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FINAL

QUALITY ASSURANCE/QUALITY CONTROL PLAN

WOODBRIDGE RESEARCH FACILITY, VIRGINIA

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U.S. Army Environmental Center

Prepared By:

EARTH TECH
1420 King Street, Suite 600
Alexandria, Virginia 22314

Prepared For:

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland 21010

August 1995

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SECTION VIII PAGES 2 of 3 AND 3 of 3, MN-I-308-A, SECTION MN-I-462, PAGE 1 of 6 ARE ALSO MISSING IN THE ORGINATOR'S AND PROJECT OFFICER'S COPY. THE PROJECT OFFICER JEFFERY WAUGH (410 671-1615) SAID SEND THE REPORT THROUGH AS IS.

JANUARY 19, 1996

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VOLUME I

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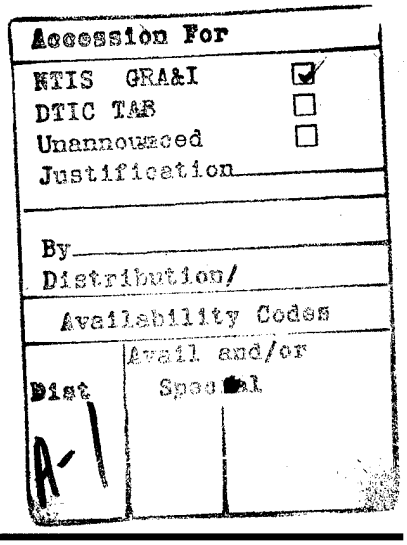

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SECTION 1.0
INTRODUCTION

This section describes the Quality Assurance (QA) and Quality Control (QC) procedures to be used throughout the sampling and analysis program for all phases of the Supplemental Site Inspection (SSI) at Woodbridge Research Facility (WRF).

1.1 PURPOSE OF DOCUMENT

The purpose of this Quality Assurance Project Plan (QAPP) is to delineate the requirements specified by U.S. Army Environmental Center (USAEC) and applicable regulatory agencies and to provide internal means for control and review so that the environmentally related measurements and data collected are valid, scientifically sound, defensible, of known acceptable documented quality, and representative of the in situ environmental conditions. This section was prepared in accordance with the U.S. Environmental Protection Agency's (USEPA's) *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* (USEPA, 1988), Department of the Army's *Chemical Data Quality Management for Hazardous Waste Remedial Activities*, ER1110-1-263 (1990), and U.S. Army Toxic and Hazardous Material Agency's (USATHAMA's) *Quality Assurance Plan* (1990).

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

A variety of activities must be completed, and several documents must be prepared, to properly complete all tasks identified in the Statement of Work for the SSI at WRF. EARTH TECH has assembled a project team who will complete the activities identified in the Statement of Work. The members of the EARTH TECH project team and their relationships are presented on Figure 1-1. The specifics of the sampling and analysis program which the EARTH TECH team will comply with during this project are further explained throughout this QA/QC Plan.

EARTH TECH typically provides technical direction of a project, on-site management of day-to-day investigation activities, and interpretation, evaluation, and reporting of the data collected. For this SSI at the WRF installation several subcontractors will be required to complete activities which, although they complement EARTH TECH data collection efforts, are not a part of the EARTH TECH Corporate structure. These subcontracted activities for the WRF SSI are soil boring and monitor well drilling and installation, geodetic surveying, and chemical and physical analytical services at certified laboratories.

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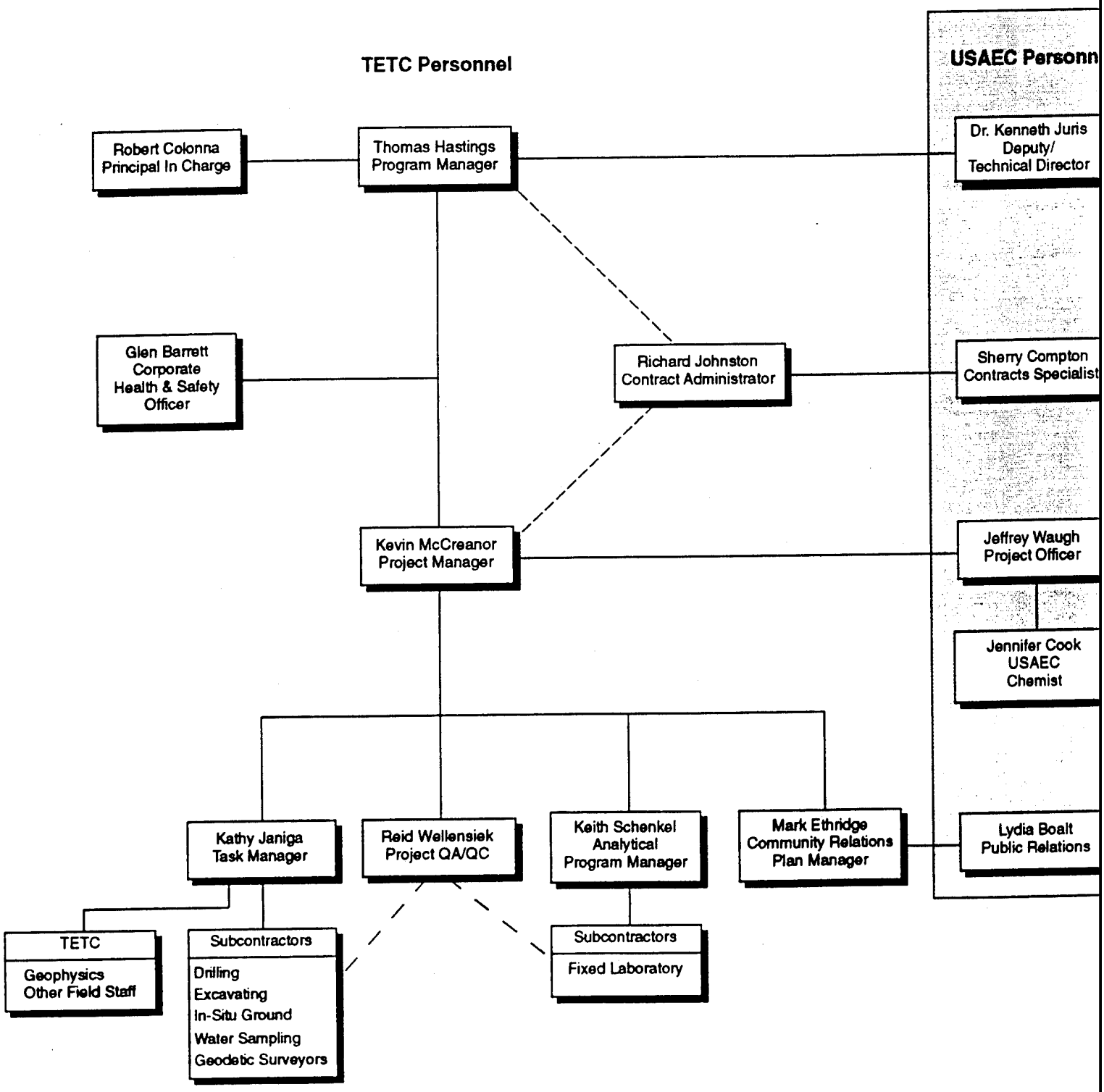
Organization
Woodbridge Research Facility -



Organizational Structure
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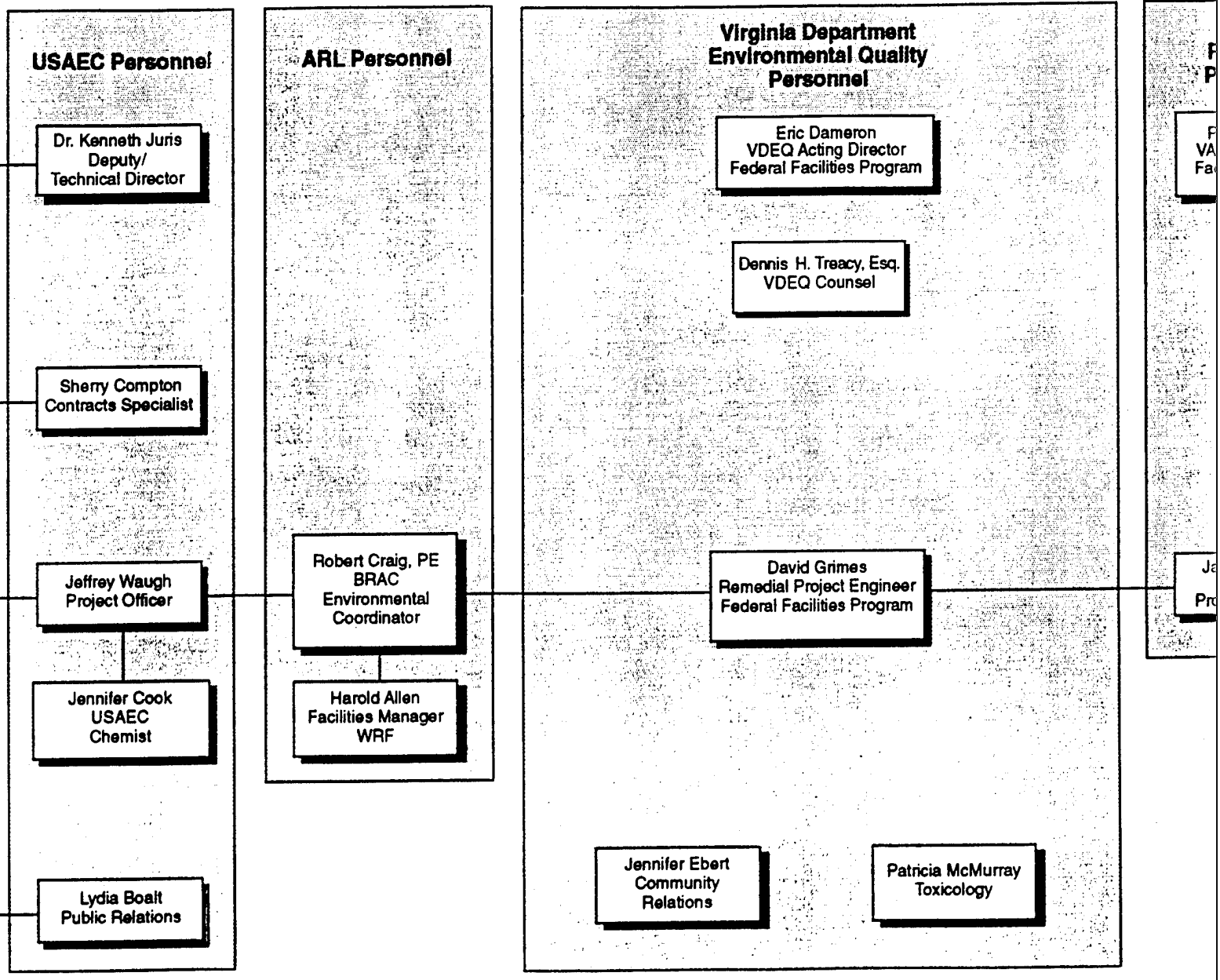

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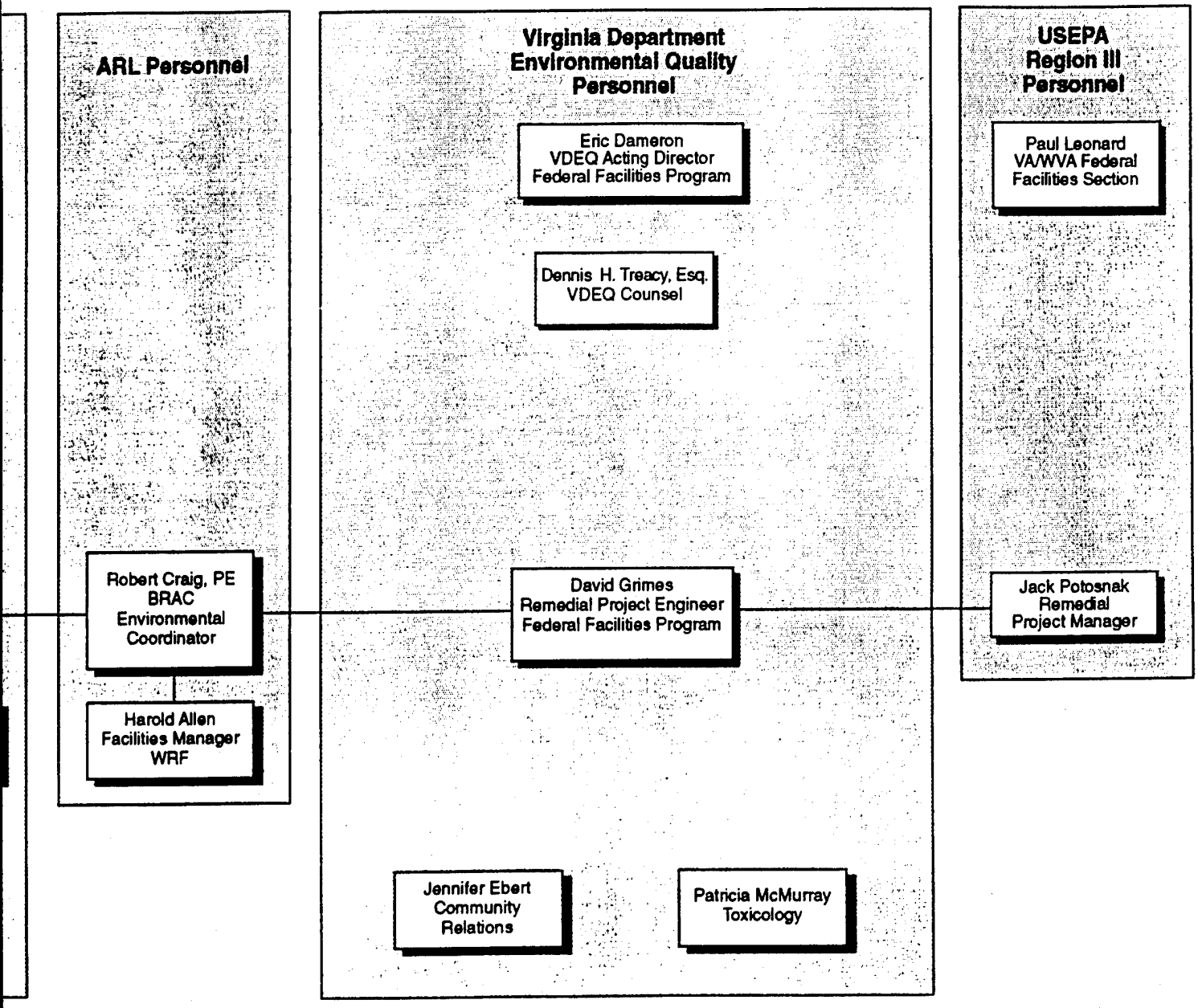

EARTH TECH	FIGURE 1-1
Organizational Structure	

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Figure 1-1 shows the members of the USAEC and their roles on this SSI project. In addition to the USAEC personnel stationed at the Aberdeen Proving Grounds facility, Mr. Harold Allen, the facility manager for the WRF has been, and will be, an asset to all phases of the USAEC/EARTH TECH data collection efforts. The primary point-of-contact at Army Research Laboratory, Adelphi, Maryland for all SSI activities will be Mr. Robert Craig, P.E. Several additional Army Research Laboratory personnel will also be sources of information to help the USAEC/EARTH TECH data collection efforts, including Mr. John Fuestle and the records/drawing repository staff, to provide additional background information should the need arise.

According to the Department of Defense and State Memorandum of Agreement (DSMOA) signed in 1990, the Commonwealth designated the Virginia Department of Waste Management (VDWM) as the lead Commonwealth agency. Since the signing of this document, several Virginia environmental regulatory agencies including the VDWM were consolidated into the VADEQ. The VADEQ, Waste Division has been retained as the lead Commonwealth regulatory component for the DSMOA for the SSI of this installation.

As the lead Commonwealth agency, VADEQ shall coordinate among other Commonwealth agencies to represent a single Commonwealth position as to remedial/removal actions at each installation. The VADEQ designated Durwood Willis, VADEQ Base Realignment and Closure Program Manager as the Commonwealth Agency Coordinator who shall be the lead technical representative for remedial program management activities. Dennis H. Treacy, Esq. has been designated the VADEQ counsel for matters arising from the remedial program management activities as specified in the implementation plan of the Cooperative Agreement. David Grimes is the Remedial Project Manager for VADEQ with responsibility for WRF.

The USEPA will also be involved during all SSI activities. WRF is located in USEPA Region III with the designated point-of-contact being Mr. Jack Potosnak.

The USAEC Project Officer, the Army Research Laboratory point-of-contact, and the Commonwealth Agency Coordinator shall be the primary point-of-contacts to coordinate the investigations and necessary removal program at WRF, including the resolution of disputes.

1.3 Data Quality Objectives (DQOs)

DQOs are qualitative and quantitative statements developed by data users to specify the quality of data required from field and laboratory data collection activities to support specific decisions or regulatory actions. The DQOs describe what data are needed, why the data are needed, and how the data will be used to address the problem being investigated. DQOs also establish numeric limits for the data to allow the data user (or reviewers) to determine whether data collected are of sufficient quality for use in their intended application.

1.3.1 General Description of DQOs

Five analytical quality control options are identified by Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and described in the USEPA document *Data Quality Objectives for Remedial Response Activities Development Process* (USEPA, 1987b). These levels are based on the type of site to be investigated, the level of precision and accuracy required, and the intended use of the data.

The useability of the data collected during this investigation depends on its quality. A number of factors relate to the quality of data, and sample collection methods are as important to consider as methods used for sample analysis. Following standard operating procedures for both sample collection and analysis reduces sampling and analytical error. Complete chain-of-custody documentation, and adherence to required sample preservation techniques, holding times and proper shipment methods ensure sample integrity. Obtaining valid and comparable data also requires adequate QA/QC procedures and documentation, as well as established detection and control limits.

1.3.2 Preliminary DQO Development

Quality criteria address the following data characteristics: accuracy, precision, completeness, representativeness, and comparability.

ACCURACY

Accuracy is the degree of agreement of a measurement or average of measurements with an accepted reference or "true" value, and is a measure of bias in the system.

For this project, accuracy of the measurement data will be assessed and controlled. Results for blank, matrix, and surrogate spikes will be the primary indicators of accuracy. These results will be used to control accuracy within acceptable limits by requiring that they meet specific criteria. The calculation formula for percent recovery is:

$$\%\ spike\ recovery = \frac{value\ of\ sample\ plus\ spike - value\ of\ unspiked\ sample}{value\ of\ spike\ added} = \times 100$$

As standard matrix spikes and surrogates are analyzed, target concentrations versus detected concentrations will be plotted, using the method of least squares linear regression, and the slope will measure the accuracy of the method.

Acceptance limits will be based upon previously established laboratory capabilities for similar samples using control chart techniques. In this approach, the control limits reflect the minimum and maximum recoveries expected for individual measurements for an in-control system. Recoveries outside the established limits indicate some assignable cause, other than normal measurement error, and possible need for

corrective action. This includes recalibration of the instrument, reanalysis of the QC sample, reanalysis of the samples in the batch, or flagging the data as suspect if the problems cannot be resolved. For highly contaminated samples, recovery of matrix spikes may depend on sample homogeneity.

PRECISION

Precision is a measure of mutual agreement among individual measurements of the same property under prescribed similar conditions. Precision of the measurement data for this project will be based upon replicate analyses (replicability), control sample analyses (repeatability), and results for duplicate/replicate field samples (sampling replicability). Precision is independent of the error (accuracy) of the analyses and reflects only the degree to which the measurements agree with one another, not the degree to which they agree with the "true" value for the parameter measured.

Field duplicates are defined as two samples collected independently at a single sampling location during a single act of sampling. Field duplicates will be collected for groundwater and surface water samples and analyzed for the same parameters as the groundwater and surface water samples. A field replicate is defined as a single sample that is collected, then divided into two equal parts for the purpose of analysis. Field replicates will be collected for soil/sediment samples and analyzed for the same parameters as the samples. Field replicates and duplicates will number 10 percent of the original sample number.

Discretely sampled field duplicates/replicates are useful in determining sampling variability. However, greater than expected differences between replicates may occur because of inhomogeneity in the sample material. In these instances a visual examination of the sample material will be performed in order to document the reason for the difference. Field sample duplicates/replicates shall be used as a quality control measure to monitor precision relative to sample collection activities. Analytical precision shall be evaluated by using duplicate spiked samples. As part of the method approval process, percent imprecision is calculated using USAEC software for Method Classes 1, 1A, and 1B. Precision is tracked for a specific method using a range (R) control chart on a daily basis.

Precision is calculated in terms of Relative Percent Difference (RPD), which is expressed as follows:

$$RPD = \frac{|X_1 - X_2|}{(X_1 + X_2)/2} \times 100$$

where X_1 and X_2 represent the individual values found for the target analyte in the two replicate analyses. RPDs must be compared to the laboratory-established RPD for the analysis. For concentrations less than 10 times the detection limit the RPD criteria are

not valid and variations may be as great as 100 percent. Precision of duplicates may depend on sample homogeneity.

The analyst or his supervisor must investigate the cause of data outside stated acceptance limits. Follow-up action includes recalibration, reanalysis of QC samples, sample reanalysis, or flagging the data as suspect if problems cannot be resolved.

COMPLETENESS

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under correct, normal conditions.

The target value for completeness of all parameters is 100 percent. Measurement data completeness is a measure of the extent to which the database resulting from a measurement effort fulfills objectives for the amount of data required. For this program, completeness will be defined as the valid data percentage of the total tests requested.

$$Completeness\ (\%) = \frac{No.\ of\ successful\ analyses}{No.\ of\ requested\ analyses} \times 100$$

Successful analyses are defined as those where the sample arrived at the laboratory intact, properly preserved, in sufficient quantity to perform the requested analyses, and accompanied by a completed chain-of-custody. Furthermore, the sample must be analyzed within the specified holding time and in such a manner that analytical QC acceptance criteria are met.

Completeness for the entire project also involves completeness of field and laboratory documentation, whether all samples and analyses specified in the Statement of Work have been processed and the procedures specified in this document and laboratory standard operating procedures (SOPs) have been implemented.

For the project as a whole, a completeness value of 90 percent will be considered acceptable. Failure to achieve this goal may necessitate resampling and reanalysis.

REPRESENTATIVENESS

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

The characteristics of representativeness are usually not quantifiable. Subjective factors to be taken into account are as follows:

- ★ Degree of homogeneity of a site
- ★ Degree of homogeneity of a sample taken from one point in a site
- ★ Available information on which a sampling plan is based.

Field duplication and field replication, as defined under precision, are also used to assess representativeness. Two samples which are collected at the same location and at the same time are considered to be equally representative of this condition, at a given point in space and time. Soil boreholes and well locations have been chosen so as to represent the areas of interest at the site. To maximize representativeness of results, sampling techniques, sample size and sample locations will be carefully chosen so they provide laboratory samples representative of the site and the specific area. Properly installed monitoring wells ensure that the water being sampled originates from the aquifer of concern. Care must be taken to ensure proper stabilization of measured water parameters, clarity and color before groundwater samples are taken. Precautions, such as not operating combustion engines near a well during sampling, must be taken so that introduction of extraneous compounds does not threaten the representativeness of the samples. Soil and sediment samples are even less homogeneous than water, and thus it is important for the sampler and analyst to exercise good judgment when removing a sample. Samples exhibiting obvious stratification or lithologic changes should not be used as replicates. Within the laboratory, precautions are taken to extract from the sample container an aliquot representative of the whole sample. For samples requiring volatiles analysis, premixing or homogenizing should be kept to a minimum.

COMPARABILITY

Comparability expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is ensured through the use of established and approved sample collection techniques and analytical methods, consistency in the basis of analysis (wet weight, volume etc.), consistency in reporting units, and analysis of standard reference materials.

Data comparability will be achieved by using standard units of measure: milligrams per liter (mg/L) for inorganics in water samples; micrograms per liter (μg/L) for organics in water; and milligrams per kilogram (mg/kg) (dry weight) for both inorganics and organics in soil samples.

The use of standard methods to collect and analyze samples (in this case American Society for Testing and Materials [ASTM] and USAEC methods), along with instruments calibrated against Standard Analytical Reference Materials (SARM) which are National Institute for Standards and Technology (NIST)-traceable standards, will also ensure comparability.

Comparability also depends on the other data quality characteristics. Only when data are judged to be representative of the environmental conditions, and when precision and accuracy are known, can data sets be compared with confidence.

1.3.3 Quantitative DQOs

Project quality objectives for the various measurement parameters associated with site characterization efforts are not quantifiable for representativeness and comparability. Accuracy and precision are tracked daily through the use of USAEC required x-bar and R control charts. A completeness factor of 90 percent is acceptable.

1.3.4 Appropriate Analytical Levels

USEPA Analytical Levels are summarized in Table 1-1. Field analysis data of qualitative or semi-quantitative nature are considered USEPA Level I quality. Data are obtained by use of approved field equipment, such as total organic vapor analyzers, dissolved oxygen meters, and geophysical survey instruments. Level I data may be used for the following: (1) delineation of contaminated zones; (2) gross determination of analytes in samples; or (3) health and safety screening. Level I data can provide information to the laboratory regarding expected concentration ranges.

Quantitative field instruments which are designed for in-situ measurements and analyses performed by mobile laboratories fall under USEPA Level II analytical levels. Data from Level II are used for site characterization, evaluation of alternatives, engineering design, and monitoring during implementation or sampling. Data collected by use of analytical field procedures (e.g. temperature and pH) are considered to be Level II. Analytical programs for Soil Organic Vapor (SOV) surveys are also considered to be Level II.

Level III provides low detection limits, a wide range of calibrated analytes, matrix recovery information, laboratory process control information, and known precision and accuracy. USEPA-accepted methods, such as those in SW-846, the National Pollutant Discharge Elimination System (NPDES), and the Contract Laboratory Program (CLP), are considered Level III. USAEC methods (Class 1, 1B, or 1A) would fall under Level III since they are based on USEPA methods. Level III can be used for risk assessment, site characterization, evaluation of alternatives, engineering design, and monitoring during implementation.

The samples to be collected as part of the SSI at WRF will be analyzed by USEPA Level I and III protocols. These results will be used for site characterization. Field equipment such as organic vapor analyzers (OVAs), geophysical instruments, and polychlorinated biphenyl (PCB) test kits will be used initially to gather data at Level I. Soil, sediment, surface water and groundwater samples will be sent to a USAEC-approved laboratory for analysis at Level III.

TABLE 1-1
SUMMARY OF USEPA ANALYTICAL LEVELS APPROPRIATE TO DATA USES

Data Uses	Analytical Level	Type of Analysis	Limitations	Data Quality
Site Characterization; Monitoring During Implementation; Health and Safety Screening	Level I	Total organic/inorganic vapor detection using portable instruments Field test kits	Instruments respond to naturally-occurring compounds	If instruments calibrated and data interpreted correctly, can provide indication of contamination
Site Characterization; Evaluation of Alternatives; Engineering Design; Monitoring During Implementation	Level II	Field instruments for variety of organics by gas chromatograph; inorganics by atomic absorption; XRF Tentative ID; analyte-specific Detection limits vary from low ppm to low ppb	Tentative ID Techniques/instruments limited mostly to volatiles, metals	Dependent on Quality Assurance/Quality Control steps employed Data typically reported in concentration ranges
Risk Assessment; Potentially Responsible Party Determination; Site Characterization; Evaluation of Alternatives; Engineering Design; Monitoring During Implementation	Level III	Organics/inorganics using Environmental Protection Agency procedures or Contract Laboratory Program; analyte-specific Resource Conservation and Recovery Act characteristics tests	Tentative ID in some cases Can provide data of same quality as Level IV	Similar detection limits to Contract Laboratory Program Less rigorous Quality Assurance/Quality Control than Level IV
Risk Assessment; Potentially Responsible Party Determination; Evaluation of Alternatives; Engineering Design	Level IV	HSL organics/inorganics by gas chromatography/mass spectrometry; atomic absorption; inductively coupled plasma Low ppb detection limit	Tentative identification of Non-HSL Parameters Some time may be required for validation of packages	Goal is data of known quality Rigorous Quality Assurance/Quality Control
Risk Assessment; Potentially Responsible Party Determination	Level V	Non-conventional parameters Method-specific detection limits Modification of existing methods Appendix 8 parameters	May require method development/modification Mechanism to obtain services requires special lead time	Method-specific

Key: USEPA = U.S. Environmental Protection Agency ppb = Parts per billion
ppm = Parts per million

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SECTION 2.0
FIELD OPERATIONS

2.1 FIELD SAMPLING PROCEDURES

The field activities to be performed as part of the SSI are described in detail in the Phase I and Phase II SSI Operations Plans (February 1995). This section outlines sample procedures, sample handling and custody protocols for soil, sediment, surface water, and groundwater samples to be collected as part of the SSI at WRF. The methodologies to be used in collecting these samples, including descriptions of field QA/QC samples, are discussed in the following subsections.

2.1.1 Soil and Sediment Sampling

During soil and sediment sampling, field personnel will fill all sample containers using the following precautions.

- ★ New gloves will be worn at each sample location.
- ★ The sampler will not lay the cap down or touch the inside of the cap.
- ★ The inside of the bottle will not come in contact with anything other than the sample (or preservative, if applicable).
- ★ After the sample volume is placed into the container, the cap will be replaced carefully.
- ★ Sample equipment will be decontaminated between sample locations.
- ★ For volatile organic analysis (VOA), the containers will be filled in a manner to minimize aeration of the samples so that no headspace exists in the container.

Following the collection of samples, containers will be placed in a cooler (4°C), and the sample custody documentation and shipping procedures will be completed as discussed in Sections 2.2.2 and 2.2.4. Samples will be collected in containers that have been cleaned according to protocols in Appendix F of USATHAMA Quality Assurance Plan (QAP) (1990). The laboratory will provide the appropriate containers. Soil sampling procedures are detailed in the Technical Sampling and Analysis Plan (TSAP) (EARTH TECH, 1995).

Subsurface soil samples will be collected using a split-spoon sampler from borings, a stainless steel trowel from an excavation, or directly from a hand auger. Surface soil and sediment samples will be collected using a stainless steel trowel.

2.1.2 Groundwater Sampling

Field personnel will fill all sample containers using the same precautions as with soil sampling. In addition, water sample containers will be rinsed three times with sample location water prior to filling the containers. Samples will be collected from the new wells no sooner than fourteen days following well development, because development methods proposed may agitate and aerate the water column, yielding samples that are non-representative. This fourteen day waiting period will allow the groundwater in the well to reach equilibrium conditions. Groundwater samples will be collected from the least likely contaminated well locations to the most likely contaminated well locations in order to lower the possibility of cross contamination. Groundwater sampling methods follow procedures described in the *RCRA Ground Water Monitoring Technical Enforcement Guidance Document* (USEPA, 1986b) and USATHAMA *Geotechnical Requirements for Drilling, Monitor Wells, Data Acquisition, and Reports* (USATHAMA, 1987).

All wells will be purged prior to sampling in order to obtain a representative sample. After the static level(s) and well depth have been measured, a pump will be lowered down the well and set in the lower portion of the submerged well screen. At least five borehole volumes will be purged from the well, unless the well is evacuated before five volumes have been purged. This method accounts for water in both the well casing and sand pack. If the well is incapable of yielding five borehole volumes, the well will be pumped until it has been evacuated and then will be allowed to recover. After the well has recovered sufficiently for a sample, the sample will be collected and tested for pH, specific conductance, and temperature. Color and odor of the discharge will also be noted. If the well is capable of yielding five borehole volumes, samples will be collected and tested for pH, specific conductance, and temperature. Samples will be measured quickly in order to minimize contact with the atmosphere.

A stainless steel submersible pump may be used for purging the wells. Other purging devices such as a bailer, peristaltic pump, gas-lift pump, centrifugal pump, or venturi pump may be used. These pumps cause some volatilization of samples, but are acceptable for purging if the water is allowed to stabilize before sampling.

Table 2-1 lists the containers to be used to collect each type of sample. Containers will be rinsed three times with sample location water prior to filling. Samples will be collected using either a Teflon™ bailer or a low flow pump.

TABLE 2-1
RECOMMENDED SAMPLE CONTAINER, PRESERVATIVE, AND HOLDING TIMES FOR SELECTED METHODS

Parameter	Container (a)	Volume Required		Preservation (b)		Maximum Holding Times (c)*
		Water (mL)	Soil (g)	Water	Soil	
Hydrogen Ion (pH)	P,G	50	NA	None Required	NA	Analyze immediately
Total Petroleum Hydrocarbons	G	2 x 1,000	50	Cool 4°C HCl to pH <2	4°C	28 days
Gasoline	G, Teflon™ lined septum	3 x 40	50	Cool 4°C HCl to pH <2	4°C	14 days
Diesel	G, Teflon™ lined septum	1,000	50	Cool 4°C	4°C	14 days until extraction, 40 days after extraction
Metals	P, G	1,000	50	Cool 4°C HNO_3 to pH <2	4°C	6 months
Lead	P,G	100	10	Cool 4°C HNO_3 to pH <2	4°C	6 months
Temperature (field)	P, G	1,000	NA	None Required	NA	Analyze immediately
Soil Moisture Content	G	NA	200 (For coarse sands or finer soil)	NA	Airtight Container	30 days
Organochlorine Pesticides/PCBs	G, Teflon™ screw cap	1,000	2 x 50	Cool 4°C	4°C	7 days until extraction, 40 days after extraction
Volatile Organics	G, Teflon™ lined septum	3 x 40	50	Cool 4°C HCl to pH <2	4°C	14 days (7 days if not pH adjusted)
Semivolatile Organics	G, Teflon™ screw cap	2 x 1,000	50	Cool 4°C	4°C	7 days (water) and 7 days (soil) until extraction, 40 days after extraction
Dioxins	G, Teflon™ screw cap	2 x 1,000	100	Cool 4°C	4°C	7 days until extraction, analyzed within 40 days after extraction
Mercury	P, G	1,000	200	Cool 4°C HNO_3 to pH <2	4°C	28 days
Cyanide	P, G	1,000	50	Cool 4°C NAOH to pH >12	4°C	14 days

TABLE 2-1
RECOMMENDED SAMPLE CONTAINER, PRESERVATIVE, AND HOLDING TIMES FOR SELECTED METHODS

Continued

Parameter	Container (a)	Volume Required		Preservation (b)		Maximum Holding Times (c)*
		Water (mL)	Soil (g)	Water	Soil	
Ethylene Glycol	G	1,000	50	Cool to 4°C	Cool to 4°C	14 days

NOTE: * Extraction holding times are from date of sample collection; analysis times are from date of extraction.

REFERENCE: This table includes the requirements of the U.S. Environmental Protection Agency, as published in the Code of Federal Regulations, Volume 49, Number 209, 40CFR 136, dated October 26, 1984, page 43260.

(a) Polyethylene (P) or amber glass (G). Soil samples may be collected in either glass jars or stainless steel liners with both ends sealed with Teflon™ paper and plastic caps.

(b) Sample preservation should be performed immediately upon sample collection. For composite chemical samples, each aliquot should be preserved at the time of collection. When use of an automatic sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting are completed.

(c) Samples should be analyzed as soon as possible after collection. The times listed are maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods of time only if permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time peri given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter period if knowledge exists to show th is necessary to maintain sample stability.

Samples for VOA will be collected in 40 milliliter glass bottles allowing no headspace. This will be accomplished by filling the bottle until a reverse meniscus is over the top, and then fitting the cap securely. Headspace will be checked by inverting the bottle and tapping the lid to see if any air bubbles are visible in the bottle.

Samples collected for inorganic analysis will be collected in the same manner as the organics but will be placed in plastic or glass containers filled to the top. Preservatives will be added following sample collection. The pH of the preserved samples will be measured and recorded in the field logbook. Filtered and unfiltered groundwater samples will be submitted for samples collected for metals analyses. Filtered samples will be filtered through a 0.45 micrometer membrane filter using an in-line positive pressure filtration within 15 minutes of sampling and prior to preservation. Bottles for filtered samples will be rinsed three times with filtered water.

The samples will be collected in order of decreasing volatilization as follows:

1. Volatile organics
2. Semivolatile organics
3. Other organics (namely PCB)
4. Inorganics.

2.1.3 Surface Water Sampling

The following procedures describe how to obtain surface water samples from surface water bodies which receive runoff (i.e., streams, ponds, and lakes).

For stream sampling, the farthest downstream sample location will be sampled first. All sample containers will be triple rinsed with the surface water prior to sample collection. The rinsing equipment precludes adding preservative to bottles before they are shipped to the sampling site. Bottles for filtered samples will be rinsed with filtered sample water and bottles for unfiltered samples will be rinsed with unfiltered water. The mouth of the sample container will be oriented upstream, while the sampling personnel stand downstream so as not to disturb any sediment that could potentially contaminate the sample. Duplicates will be collected immediately after the sample by repeating the procedure.

All surface water samples will be collected before sediment samples to avoid excess suspended particles from the sediment sampling locations. Preservatives will be added and caps secured. The sample containers will be placed in a temperature controlled (4°C) chest immediately after sampling. All sampling equipment will be rinsed in accordance with decon procedures given in Section 2.1.4.

2.1.4 Sampling Equipment Decontamination

All sampling equipment, including internal components, will be thoroughly decontaminated prior to use and between sample points to avoid cross contamination. All equipment used for water sampling will be decontaminated by scrubbing and rinsing with distilled or USAEC-approved water.

Ample time will be given for the equipment to dry prior to reuse. Equipment will be protected from ground contamination by placing it on plastic sheeting. Sampling equipment that is not readily decontaminated will be discarded after each use. Discarded materials, including decontamination solutions, will be accumulated and stored in appropriate receptacles for proper disposal.

Purge equipment, including bailers and pumps, will be decontaminated by flushing/pumping distilled water through the components. The exterior of the pump inlet hose will also be rinsed.

All measuring equipment and apparatus will be thoroughly decontaminated prior to use and between sampling points to avoid cross contamination. Groundwater meters, such as the conductivity meter, will be thoroughly rinsed with distilled water after each use. Discarded materials, including paper towels and decontamination fluids, will be disposed of in accordance with applicable regulations.

If a rig is used to handle equipment during purging or sampling, any grease that may contact equipment going into the well will be removed with distilled water. The rig will then be steam cleaned and rinsed with potable water.

2.2 SAMPLE HANDLING

Preservation of samples is required to retain integrity. The most common preservation techniques include pH adjustment and temperature control. Field personnel will use USEPA-recommended container types and adhere to USEPA-recommended preservation techniques for the parameters of concern (Table 2-1). Minimum sample volumes required for each analysis are also specified and must be observed. Pre-cleaned sample containers for soil and groundwater samples will be provided by the laboratory. The containers are pre-cleaned and laboratory certified (I-Chem Superfund Analyzed) with certificate of analysis. The cleaning procedure is in accordance with USAEC specifications for glassware cleaning. The certificate of analysis will be on file at the laboratory. Sample containers will be packaged according to procedures outlined in Section 2.2.2. Samples are to be analyzed within the holding times defined in certified laboratory methods, and are never to exceed the prescribed holding times given in Appendix H of the USATHAMA QAP.

2.2.1 Sample Identification

Unique field sample identification numbers will be designated by a four-part code. The first two digits represent the area requiring environmental evaluation (AREE) number, the middle four digits designate the sampling location (type of sample location and its number), and the last two digits state the sample number taken sequentially from the location. Sample numbers will be consecutive as they are collected at a location. An example of the sample identification is described below:

03MW0201

Where:	03	=	The AREE Number (AREE 3)
	MW	=	Type of Sample Location (Monitoring Well)
	02	=	Sample Location Number (Monitoring Well 2)
	01	=	Sample Number (First Sample from MW02).

The following are abbreviations for the sample location types:

BH	=	Borehole	SE	=	Sediment
MW	=	Monitor Well	SW	=	Surface Water
SS	=	Surface Soil	EX	=	Excavation
DP	=	Direct Push Sample			

The samples will also be labeled with a site type and identification required by Installation Restoration Data Management Information System (IRDMIS) to describe the sampling location. Each sampling location will be assigned a site type and ID before sampling takes place. A complete list is given in Section 9.17 of the IRDMIS Data Dictionary (IRDMIS, 1995).

If more than one container is collected from the same location on one day to provide the laboratory with enough sample to analyze or due to different analyses requirements, all containers should be labeled with the same identification number. The sample number, along with the date and time the sample was obtained, will be recorded in the field log and written on the sample label. After collection and identification, the samples will be maintained under chain-of-custody procedures (see Section 2.2.3).

Quality control samples will be labeled sequentially with the sample type preceding the sample number. The abbreviations for sample type are TB for Trip Blanks, RB for Rinsate Blanks, and AB for Ambient Blanks. An example of a field identification number is TB01. The rinsate blanks should include a note in the field log as to which samples it is associated.

Samples are identified by a sample label. The information recorded on the sample tag includes:

- ★ Project name and project number
- ★ Site type and identification
- ★ Field identification sample number
- ★ Date and time of sample collection
- ★ Sampler's initials
- ★ Sample type (soil, water, air, etc.) and depth at which obtained
- ★ Analyses to be performed on the sample
- ★ Preservative used and whether the sample is filtered or unfiltered (for water).

Sample tags will be affixed by the sampler to the sample container used.

2.2.2 Sample Packaging and Shipping

All samples will be packaged carefully to avoid breakage or contamination and will be shipped to the laboratory at the proper temperatures. The sample packaging requirements listed below will be followed.

- ★ Sample bottle lids will not be mixed. All sample lids will stay with the original containers. All lids will be secured with custody seals.

- ★ If the sample volume level is low because of limited sample availability, the level will be marked with a grease pencil. This procedure will help the laboratory determine if any leakage occurred during shipment.

- ★ Samples collected during the SSI are anticipated to be low concentration samples. All sample containers will be placed in plastic bags. All glass sample bottles will be wrapped in bubble pack and placed in plastic bags to minimize the potential for breakage and contamination during shipment. Plastic bottles will not be wrapped in bubble pack, but will be placed in plastic bags.

- ★ All samples will be cooled unless "no cooling" has been specified. The sample containers will be packed in coolers. Empty space around the samples will be filled with inert packing material. The coolers will then be filled with ice within Zip-lock™ bags or blue ice.

- ★ The chain-of-custody record will be placed in a plastic bag and taped to the inside of the cooler lid.

- ★ All shipping containers will be locked or custody sealed for shipment to the laboratory. Custody seals should be placed on all sides of the shipping container (except side with hinges). The custody seal will consist of a regular paper custody seal or filament tape wrapped around

the shipping container at least twice, with the end of the tape signed before the samples are shipped.

2.2.3 Sample Custody in the Field

In order to maintain and document sample custody, the following chain-of-custody procedures will be strictly followed. A sample is considered to be under custody if:

- ★ It is in actual possession of the responsible person
- ★ It is in view, following physical possession
- ★ It is in the possession of a responsible person and is locked or sealed to prevent tampering
- ★ It is in a secure area.

2.2.4 Chain-of-Custody Record

Sample custody is maintained by a "Chain-of-Custody Record". See Figure 2-1 for the custody record which is completed by the individual collecting the sample.

2.3 Calibration Procedures and Frequencies for Field Test Equipment

Field equipment will be calibrated prior to use in the field as appropriate. The calibration procedures will follow standard manufacturers' instructions and/or EARTH TECH's Calibration/Service Specification (C/SS) to ensure that the equipment is functioning within tolerances established by the manufacturers and required by the project. In addition to regularly scheduled calibration, some instruments such as pH meters require calibration checks before use. All instruments will be monitored for evidence of non-reproducible or erratic readings, and recalibration performed as required. Calibration procedures and the frequency of calibration are described in the TSAP (February 1995). Copies of the instrument manuals will be maintained in the field office. A daily record of field analytical instrument (e.g., pH meter and conductivity meter) daily calibration will be maintained in the field logbook or calibration logbook by field personnel. Copies of calibration records for equipment that only needs periodic calibration (e.g., thermometers and sounders) will be available in the field office. These records will be subject to QA audit. In addition, any notes on unusual results, changing of standards, battery charging, and operation and maintenance will be included in the logbook.

All instruments are to be stored, transported, and handled with care to preserve equipment accuracy. Damaged instruments will be taken out of service immediately and not used again until a qualified technician repairs and recalibrates the instruments.

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pace
INCORPORATED
THE ASSURANCE OF QUALITY

U-01040

USATHAMA
CHAIN-OF-CUSTODY RECORD (COC)
Analytical Request

Installation

Prime Contractor

Sample Program

Report To:

Bill To:

P.O. # / Billing Reference

Pace Client No.

Pace Project Manager

Pace Project No.

Sampled By (PRINT):

Sampler Signature

Date Sampled

FILE NAME	SITE TYPE	SITE ID	FIELD SAMPLE NO.	MTRX	SAMPLE DEPTH	SMPL TECH	PACE NO.	NO. OF CONTAINERS	PRESERVATIVES: UNPRESERVED	H_2SO_4	HNO_3	HCl	NaOH	UM05 VOA GC/MS	UG03 VOA GC/HALL	UP01 VOA GC/PID	UM06 BNA GC/MS	UH21 OCP GC/ECD	UH22 HERB GC/ECD	SS15 METALS ICP	SB07 MERCURY CVAA	SD08 METALS GFAA	TY03 CYANIDE	TPH 418.1	TT12 ANIONS-IC	TY11 TOTAL PO_4	TF15 ORTHO PO_4	LM05 VOA GC/MS	LG03 VOA GC/HALL	LP01 VOA GC/PID	LM06 BNA GC/MS	LH19 OCP GC/ECD	LH20 HERB GC/ECD	JS14 METALS ICP	JB06 MERCURY CVAA	JC02 METALS FIAA	KY04 CYANIDE	TCLP SW1311	EXPLOSIVES H_2O	EXPLOSIVES SOIL	LABORATORY REMARKS

SHIPPING AIRBILL NO.	NO. OF COOLERS	NO. OF COC IN SHIPMENT

TOTAL CONT.	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

Field Sampling Remarks:

EARTH TECH

FIGURE 2-1

Chain of Custody Record

SEE REVERSE SIDE FOR INSTRUCTIONS

WHITE: PACE FILE YELLOW: PRIME CONTRACTOR PROJECT MANAGER PINK: PACE PROJECT MANAGER GOLD: RETAIN IN FIELD

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2.4 Field Data Reduction, Validation, and Reporting

Field observations, direct reading instrument responses, and other measurements will be recorded either in field logbooks or on the field data forms appropriate for the activity. The Task Manager will be responsible for ensuring that all necessary data and information is incorporated into the logbooks and forms as each field activity occurs. On a daily basis, the Task Manager will check the logbooks and forms for completeness.

Field measurement data review will be the responsibility of the Task Manager. Criteria to consider when reviewing measurement data includes:

- ★ Calibration information in logbooks; and
- ★ Reasonableness of results based on what is known for the site relative to the magnitude and implications of the result.

To present field data in the site characterization reports, data in logbooks and on forms will need to be summarized and transferred to tables, figures, maps, or logs. The Project Manager and Task Manager will be responsible for the data transfer activities pertinent to their project roles. The QC Coordinator will be responsible for performing spot checks of transfer activities and for ensuring the data transfers are performed accurately. The data will also be entered into IRDMIS map and geotechnical files. IRDMIS map files will be completed prior to sampling and updated as needed.

2.5 Quality Control for Field Activities

The field QA/QC program will include the following.

- ★ Trip blanks will accompany each cooler shipment of samples sent to the laboratory for analysis of volatile organic compounds. A trip blank is a VOA sample bottle filled by the laboratory with Type II reagent grade water. The trip blank is transported to the sampling site, handled like a sample, and returned to the laboratory with samples submitted for volatile organic compounds (VOCs). The trip blank will not be opened in the field. The trip blank will be analyzed for the same VOCs as the samples to insure that no cross contamination occurred during shipment between samples. The trip blanks are only required for water samples.

- ★ Ambient conditions blanks will be collected at each site or area during each round of water sampling for volatile organic contaminants to insure that no outside sources contributed to the possible VOC contamination. Ambient conditions blanks are prepared by pouring Type II reagent grade water into sample containers at a sampling site. These blanks are

handled as samples and then sent to the laboratory for analysis. Ambient conditions blanks are analyzed for VOCs only.

- One set of rinsate blanks will be collected for each matrix per equipment type every day of sampling (all parameters to be analyzed). After sampling equipment is deconned, rinsate blanks are prepared by pouring or pumping Type II reagent grade water through the sampling device into the sample bottle. The blank is then transported to the laboratory for analysis. Rinsate blanks serve as a check that no cross contamination between sites occurs from using the same equipment type during sampling procedures.

- Duplicate water samples will be collected at a frequency of 10 percent to provide a measure of method variability (i.e., total variability due to imprecision in both sampling and analytical procedures). Two samples will be collected independently at one sampling location during one act of sampling. The sample and the duplicate will be analyzed for the same parameters. The duplicates will be collected by the same procedures as the sample immediately following its collection.

- Replicate (i.e., split) soil samples will be collected at a frequency of 10 percent to provide a measure of method variability (i.e., precision). A single sample will be collected, then divided into two equal parts for the analysis (all parameters analyzed). For split-spoon samples, the composite soil will be split into the sample and replicate. For surface soil samples, sediment, and direct push samples, composite samples will be blended and split in the field except for volatile organic samples, which will be collected from adjacent locations before they are composited.

- Chain-of-custody forms will accompany all samples and will be placed in a sealed plastic bag and taped to the inside lid of the cooler.

- Sampling apparatus will be thoroughly cleaned between each sampling event to prevent cross contamination of the samples. Sampling equipment used to collect samples for volatile organic analysis will not be allowed to come in contact with any type of plastic (e.g., plastic storage bags). Decontamination of sampling equipment is detailed in Section 2.1.4.

2.6 FIELD AUDITS

During the course of this project a field audit may be conducted by EARTH TECH (internal field audit) or by the USAEC Geology and Chemistry Branch (external audit). The Field Sampling Checklist (Appendix W) of the USATHAMA QAP may be used as a guideline when performing the audit.

The results of the field audit will be documented in a written report and noted deficiencies will be attached with a notice of nonconformance or an equivalent form. The report will be submitted to the following:

- ★ USAEC Project Officer;
- ★ EARTH TECH Program Manager;
- ★ EARTH TECH Project Manager; and
- ★ EARTH TECH Task Manager.

Correctives actions, discussed in the following section, will be implemented if required by the audit.

2.7 Corrective Action for Field Activities

During the course of the SSI field program at WRF, it will be the responsibility of the Project Manager and sampling team members to see that all procedures are followed as specified and that measurement data meet the prescribed acceptance criteria. In the event a problem arises, it is imperative that prompt action be taken to correct the problem. Engineering and scientific calculations will be checked and corrected as required by technical personnel, and normally require no QA reporting.

A nonconformance exists if there is a deviation from or noncompliance with contract specifications, the QA program, approved procedures, work plans or sampling and analysis plans. Nonconformances also include major errors in documented analysis, data, or results, and deficiencies in documentation or any other aspect of the project that affects quality. Personnel who identify a nonconformance shall report the condition to responsible management. The sample numbers of any samples affected by the nonconformance should be noted on the Nonconformance Report.

If a deficiency is noted and a corrective action is required, the person responsible for implementing the action will be listed in the nonconformance report. The auditor will be notified of the corrective action, by the named person, within 10 days of the date of the nonconformance report.

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SECTION 3.0
LABORATORY OPERATIONS

Pace, Incorporated will be performing all analyses. The Pace Minnesota regional laboratory is a full service laboratory housed in a 61,000 square foot facility with 149 employees. The laboratory is equipped with state-of-the-art instrumentation. The laboratory holds many national and state certifications including USAEC, U.S. CLP, and U.S. Army Corps of Engineers, Missouri River Division.

3.1 LABORATORY SAMPLE CUSTODY

All sample log-in, storage, and chain-of-custody documentation are the responsibility of the sample control supervisor. Any laboratory employee in sample control is authorized to sign for incoming samples. The sample control supervisor is responsible for retaining documents of shipment, and verifying data entered into the sample custody records. In addition, the sample control supervisor will ensure that sample storage is secure and maintained at the proper temperature.

3.1.1 Sample Handling

Upon receipt in the laboratory the integrity of the shipping container is checked by verifying that the custody seal is not broken. The presence of ice is noted and the temperature measured. The samples are checked for breakage, leakage, and damage, and the contents of the shipping container are verified against the chain-of-custody documentation. Documentation of custody seal integrity, temperature or presence of ice, and sample preservations are made on the sample log-in form. A bound permanent logbook will be maintained by the sample custodian to document the following:

- ★ Date of sample receipt
- ★ Source of sample
- ★ Sample accession number
- ★ Analytical test requested
- ★ Matrix
- ★ Number of samples
- ★ Final disposition of sample (45 days after report issuance)

Any problems are documented on the chain-of-custody and the EARTH TECH Analytical Project Manager is contacted immediately. The USAEC Base Closure

Project Officer and the USAEC Geology and Chemistry Branch Project Officer will be informed if cooler temperature exceeds 4°C ± 2°C. Analysis of the samples in this cooler will only be performed after permission by the Project Officer is received.

Samples are then placed in the appropriate 4°C sample refrigerator. Information about samples with suspected high contamination levels will be noted by the sample collectors on the chain-of-custody forms. Samples identified as having high contamination levels are stored separately as are samples submitted for volatile analysis. All refrigerators are maintained at 4°C ± 2°C, and temperatures are monitored and recorded daily by sample control personnel. Preservatives, containers, holding times, and volume requirements for project-required tests are given in Table 2-1. All samples are kept under the proper environmental control until the data associated with the samples are accepted into IRDMIS Level 3.

3.1.2 Sample Identification

The USAEC analytical reporting system uses a seven-character identification code to identify each sample. The first four characters of this code are alpha and represent the analytical lot code assigned by the laboratory and USAEC. Each analytical lot has a different set of alpha characters. For example a set of groundwater samples for metals analysis by inductively coupled plasma (ICP) would be designated AAAA, while groundwater samples for organic gas chromatography/mass spectrometry (GC/MS) analysis would be designated BBBB (multi-analyte methods, such as GC/MS, will have the same alpha designator for each analyte in a single sample). Three characters can be used as a minimum.

The second half of the seven-character code will be numeric characters that represent the individual samples within the lot (i.e., the third groundwater sample for metals analysis by ICP would be labeled as AAAA003). Total lot size is determined and approved by the USAEC when the analytical method is approved.

3.1.3 Sample Custody Records

All samples shall be accompanied by a chain-of-custody record. A chain-of-custody record must also be used if the laboratory relinquishes control of the samples to subcontractor laboratories or returns the samples to the originator. A laboratory chain-of-custody is used to track the samples within the laboratory. All chain-of-custody records are filed permanently with the analytical data. The completed original chain-of-custody will be forwarded to EARTH TECH with the final report.

3.2 LABORATORY CALIBRATION

Prior to sample analysis, chemical calibration of each target analyte must be performed to ensure analytical instrumentation is functioning properly within the

established sensitivity range. Protocols defining the procedures and QC measurements for instrument calibration will be in accordance with criteria specified in the 1990 USATHAMA QAP and the individual certified methods. The acceptable ranges for the daily calibration and check standards, discussed below, are specified in Table 3-1. Numbers and concentrations of standards to be analyzed during calibrations performed for different ranges (linear and zero-intercept) and different certification classes are summarized in Table 3-2.

3.2.1 Initial Calibration

Initial calibration for the methods to be used in this project will be performed routinely by Pace as part of the certified analytical protocol. New initial calibrations are not required unless the instrument fails the daily calibration test procedure. The initial calibration procedure also requires the analysis of a calibration check standard (in accordance with the 1990 USATHAMA QAP, Section 8.2) before sample analysis can begin.

3.2.2 Daily

For Class 1, 1A, and 1B methods, prior to analysis all instruments will be calibrated to ensure that the instrumental response has not changed significantly from the previous calibration. Analysis should be performed on the highest concentration standard. A response within the required percentage or two standard deviations of the mean response for the same concentration as determined from precertification, certification, and prior initial/daily calibrations, indicates the instrument calibration is acceptable and sample analysis may proceed. If the response fails the percentage or two standard deviation criterion, the daily standard will be reanalyzed. Failure of the second analysis requires initial calibration to be performed as specified in the 1990 USATHAMA QAP.

3.2.3 Continuing Calibration

Continuing calibration will be performed in accordance with USEPA CLP Statement of Work and will occur as follows (USEPA, 1991):

- When inorganic analyses are performed, a blank and a continuing calibration standard should be analyzed after every 10th sample, or every 2 hours, whichever is more frequent.

- When GC/MS volatile analyses are conducted, a blank and a continuing calibration standard should be analyzed every 12 hours.

- When GC/MS semivolatiles are analyzed, a continuing calibration standard should be analyzed every 12 hours.

TABLE 3-1
LIMITS OF ACCEPTABILITY

Analysis	Daily Calibration Standard	Certified Check Standard[1]
Organics	±25%	±25%
Inorganics	±10%	±10%
Mercury, Cyanide, and Anions	±15%	±15%

(1) Certified check standard is available from EPA or some other source with the true volume specified by the supplier. If the limits of acceptability are specified by the supplier and are lower than the limits shown, the results must fall within the lower limits.

TABLE 3-2
NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS (LINEAR AND ZERO-INTERCEPT)

Initial Calibration - Class 1A
Minimum Testing Range (MTR): 5 Standards Blank, *0.5, 2, *10, and *10 TRL MTR + 1 Order of Magnitude Extension: 7 Standards Blank, *0.5, 2, 10, 50, *200, and *200 TRL MTR + 2 Orders of Magnitude Extension: 9 Standards Blank, *0.5, 2, 10, 50, 200, 500, *2000, and *2000 TRL
Initial Calibration - Class 1B
Minimum Testing Range (MTR): 5 Standards + 1 Check Standard (CS) Blank, *0.5, 2, *10, and *10 TRL + CS MTR + 1 Order of Magnitude Extension: 7 Standards + 1 Check Standard Blank, *0.5, 2, 10, 50, *200, and *200 TRL + CS MTR + 2 Orders of Magnitude Extension: 9 Standards + 1 Check Standard Blank, *0.5, 2, 10, 50, 200, 500, *2000, and *2000 TRL + CS
Daily Calibration - Class 1/Class 1A/Class 1B
Minimum Testing Range (MTR): 2 Standards, *10 and *10 TRL MTR + 1 Order of Magnitude Extension: 2 Standards, *100 and *100 TRL MTR + 2 Orders of Magnitude Extension: 2 Standards, *1000 and *1000 TRL
Certification - Class 1
Minimum Testing Range (MTR): 9 Initial, 6 Daily MTR + 1 Order of Magnitude Extension: 12 Initial, 6 Daily MTR + 2 Orders of Magnitude Extension: 15 Initial, 6 Daily
Certification - Class 1A
Minimum Testing Range (MTR): 5 Initial MTR + 1 Order of Magnitude Extension: 7 Initial MTR + 2 Orders of Magnitude Extension: 9 Initial
Certification - Class 1B
Minimum Testing Range (MTR): 6 Initial, 6 Daily MTR + 1 Order of Magnitude Extension: 8 Initial, 6 Daily MTR + 2 Orders of Magnitude Extension: 10 Initial, 6 Daily
Initial Field Sample Lot - Class 1
Minimum Testing Range (MTR): 9 Initial MTR + 1 Order of Magnitude Extension: 12 Initial MTR + 2 Orders of Magnitude Extension: 15 Initial
Initial Field Sample Lot - Class 1A
Minimum Testing Range (MTR): 5 Initial MTR + 1 Order of Magnitude Extension: 7 Initial MTR + 2 Orders of Magnitude Extension: 9 Initial

TABLE 3-2
NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS
(LINEAR AND ZERO-INTERCEPT)

Continued

Initial Field Sample Lot - Class 1B
Minimum Testing Range (MTR): 6 Initial MTR + 1 Order of Magnitude Extension: 8 Initial MTR + 2 Orders of Magnitude Extension: 10 Initial
Additional Field Sample Lot - Class 1/Class 1A/Class 1B
Minimum Testing Range (MTR): 2 Daily MTR + 1 Order of Magnitude Extension: 2 Daily MTR + 2 Orders of Magnitude Extension: 2 Daily

Key: TRL = Target Reporting Limit
* = 10 percent to 25 percent Range Extension

- When pesticides and PCBs are analyzed, a blank should be analyzed every 12 hours. The laboratory should also alternately analyze a Performance Evaluation Mixture or Standard Mixtures A and B as defined in the USEPA CLP requirements.

- For all other organic methods, a blank and a continuing calibration standard should be analyzed every 12 hours.

In all cases, the standard should meet the limits of acceptability as specified by USAEC Guidelines. If a continuing calibration standard does not meet limits of acceptability after two attempts, analysis should stop until such time as the cause of the abnormality can be corrected. Samples analyzed since the last acceptable calibration should be reanalyzed. Such occurrences will be documented in accordance with USAEC Guidelines.

3.3 Analytical Procedures

Analytical procedures concerning sample preparation, analysis, and reporting must be in accordance with guidelines given in USATHAMA QAP. Analytical methods to be performed at Pace are given in Table 3-3 and are discussed below. USAEC-certified methods and USEPA Methods (Non-THAMA Approved Methods (NTAMs)) will be performed on the samples collected. Pace's SOPs for all analytical methods to be performed on samples from WRF are included in Appendix B.

3.3.1 Analytical Methods

Standard analytical methods to be used for the sample analyses are approved by USAEC and are similar in scope to USEPA methods. NTAMs (SW846 Methods) may be used if lower detection limits are required or if a USAEC method is not available. USEPA guidelines are followed for the analytical procedures of NTAMs. Reporting is accomplished with the NTAM database management system. All NTAM data will be 100% manually validated by EARTH TECH.

The purpose of the laboratory analyses is to identify the types and concentrations of contaminants in soil, sediment, and groundwater. The analytical methods to be performed on soil and water samples collected during the SSI at WRF were chosen based on the site history and the contaminants which have been identified during previous investigations. The contaminants of potential concern include fuels, PCBs and various metals.

3.3.2 Detection Limits

Certified reporting limits (CRLs) are required for all methods prior to sample analysis of USAEC projects to evaluate method performance. Before any analytical system is employed in a survey, sufficient spikes and blanks will be run to statistically establish

TABLE 3-3
SUMMARY OF SOIL AND GROUNDWATER SAMPLE ANALYSES FOR SUPPLEMENTAL SITE INSPECTION ACTIVITIES

Soil	Number of Samples[1]	Number of Replicates/ Duplicates	Number of Rinsate Blanks	Number of Trip Blanks	Number of Ambient Blanks	Total
PHASE I						
Metals by Inductively Coupled Argon Plasma (JS14)	83	8	8	NA	NA	99
Total Petroleum Hydrocarbons (E418.1)	20	2	2	NA	NA	24
Ethylene Glycol by Gas Chromatograph (Modified 8015)	6	1	1	NA	NA	8
Volatile Organic Compounds by Purge and Trap (LM33)	22	2	2	2	NA	28
Acid & Base Neutrals (LM30)	22	2	2	NA	NA	26
Polychlorinated Biphenyls/Pesticides by Gas Chromatograph (LH19)	50	5	5	NA	NA	60
Lead (SW6010)	83	8	8	NA	NA	99
Water	**Number of Samples[1]**	**Number of Replicates/ Duplicates**	**Number of Rinsate Blanks**	**Number of Trip Blanks**	**Number of Ambient Blanks**	**Total**
Metals by Inductively Coupled Argon Plasma (SS15)	1	0	1	NA	NA	2
Total Petroleum Hydrocarbons (E418.1)	1	0	1	NA	NA	2
Ethylene Glycol by Gas Chromatograph (Modified 8015)	1	0	1	NA	NA	2
Volatile Organic Compounds by Purge and Trap (UM05)	1	0	1	1	1	4
Acid & Base Neutrals (UM06)	1	0	1	NA	NA	2
Polychlorinated Biphenyls/Pesticides by Gas Chromatograph (UH21)	1	0	1	NA	NA	2
Lead (SW6010)	1	0	1	NA	NA	2

TABLE 3-3
SUMMARY OF SOIL AND GROUNDWATER SAMPLE ANALYSES FOR SUPPLEMENTAL SITE INSPECTION ACTIVITIES

Continued

Soil	Number of Samples[1]	Number of Replicates/ Duplicates	Number of Rinsate Blanks	Number of Trip Blanks	Number of Ambient Blanks	Total
PHASE II						
Metals by Inductively Coupled Argon Plasma (JS14)	54	6	10	NA	NA	70
Total Petroleum Hydrocarbons (E418.1)	51	5	10	NA	NA	66
Volatile Organic Compounds by Purge and Trap (LM33)	54	6	10	10	10	90
Acid & Base Neutrals (LM30)	54	6	10	NA	NA	70
Polychlorinated Biphenyls/Pesticides by Gas Chromatograph (LH19)	54	6	10	NA	NA	70
Lead (SW6010)	54	6	10	NA	NA	70
Chlorinated Dioxins and Furans (SW8280)	7	1	1	NA	NA	9
Arsenic (SW7060)	54	6	10	NA	NA	70
Mercury (JB06)	54	6	10	NA	NA	70
Cyanide (KY04)	54	6	10	NA	NA	70
Water	**Number of Samples[1]**	**Number of Replicates/ Duplicates**	**Number of Rinsate Blanks**	**Number of Trip Blanks**	**Number of Ambient Blanks**	**Total**
Metals by Inductively Coupled Argon Plasma (SS15)	1	0	1	NA	NA	2
Total Petroleum Hydrocarbons (E418.1)	1	0	1	NA	NA	2
Volatile Organic Compounds by Purge and Trap (UM05)	1	0	1	1	1	4
Acid & Base Neutrals (UM06)	1	0	1	NA	NA	2
Polychlorinated Biphenyls/Pesticides by Gas Chromatograph (UH21)	1	0	1	NA	NA	2
Lead (SW6010)	1	0	1	NA	NA	2
Antimony (SW7041)	1	0	1	NA	NA	2
Selenium (SW6010)	1	0	1	NA	NA	2
Thallium (SW7840)	1	0	1	NA	NA	2
Arsenic (SW6010)	1	0	1	NA	NA	2
Mercury (SB07)	1	0	1	NA	NA	2
Cyanide (TY03)	1	0	1	NA	NA	2

TABLE 3-3
SUMMARY OF SOIL AND GROUNDWATER SAMPLE ANALYSES FOR SUPPLEMENTAL SITE INSPECTION ACTIVITIES

Continued

Soil	Number of Samples[1]	Number of Replicates/ Duplicates	Number of Rinsate Blanks	Number of Trip Blanks	Number of Ambient Blanks	Total
VADEQ RESPONSE ACTION						
Total Petroleum Hydrocarbons (E418.1)	37	4	4	NA	NA	45
Polychlorinated Biphenyls/Pesticides by Gas Chromatograph (LH19)	37	4	4	NA	NA	45
Lead (SW6010)	37	4	4	NA	NA	45
Benzene, Toluene, Ethylbenzene, Xylenes (SW8020)	37	4	4	4	NA	49
Water	**Number of Samples[1]**	**Number of Replicates/ Duplicates**	**Number of Rinsate Blanks**	**Number of Trip Blanks**	**Number of Ambient Blanks**	**Total**
Total Petroleum Hydrocarbons (E418.1)	19	2	2	NA	NA	23
Benzene, Toluene, Ethylbenzene, Xylenes (SW8020)	19	2	2	2	2	27
Lead (SW6010)	19	2	2	NA	NA	23

Key: NA = Not Applicable

the lowest sample concentration which may be reported. This concentration is the CRL. For USAEC projects, CRLs are determined by using the USAEC program with 95 percent confidence limits. This CRL is associated with the entire method and reflects all sample preparation and measurement steps. Therefore, if any procedures or sample preparations used in the method change, the method must be recertified. USEPA methods will be used for samples collected as part of the Virginia Department of Environmental Quality (VADEQ) Response Action due to lower detection limit requirements. Analytical methods and their associated CRLs used at Pace for WRF are listed in Appendix A.

3.4 Laboratory Data Reduction, Validation, and Reporting

A typical sequence of sample analysis through data transmission is shown in Figure 3-1.

3.4.1 Data Reduction

Chemical results in data packages will be submitted to the USAEC Geology and Chemistry Branch from the analytical laboratory. It will be the responsibility of the laboratory data coordinator to check the raw laboratory data for completeness and accuracy. Raw laboratory data will be transferred from the laboratory reports to the IRDMIS chemical data files.

It will be the responsibility of the QA Coordinator and Data Manager to ensure that all data transferred to IRDMIS are transferred correctly. All data transferred will be checked at least once for completeness and accuracy of transfer. IRDMIS data will be record and group checked by the IRDMIS PC Data Entry and Validation System and submitted to Potomac Research, Incorporated when correct.

3.4.2 Data Validation/Review

Pace's system for ensuring valid data includes several levels of review. Each level commands specific action to prevent the unqualified release of erroneous data and to correct any problems discovered during the review process.

All analytical data generated at Pace are extensively checked for accuracy and completeness. The data validation process consists of data generation, reduction, and three levels of review, as described below. All data are ultimately compared to the criteria in 1990 USATHAMA QAP and the specific approved USAEC method. The 1990 USATHAMA QAP also includes a checklist in Appendix T to use in the data review process.

The analyst who generates the analytical data has the prime responsibility for the correctness and completeness of the data. All data are generated and reduced following protocols specified in laboratory SOPs. Each analyst reviews the quality of

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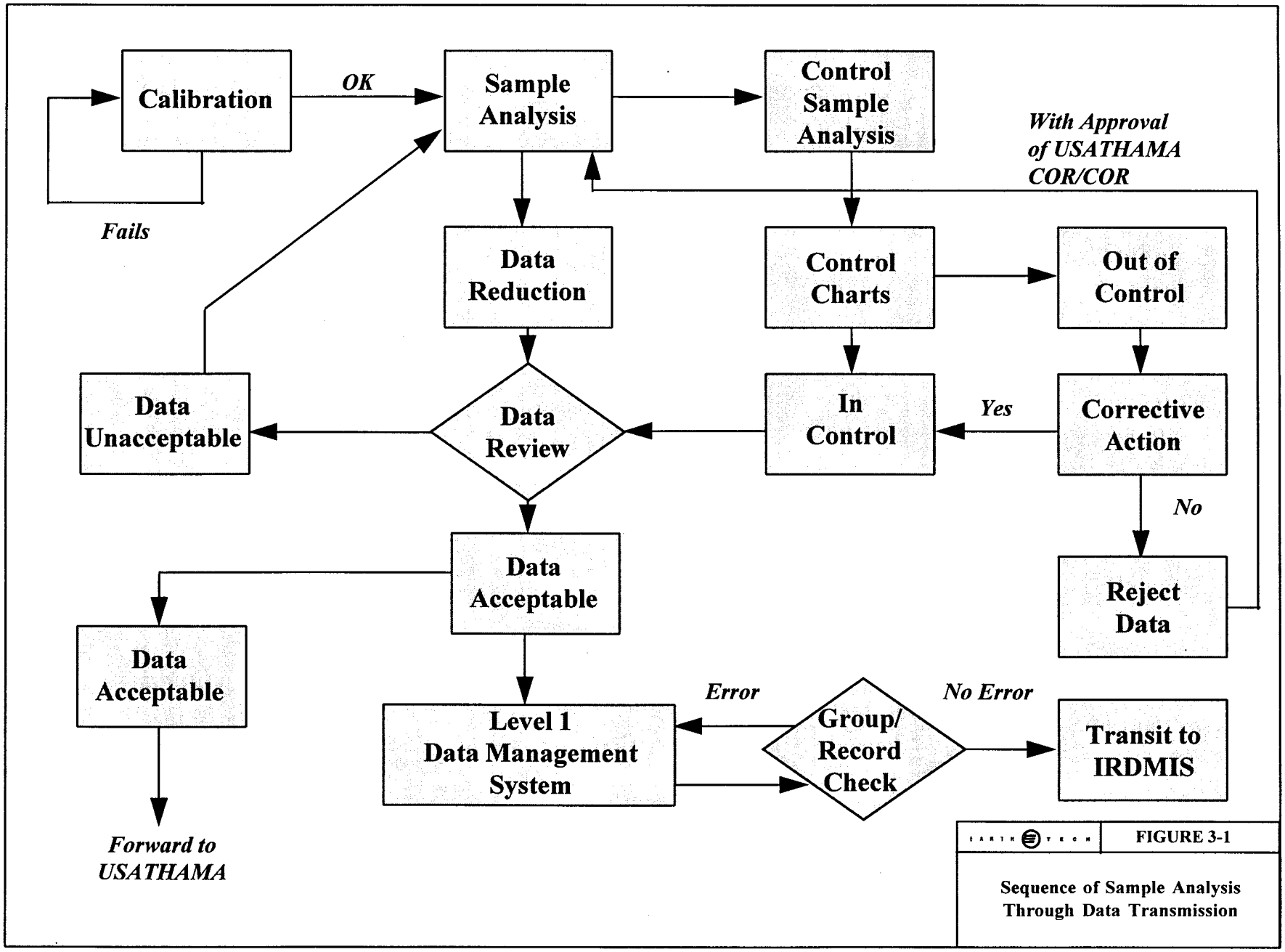

FIGURE 3-1

Sequence of Sample Analysis Through Data Transmission

#0529FIG.3-1

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his or her work based on an established set of guidelines. The analyst reviews the data package to ensure the following items are checked.

- ★ Sample preparation information is correct and complete analysis information is correct and complete.
- ★ The appropriate SOPs have been followed.
- ★ Analytical results are correct and complete.
- ★ QC samples are within established control limits.
- ★ Special sample preparation and analytical requirements have been met.
- ★ Documentation is complete (e.g., all anomalies in the preparation and analysis have been documented, out of control forms, if required, are complete, holding times are documented, etc.).

Upon completion of this initial review step, the analyst will sign Pace's "Data Packet Signoff Sheet". The analyst then passes the data package to a technical reviewer who reviews the package for accuracy. This technical review is structured to ensure the following items.

- ★ Calibration data are scientifically sound, appropriate to the method, and completely documented.
- ★ QC samples are within established guidelines.
- ★ Qualitative identification of sample components is correct.
- ★ Quantitative results are correct.
- ★ Documentation is complete and correct (e.g., anomalies in the preparation and analysis have been documented, out-of-control forms, if required, are complete, holding times are documented, etc.).
- ★ The data are ready for incorporation into the final report.
- ★ The data package is complete and ready for data archive.

If no problems are found with the data package, the review is considered complete. If any problems are found with the data package, an additional 10 percent of the samples are checked to the bench sheet. The process continues until no errors are found or until the data package has been reviewed in its entirety. The signature of

the reviewer and the date of review is recorded on an "Analytical Review" form. The reviewed data are then approved for release and a final report is prepared.

Before the report is released to the client, the Laboratory Project Manager who is responsible for interfacing directly with EARTH TECH reviews the report to ensure that the data meets the overall objectives of the project.

Each step of this review process involves evaluation of data quality based on both the results of the QC data and the professional judgement of those conducting the review. This application of technical knowledge and experience to the evaluation of the data is essential in ensuring that data of high quality are generated consistently.

Due to the necessity to use standard USEPA methods on occasion, EARTH TECH will validate all these data. The validation verifies that holding times have been met, calibration checks are adequate, qualitative and quantitative results are correct, documentation is complete, and QC results are complete and accurate. An additional 10 percent of the USAEC data will be hand validated by EARTH TECH using USEPA Region III Data Validation guidelines.

Data reduction and validation completes the data useability determination. Validation of data requires that appropriate QA/QC and documentation steps were performed in both the laboratory and the field. USAEC chemists trained in validation procedures review control charts to assign data qualifiers. Qualifiers indicate data acceptance, potential limitations of data usage, or rejection when QA/QC criteria are not met. Qualifiers for holding time violations are added automatically by IRDMIS. Flagging codes are assigned by the laboratory to indicate other than usual conditions or results. Data qualifiers and flagging codes become a permanent part of the numeric data (i.e., a value of 7 qualified with an A is always represented as 7A). The following flagging codes are available for use during this effort:

- A Analyte found in trip blank as well as in field samples
- B Analyte found in the method blank or QC blank as well as the sample
- C Analysis was confirmed
- D Duplicate analysis
- F Sample filtered prior to analysis
- G Analyte found in rinse blank as well as field sample
- I Interferences in sample make quantitation and/or identification to be suspect
- J Value is estimated
- K Reported results are affected by interferences or high background
- N Tentatively identified compound (TIC) (match greater than 70 percent)
- P Results less than reporting limit but greater than instrument detection limit (IDL)
- Q Sample interference obscured peak of interest
- R Nontarget compound analyzed for but not detected (GC/MS methods)

S Nontarget compound analyzed for and detected (GC/MS methods)
T Nontarget compound analyzed for but not detected (non-GC/MS methods).
U Analysis is unconfirmed
V Sample subjected to unusual storage/preservation conditions
W Single analyte required from a multi-analyte method
X Analyte recovery outside of certified range but within acceptable limits
Y TIC (match less than 70 percent)
Z Nontarget compound analyzed for and detected (non-GC/MS methods)
1 Result less than CRL but greater than criteria of detection (COD)
2 Ending calibration not within acceptable limits
3 Internal standard(s) not within acceptable limits
4 Analyte quantitated on the secondary column
9 Non-demonstrated/validated method performed for USAEC.

In addition, the following qualifier codes were assigned to some results by the USAEC Chemist to indicate data acceptance or rejection based on IRDMIS errors or problems with control charts.

? Control chart not yet approved by USAEC.
1-9 Number of surrogates failing USEPA CLP criteria (used with Data Qualifier Q).
I The low-spike recovery is high.
J The low-spike recovery is low.
K Missed holding time for extraction and preparation.
L Missed holding time for sample analysis.
M The high-spike recovery is high.
N The high-spike recovery is low.
O Low spike recoveries excessively different.
P High spike recoveries excessively different.
Q Surrogate recovery is outside of normal limits (field samples only)
R Datum is rejected.

The documentation provided by Pace in conjunction with EARTH TECH field records were used to evaluate the following data quality indicators:

- Integrity and stability of the samples
- Instrument performance during sample analyses
- Precision
- Accuracy
- Representativeness
- Completeness
- Comparability.

PROCEDURES FOR HANDLING UNACCEPTABLE DATA

Control charts and calibration curves will be used to review the data and identify outlying results. Quality control charts are prepared by adding a known amount of analyte (spike amount) to reagent water or standard soil (supplied by USAEC). Control limits are statistically calculated using a USAEC-required software package. Out of control samples will be investigated by the analysts.

Results which exceed the warning limits but not the control limits alert the analyst to a potential problem. Sample results are accepted when they fall between warning limits and control limits, but the procedures and standards are checked. If the laboratory control sample exceeds the control limit, the analyst will stop work on the analysis. The analyst and supervisor should investigate potential causes of the problem. After the cause is determined and corrected, samples from the original set are rerun along with duplicate spiked samples and a laboratory control sample.

All QC information will be recorded in the notebooks and printouts in the same format used for sample results. It is the analyst's responsibility to check the QC information against limits for the analysis. When an analysis of a QC sample (blank, spike, check standard, USEPA-traceable standard, replicate, or similar sample) shows that the analysis of that batch of samples is not in control, the analyst will immediately bring the matter to the attention of the supervisor. The supervisor will, if necessary, consult with the QA manager and/or the Laboratory Project Manager to determine whether the analysis can proceed, if selected samples should be rerun, or specific corrective action needs to be taken before analyzing additional samples. Out-of-control analyses must be documented by the supervisor. The analyst or supervisor will file an "Anomaly Report" with the QA Manager.

3.4.3 Laboratory Data Reporting

Reports from Pace shall include the following.

- ★ A copy of the signed chain-of-custody form showing date and time of sample receipt in laboratory.
- ★ A glossary to define the symbols and terms used in the laboratory report.
- ★ Sample collection, extraction and analysis dates.
- ★ A sample data summary (the analytical results for the sample).
- ★ For GC analyses, a separate data summary report shall be provided for each confirmational analysis.

- ★ A QA/QC summary report, providing data on method blanks, check samples, surrogate recoveries, laboratory duplicates, matrix spikes, or matrix spike duplicates (whichever are applicable to the particular method). The QA/QC summary report shall also list laboratory control limits and discuss the corrective actions taken whenever laboratory control limits are exceeded. Results of the standard matrix QC spikes, plotted on control charts, will be submitted to the USAEC Geology and Chemistry Branch no later than 5 days following the week in which they are analyzed.

- ★ The required IRDMIS chemical data files.

- ★ A weekly list of the chemical lots analyzed and the IRDMIS files sent to Potomac Research, Incorporated.

- ★ A weekly list of control charts sent to the USAEC Geology and Chemistry Branch.

- ★ A list of field sample numbers contained in each lot.

3.5 Quality Control For Laboratory Analyses

Internal quality control focuses on ensuring that each chemical measurement has the highest probability of exceeding method protocol in terms of precision and accuracy. Quality control samples such as method blanks, spikes, and duplicates are evaluated and documented on a routine basis. Spike and surrogate recoveries and relative percent difference, as appropriate, are calculated, and this quality control data is compared on an ongoing basis to laboratory-established control limits. Spiking compounds and surrogates must be traceable to SARMs.

3.5.1 Laboratory QA/QC Samples

The following types of QC samples are included in each analytical lot, depending on method class. Table 3-4 specifies the number and concentrations of QC samples required per lot.

- ★ ***Analytical Lot.*** The basic unit for analytical quality control is the analytical lot. Lot size, maximum, is defined as the number of samples, including QC samples, that can be processed through a step of the analytical method during a single time period (not to exceed 1 day) as determined by the time or by the equipment- limiting step of the method. Samples in each lot should be of similar composition.

TABLE 3-4
NUMBERS AND CONCENTRATIONS OF QUALITY CONTROL SAMPLES PER LOT

Class 1
1 - Standard Matrix Method Blank 3 - Standard Matrix Spikes (2, 10, and 10 Certified Reporting Limit) 1 - Standard Matrix Spikes (Extended Range 100 Certified Reporting Limit or Near Method Maxima)
Class 1A
1 - Standard Matrix Method Blank/Spike (0 Certified Reporting Limit Non-surrogate/10 Certified Reporting Limit Surrogate) All - Natural Matrix (Field Sample) Spikes (10 Certified Reporting Limit Surrogate)
Class 1B
1 - Standard Matrix Method Blank 1 - Standard Matrix Spike (10 Certified Reporting Limit)

★ ***Method Blank***. A method blank is an artificial, matrixless sample used to monitor the system for interferences and contamination from glassware, reagents, etc. The method blank is taken through the entire sample preparation process, and is included with each lot of extractions/digestions prepared.

★ ***Spikes***. A matrix spike is a sample to which a known amount of analyte is added and is then carried through the complete analytical method.

★ ***Surrogate Compounds***. For Class 1A only, the analytical process includes the addition, subsequent detection, and recovery calculations of surrogate spiking compounds. Surrogate compounds are added to every sample at the beginning of the sample preparation, and the surrogate recovery is used to monitor matrix effects and sample preparation. Compounds that meet the following criteria are suitable surrogate compounds:

- Compounds not requested for analysis
- Compounds that do not interfere with the determination of required analytes
- Compounds that are not naturally occurring, yet are chemically similar to the required analytes.

★ ***Reagents***. Laboratory reagent water that meets the requirements of ASTM Type II water, as described in the USATHAMA QAP, is checked daily. The resistivity of the water is measured and recorded in a logbook. Blanks are routinely analyzed for purity and accompany each lot tested.

High-purity reagents are purchased as dictated by each test method and are documented by batch, lot number, and supplier, as well as time period of laboratory use (date opened, date depleted). SARMs should be acquired by the laboratory when analyzing samples under the USAEC program, and used whenever possible for internal QC and calibration samples. Standard soil samples are provided by the USAEC Geology and Chemistry Branch.

3.5.2 Control Charts

Where applicable, control charts will be used to monitor the trends and variations in the accuracy and precision of analytical analyses. The control chart shall contain the following:

- Title, analyte, method number, and laboratory name;
- Spike concentration;
- Three-letter lot designation and analysis date for each point along the abscissa;
- Percent recovery (X charts) or Range (R charts) along the ordinate;
- Upper and lower control limits; and
- Upper and lower warning limits.

Criteria and formats for control chart construction can be found in the USAEC Guidelines. Example control charts are included in Appendix C.

3.6 Laboratory Performance and Systems Audits

Performance and systems audits will be used to monitor project activities to assure compliance with the QA objectives and procedures. Audits may be performed by USAEC or EARTH TECH. USATHAMA PAM 11-41 Revision No. 0, dated January 1990, describes external and internal audits as below.

External

External audits are conducted by representatives of the USAEC Geology and Chemistry Branch or their representatives. After reviewing the proposed QAPP, Pace may be visited to ensure that all procedures and practices are being followed. During this visit, the USAEC representatives will complete an audit checklist. Copies of the completed checklist will be provided to the USAEC Project Officer, the EARTH TECH Project Manager, the EARTH TECH Analytical Project Manager, and the USAEC Geology and Chemistry Branch. If deficiencies are of a serious nature, copies will be forwarded to the procurement contracting officer for official documentation and action. The visit may occur before analyses of field samples are initiated by the laboratory.

After initiation of the analyses by the contractor laboratory, a USAEC representative may visit the field activities or the laboratory to evaluate the effective implementation of the QAPP. Any project-related activities may be evaluated during the visit. Any documents or data required by the QAPP are eligible for inspection. Any aspect of the internal audit may be monitored. Findings will be reported to the USAEC Project Officer, the EARTH TECH Project Manager, the EARTH TECH Analytical Project Manager, and the USAEC Geology and Chemistry Branch. If deficiencies are of a serious nature, copies may be forwarded to the procurement contracting officer for official documentation and action.

Scheduling/completion of the visits noted above does not preclude additional visits, as deemed necessary or desirable.

INTERNAL

Audits of critical functions by the laboratory QA staff will include the following.

- ★ Verification that standards, procedures, records, charts, magnetic tapes, etc. are properly maintained.

- ★ Verification that actual practice agrees with written instructions, accomplished through the use of a systems audit where a selected method is monitored through all the steps of its performance. This systems audit must be accomplished at least once each quarter if the laboratory effort is long term, or once a month if the laboratory effort is short term. Methods must be selected so that all phases of a laboratory's effort are monitored to include, but not be limited to, sample logging, chain-of-custody, sample preparation, standard preparation, extract storage and analysis, and data reduction.

- ★ Verification that QA records are adequately filed and maintained so as to assure protection and retrievability.

- ★ Assessment of results of QA sample analyses.

Auditing will consist of observations and notations as to whether approval practices are followed. A formal audit report comprised of summary findings shall be distributed to the Project Manager, Analytical Project Leader, and USAEC. Deviations will be noted and discussed with staff members, appropriate management, and with USAEC. The audit and findings, both compliance and noncompliance, must be documented in a bound logbook, or permanently attached and maintained as part of the QA documentation. The QA office will maintain by project, a file of audit reports and findings. Copies of the report and findings that cover more than one project shall be maintained in each project file. At the conclusion of a project or task order, copies of the QA file shall be transmitted to the USAEC Geology and Chemistry Branch, along with the data packages.

3.7 Corrective Action for Laboratory Activities

Corrective action is dictated by the type and extent of the nonconformance. Corrective action may be initiated and carried out by non-supervisory staff, but final approval and data review by management is necessary before reporting any information. All potentially affected data must be thoroughly reviewed for acceptance or rejection.

A nonconformance is any event whose results fall outside of established laboratory limits. A nonconformance may result from a number of factors including method procedural problems, equipment malfunctions, and operator error. Regardless of the

cause, any activity in the laboratory which adversely affects data quality is considered a nonconformance.

Spike recovery (accuracy) and replicability (precision) plotted on control charts are a means of determining a nonconforming situation. A single mean outside of the modified limits constitutes a nonconformance. QC criteria are included in Appendix D.

Nonconformance may also be encountered in shipping and receiving. If the chain-of-custody is not properly filled out, or if the samples are broken or received without required preservation, a receiving nonconformance report is filled out, and the EARTH TECH Project Manager or the EARTH TECH Analytical Project Manager is informed. Corrective action includes correcting the chain-of-custody, using alternate samples, or even resampling.

Exceeding the required holding times is another example of a nonconformance. The EARTH TECH Project Manager or the EARTH TECH Analytical Project Manager will be informed immediately by the laboratory, so that resampling can be done as soon as possible.

A nonconformance/corrective action report is required to document any nonconforming situation and the corrective actions taken. The documentation must include:

- ★ Definition of the out-of-control event and identification of all affected samples.
- ★ Where the out-of-control incident occurred (department and test name)
- ★ Date of occurrence
- ★ Corrective action taken
- ★ Verification of corrective action and reestablishment of control
- ★ Initials of operating analyst, supervisor, and laboratory QA officer.

Corrective action may take several forms, but the following steps are almost always included:

1. Check the calculations.
2. Check the instrument for proper setup.
3. Reanalyze the control item.

All data generated during an out-of-control situation must be flagged, and when control has been reestablished, a decision made as to whether the data can be used or if reanalysis is required. The decision must be documented on the nonconformance/corrective action report.

SECTION 4.0
IRDMIS DATA MANAGEMENT PLAN

The IRDMIS computerized, environmental database will be used to manage data collected during the SSI. It is an interactive, electronic data management system that stores, checks, and manipulates laboratory analytical results and field data. The IRDMIS provides the advantage of electronic data management to help ensure data integrity, consistency, and completeness.

EARTH TECH and Pace will coordinate field data collection and laboratory analysis to produce the IRDMIS map, geotechnical, and chemical data files that will be used to complete the SSI. The following sections describe the data management that will be used by EARTH TECH and Pace to produce the IRDMIS map, geotechnical, and chemical files.

4.1 THE MAP DATA FILE

The map data file is an integral component of IRDMIS that ensures chemical and geotechnical data correspond to sampling locations at WRF. The map file will also be used to help construct groundwater level elevation and isoconcentration maps.

EARTH TECH will obtain the existing map data file for the WRF and identify the unique designators for each existing monitoring well that will be sampled by EARTH TECH during the SSI.

Once all the sample locations that will be used in the SSI have been identified, EARTH TECH will construct a new map file. The coordinates used in the map file for each new sampling location will initially be derived from the facility map. EARTH TECH will submit this map file to USAEC and Pace. Once the sampling locations are surveyed by EARTH TECH, a new map file containing surveyed coordinates will be submitted to USAEC.

Before any samples are sent to the laboratory for analysis, EARTH TECH field personnel will be given the complete list of sampling location designators recorded in the new map file. These designators will be used on chain-of-custody forms that accompany all samples sent from the field to Pace. The map data file will allow Pace to perform the IRDMIS group checking on chemical data files. IRDMIS group checking requires that the sample designator assigned to an analytical result corresponds to a sample location recorded in the map data file.

4.2 THE GEOTECHNICAL DATA FILES

The following three geotechnical data files are included in the IRDMIS system:

- ★ Field drilling data file
- ★ Well construction data file
- ★ Groundwater stability data file.

The field drilling data file will record all the IRDMIS-required information pertaining to the boreholes that may be drilled during the SSI activities. The well construction file will record all the IRDMIS-required information pertaining to the monitoring wells that may be installed during the SSI activities. The groundwater stability data file records measurements from the ground surface to the potentiometric surface of the aquifer being assessed.

EARTH TECH field personnel will be provided with pre-printed field data forms to ensure that field personnel collect the information required for the IRDMIS geotechnical files. The field data forms will be sent from the field to EARTH TECH to construct the IRDMIS geotechnical data files.

EARTH TECH will use the IRDMIS PC Data Entry and Validation Subsystem to enter the geotechnical data from the field data forms. As an alternative, EARTH TECH will download geotechnical data from the gINT software package which is used to produce computer-based borehole logs. EARTH TECH will use the data codes identified in the IRDMIS User's Guide, Volume II, Data Dictionary.

EARTH TECH will also use the IRDMIS PC Data Entry and Validation Subsystem to perform record and group checking on all constructed geotechnical data files before submittal to the IRDMIS. When performing group checking, the EARTH TECH map data file will be used. If errors are discovered during record and group checking, EARTH TECH will coordinate with the USAEC Project Geologist to identify acceptable and unacceptable errors. EARTH TECH will correct all unacceptable errors before submitting the geotechnical data files electronically to the IRDMIS.

4.3 THE CHEMICAL DATA FILES

Pace will provide the analytical results in chemical data files to the IRDMIS database. These chemical data files will contain all the IRDMIS-required information that results from the analysis of all normal environmental and QA/QC samples collected during the SSI. The chemical files will fully comply with all the IRDMIS requirements with regard to analytical methods, QA/QC information, duplicate and blank sample analyses, lot size, and data reporting. Pace will use the data codes identified in the IRDMIS User's Guide, Volume II, Data Dictionary.

To construct the IRDMIS chemical data files, Pace will interface its laboratory information management system with the IRDMIS to download laboratory data and/or it will use the IRDMIS PC Data Entry and Validation Subsystem to manually enter analytical data.

Pace will use the IRDMIS PC Data Entry and Validation Subsystem to perform record and group checking on all constructed chemical data files before submittal to the IRDMIS. When performing group checking, Pace will use the map data file that EARTH TECH constructed and submitted to the IRDMIS. If errors occur during record and group checking, Pace will coordinate with the USAEC Geology and Chemistry Branch to identify acceptable and unacceptable errors. Once Pace corrects all unacceptable errors for a chemical data file, it will submit the chemical data file electronically to the IRDMIS.

For NTAM samples, the data will be entered into the NTAM database management system. The laboratory is able to customize a NTAM database for use with the IRDMIS PC Data Entry and Validation Subsystem by selecting the desired methods, detection limits, and required minimum and maximum recoveries.

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SECTION 5.0
PREVENTIVE MAINTENANCE

The primary objective of a preventive maintenance program is to help ensure the timely and effective completion of a measurement effort by minimizing the down time of crucial sampling and/or analytical equipment due to expected or unexpected component failure. In implementing this program, efforts are focused in three primary areas: maintenance responsibilities; maintenance schedules; and adequate inventory of critical spare parts and equipment.

5.1 MAINTENANCE RESPONSIBILITIES

Maintenance responsibilities for field equipment are coordinated through an instrument technician who has, as his or her primary duty, responsibility for ensuring that available equipment and instrumentation are ready for use, and that returned equipment is checked out, serviced, and returned to available inventory in a timely manner. Maintenance during use is the responsibility of the project team using the equipment.

Maintenance responsibilities for laboratory equipment are assigned to the respective laboratory managers. The laboratory managers then establish maintenance procedures and schedules for each major equipment item. These are contained in the maintenance logbooks assigned to each instrument.

5.2 MAINTENANCE SCHEDULES

The effectiveness of any maintenance program depends to a large extent on adherence to specific maintenance schedules for each major equipment item. A specific schedule is established for all routine maintenance activities. Other maintenance activities may also be identified as requiring attention on an as-needed basis. Manufacturers' recommendations and/or sample throughput provide the basis for the established maintenance schedules, and manufacturers' service contracts provide primary maintenance for many major instruments (e.g., GC/MS instruments, atomic absorption spectrometers, analytical balances, etc.). Maintenance activities for each instrument are documented in a maintenance log which indicates the required frequency for each procedure and provides for dated entries.

5.3 SPARE PARTS

Along with a schedule for maintenance activities, an adequate inventory of spare parts is required to minimize equipment down time. This inventory emphasizes those parts (and supplies) which are subject to frequent failure, have limited useful lifetimes, or cannot be obtained in a timely manner should failure occur. Backup equipment, spare parts, and other supplies should be brought to the field to every extent possible.

The respective laboratory managers are responsible for maintaining an adequate inventory of necessary spare parts. Sufficient equipment should be on hand to continue analyses in the event that an instrument encounters problems. In addition to backup instrumentation, a supply of spare parts such as gas chromatography columns, fittings, septums; atomic absorption lamps, mirrors, diaphragms; graphite furnace tubes; and other ancillary equipment should be maintained.

SECTION 6.0
QUALITY ASSURANCE REPORTS

Effective management of a field sampling and analytical effort requires timely assessment and review of field and laboratory activities. This will require effective interaction and feedback between the field team members, the Project Manager, the laboratories, and the laboratory QA coordinator.

6.1 QUALITY ASSURANCE REPORTING PROCEDURE

The laboratory project managers and appropriate project team members will be responsible for keeping the Project Manager and project QA coordinator up to date regarding the status of their respective tasks so that quick and effective solutions can be implemented should any data quality problems arise.

Sampling activities will be reviewed on a daily basis by the onsite task leader to determine if the sampling quality control requirements are being fulfilled, such as the proper numbers of blanks and duplicate samples taken for each parameter sampled. All data sheets and logbooks will be reviewed daily. Any needed corrective action will be initiated and documented daily.

The laboratory project managers/QA officers have the responsibility of reviewing all laboratory analytical activities to ensure compliance with the QC requirements outlined in this QAPP. This review serves as a control function in that it should be conducted frequently so deviations from method requirements will be immediately identified and corrected.

A summary report detailing the sampling and analysis status and any QA/QC problems will be prepared by the project QA coordinator after receipt of the field and laboratory reports and review of the analytical data reports, and sent to the Project Manager.

6.2 REPORT CONTENT

As appropriate, the required periodic reports shall contain information on the status of the project and any quality problems. This includes:

- ★ Activities and general program status
- ★ Calibration and QC data problems
- ★ Unscheduled maintenance activities

- ★ Corrective action activities
- ★ Status of any unresolved problems
- ★ Assessment and summary of data completeness
- ★ Any significant QA/QC problems and recommended and/or implemented solutions not included above.

The auditor will prepare audit reports following each performance and systems audit which address the audit results and provide a qualitative assessment of overall system performance. These reports will be submitted to the laboratory project manager for laboratory audits, and to the EARTH TECH Project Manager for field audits.

Problems requiring swift resolution will be brought to the immediate attention of the appropriate manager via the nonconformance reporting/corrective action scheme discussed in Section 2.6.

SECTION 7.0
REFERENCES AND ACRONYMS AND ABBREVIATIONS

EARTH TECH, 1995. Final Phase I Supplemental Site Inspection Operations Plan.

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LIST OF ACRONYMS AND ABBREVIATIONS

AB	Ambient Blanks
AREE	Area Requiring Environmental Evaluation
ASTM	American Society for Testing and Materials
C/SS	Calibration/Service Specification
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
COD	Criteria of Detection
CRL	Certified Reporting Limit
DQO	Data Quality Objective
DSMOA	Department of Defense and State Memorandum of Agreement
GC/MS	Gas Chromatography/Mass Spectrometry
ICP	Inductively Coupled Plasma
IDL	Instrument Detection Limit
IRDMIS	Installation Restoration Data Management Information System
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
NIST	National Institute for Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NTAM	Non-THAMA Approved Method
OVA	Organic Vapor Analyzer
PCB	Polychlorinated Biphenyl
QA	Quality Assurance
QAP	Quality Assurance Plan
QAPP	Quality Assurance Project Plan
QC	Quality Control
RB	Rinsate Blanks
RPD	Relative Percent Difference
SARM	Standard Analytical Reference Material
SOP	Standard Operating Procedure
SOV	Soil Organic Vapor
SSI	Supplemental Site Inspection
TB	Trip Blanks
TIC	Tentatively Identified Compound
TSAP	Technical Sampling and Analysis Plan
µg/L	Micrograms per liter
USAEC	U.S. Army Environmental Center
USATHAMA	U.S. Army Toxic and Hazardous Material Agency
USEPA	U.S. Environmental Protection Agency
VADEQ	Virginia Department of Environmental Quality
VDWM	Virginia Department of Waste Management
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WRF	Woodbridge Research Facility

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FINAL

QUALITY ASSURANCE/QUALITY CONTROL PLAN

WOODBRIDGE RESEARCH FACILITY, VIRGINIA

VOLUME II: APPENDICES

Prepared By:

EARTH TECH
1420 King Street, Suite 600
Alexandria, Virginia 22314

Prepared For:

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland 21010

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APPENDIX A

PACE, INCORPORATED ANALYTICAL METHODS AND CRLS

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TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
JS14	METALS/SOIL/ICP	Aluminum	SO	µg/g	10.7
	METALS/SOIL/ICP	Barium	SO	µg/g	5.42
	METALS/SOIL/ICP	Beryllium	SO	µg/g	0.25
	METALS/SOIL/ICP	Calcium	SO	µg/g	118
	METALS/SOIL/ICP	Cadmium	SO	µg/g	1.0
	METALS/SOIL/ICP	Cobalt	SO	µg/g	2.5
	METALS/SOIL/ICP	Chromium	SO	µg/g	1.0
	METALS/SOIL/ICP	Copper	SO	µg/g	3.77
	METALS/SOIL/ICP	Iron	SO	µg/g	12.0
	METALS/SOIL/ICP	Potassium	SO	µg/g	142.0
	METALS/SOIL/ICP	Magnesium	SO	µg/g	138.0
	METALS/SOIL/ICP	Manganese	SO	µg/g	0.5
	METALS/SOIL/ICP	Molybdenum	SO	µg/g	4.0
	METALS/SOIL/ICP	Sodium	SO	µg/g	50.0
	METALS/SOIL/ICP	Nickel	SO	µg/g	7.5
	METALS/SOIL/ICP	Lead	SO	µg/g	10.0
	METALS/SOIL/ICP	Antimony	SO	µg/g	82.9
	METALS/SOIL/ICP	Selenium	SO	µg/g	18.8
	METALS/SOIL/ICP	Thallium	SO	µg/g	12.5
	METALS/SOIL/ICP	Vanadium	SO	µg/g	2.0
	METALS/SOIL/ICP	Zinc	SO	µg/g	4.0
	METALS/SOIL/TCP	Arsenic	SO	µg/g	12.7
LH19	ORGANIC/SOIL/ECD	∝-Benzene Hexachloride	SO	µg/g	0.0225
	ORGANIC/SOIL/ECD	∝-Chlordane	SO	µg/g	0.0040
	ORGANIC/SOIL/ECD	Endosulfan I	SO	µg/g	0.0047
	ORGANIC/SOIL/ECD	Aldrin	SO	µg/g	0.0130
	ORGANIC/SOIL/ECD	β-Benzenehexachloride	SO	µg/g	0.0054
	ORGANIC/SOIL/ECD	Endosulfan II	SO	µg/g	0.0071
	ORGANIC/SOIL/ECD	Decachlorobiphenyl	SO	µg/g	0.0069
	ORGANIC/SOIL/ECD	2,4,5,6-Tetrachlorometaxylene	SO	µg/g	0.0071

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
LH19 (Cont.)	ORGANIC/SOIL/ECD	Δ-Benzenehexachloride	SO	µg/g	0.0228
	ORGANIC/SOIL/ECD	Dieldrin	SO	µg/g	0.0078
	ORGANIC/SOIL/ECD	Endrin	SO	µg/g	0.0111
	ORGANIC/SOIL/ECD	Endrin Aldehyde	SO	µg/g	0.0276
	ORGANIC/SOIL/ECD	Endrin Ketone	SO	µg/g	0.0061
	ORGANIC/SOIL/ECD	Endosulfan Sulfate	SO	µg/g	0.0130
	ORGANIC/SOIL/ECD	V-Chlordane	SO	µg/g	0.0214
	ORGANIC/SOIL/ECD	Heptachlor	SO	µg/g	0.0096
	ORGANIC/SOIL/ECD	Heptachlor Epoxide	SO	µg/g	0.0039
	ORGANIC/SOIL/ECD	Lindane	SO	µg/g	0.0200
	ORGANIC/SOIL/ECD	Methoxychlor	SO	µg/g	0.211
	ORGANIC/SOIL/ECD	ppDDD	SO	µg/g	0.0112
	ORGANIC/SOIL/ECD	2,2-Bis(p-chlorophenyl)-1,1-dichloroethene	SO	µg/g	0.014
	ORGANIC/SOIL/ECD	2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane	SO	µg/g	0.0096
	ORGANIC/SOIL/ECD	Toxaphene	SO	µg/g	0.250
	ORGANIC/SOIL/ECD	PCB-1016	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1221	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1232	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1242	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1248	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1254	SO	µg/g	0.0500
	ORGANIC/SOIL/ECD	PCB-1260	SO	µg/g	0.0500
LM30	SEMIVOLATILES/SOIL/GCMS	1,2,4-Trichlorobenzene	SO	µg/g	0.29
	SEMIVOLATILES/SOIL/GCMS	1,2-Dichlorobenzene	SO	µg/g	0.32
	SEMIVOLATILES/SOIL/GCMS	1,3-Dichlorobenzene	SO	µg/g	0.58
	SEMIVOLATILES/SOIL/GCMS	1,4-Dichlorobenzene	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	2,4,5-Trichlorophenol	SO	µg/g	0.24
	SEMIVOLATILES/SOIL/GCMS	2,4,6-Tribromophenol	SO	µg/g	0.35
	SEMIVOLATILES/SOIL/GCMS	2,4,6-Trichlorophenol	SO	µg/g	0.29

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
LM30 (Cont.)	SEMIVOLATILES/SOIL/GCMS	2,4-Dichlorophenol	SO	µg/g	0.28
	SEMIVOLATILES/SOIL/GCMS	2,4-Dimethylphenol	SO	µg/g	0.34
	SEMIVOLATILES/SOIL/GCMS	2,4-Dinitrotoluene	SO	µg/g	0.31
	SEMIVOLATILES/SOIL/GCMS	2,6-Dinitrotoluene	SO	µg/g	0.20
	SEMIVOLATILES/SOIL/GCMS	2-Chlorophenol	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	2-Chloronaphthalene	SO	µg/g	0.33
	SEMIVOLATILES/SOIL/GCMS	2-Fluorobiphenyl	SO	µg/g	0.18
	SEMIVOLATILES/SOIL/GCMS	2-Fluorophenol	SO	µg/g	0.35
	SEMIVOLATILES/SOIL/GCMS	2-Methylnaphthalene	SO	µg/g	0.14
	SEMIVOLATILES/SOIL/GCMS	2-Cresol	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	2-Nitroaniline	SO	µg/g	0.36
	SEMIVOLATILES/SOIL/GCMS	2-Nitrophenol	SO	µg/g	0.26
	SEMIVOLATILES/SOIL/GCMS	2-Methyl-4,6-dinitrophenol	SO	µg/g	0.84
	SEMIVOLATILES/SOIL/GCMS	4-Bromophenyl phenyl ether	SO	µg/g	0.13
	SEMIVOLATILES/SOIL/GCMS	3-Methyl-4-chlorophenol	SO	µg/g	0.23
	SEMIVOLATILES/SOIL/GCMS	4-Chlorophenyl phenyl ether	SO	µg/g	0.20
	SEMIVOLATILES/SOIL/GCMS	4-Cresol	SO	µg/g	0.18
	SEMIVOLATILES/SOIL/GCMS	4-Nitrophenol	SO	µg/g	2.4
	SEMIVOLATILES/SOIL/GCMS	Acenaphthene	SO	µg/g	0.27
	SEMIVOLATILES/SOIL/GCMS	Acenaphthylene	SO	µg/g	0.27
	SEMIVOLATILES/SOIL/GCMS	Anthracene	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Bis(2-chloroethyoxy)methane	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Bis(2-chloroisopropyl)ether	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Bis(2-chloroethyl)ether	SO	µg/g	1.6
	SEMIVOLATILES/SOIL/GCMS	Bis(2-ethylhexyl)phthalate	SO	µg/g	0.19
	SEMIVOLATILES/SOIL/GCMS	Benzo[a]anthracene	SO	µg/g	0.12
	SEMIVOLATILES/SOIL/GCMS	Benzo[a]pyrene	SO	µg/g	0.24

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
LM30 (Cont.)	SEMIVOLATILES/SOIL/GCMS	Benzo[b]fluoranthene	SO	µg/g	0.73
	SEMIVOLATILES/SOIL/GCMS	Butlybenzyl Phthalate	SO	µg/g	0.20
	SEMIVOLATILES/SOIL/GCMS	Benzoic Acid	SO	µg/g	0.92
	SEMIVOLATILES/SOIL/GCMS	Benzo[g,h,i]perylene	SO	µg/g	0.25
	SEMIVOLATILES/SOIL/GCMS	Benzo[k]fluoranthene	SO	µg/g	0.40
	SEMIVOLATILES/SOIL/GCMS	Benzyl Alcohol	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Chrysene	SO	µg/g	0.26
	SEMIVOLATILES/SOIL/GCMS	Hexachlorobenzene	SO	µg/g	0.26
	SEMIVOLATILES/SOIL/GCMS	Hexachlorocyclopentadiene	SO	µg/g	1.8
	SEMIVOLATILES/SOIL/GCMS	Hexachloroethane	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Dibenz[a,h]anthracene	SO	µg/g	0.27
	SEMIVOLATILES/SOIL/GCMS	Dibenzofuran	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Diethyl Phthalate	SO	µg/g	0.35
	SEMIVOLATILES/SOIL/GCMS	Dimethyl Phthalate	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Di-n-butyl Phthalate	SO	µg/g	0.52
	SEMIVOLATILES/SOIL/GCMS	Di-n-octyl Phthalate	SO	µg/g	0.22
	SEMIVOLATILES/SOIL/GCMS	Fluoranthene	SO	µg/g	0.60
	SEMIVOLATILES/SOIL/GCMS	Fluorene	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Hexachlorobutadiene	SO	µg/g	0.28
	SEMIVOLATILES/SOIL/GCMS	Indeno[1,2,3-c,d]pyrene	SO	µg/g	0.15
	SEMIVOLATILES/SOIL/GCMS	Isophorone	SO	µg/g	0.32
	SEMIVOLATILES/SOIL/GCMS	Naphthalene	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Nitrobenzene	SO	µg/g	0.19
	SEMIVOLATILES/SOIL/GCMS	Nitrobenzene-d5	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	N-nitrosodi-n-proplamine	SO	µg/g	1.1
	SEMIVOLATILES/SOIL/GCMS	N-nitrosodiphenylamine	SO	µg/g	0.13
	SEMIVOLATILES/SOIL/GCMS	Pentachlorophenol	SO	µg/g	0.48
	SEMIVOLATILES/SOIL/GCMS	Phenanthrene	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Phenol-d5	SO	µg/g	0.17
	SEMIVOLATILES/SOIL/GCMS	Phenol	SO	µg/g	0.17

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
LM30 (Cont.)	SEMIVOLATILES/SOIL/GCMS	Pyrene	SO	µg/g	0.97
	SEMIVOLATILES/SOIL/GCMS	Terphenyl-d14	SO	µg/g	0.74
LM33	VOLATILES/SOIL/GCMS	1,1,1-Trichloroethane	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	1,1,2-Trichloroethane	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	1,1-Dichloroethene	SO	µg/g	0.032
	VOLATILES/SOIL/GCMS	1,1-Dichloroethane	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	1,2-Dichloroethane-d4	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	1,2-Dichloroethane	SO	µg/g	0.0027
	VOLATILES/SOIL/GCMS	1,2-Dichloropropane	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	4-Bromofluorobenzene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Acetone	SO	µg/g	0.044
	VOLATILES/SOIL/GCMS	Bromodichloromethane	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	cis-1,2-Dichloroethene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	cis-1,3-Dichloropropene	SO	µg/g	0.0030
	VOLATILES/SOIL/GCMS	Chloroethene	SO	µg/g	0.0038
	VOLATILES/SOIL/GCMS	Chloroethane	SO	µg/g	0.0029
	VOLATILES/SOIL/GCMS	Benzene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Carbon Tetrachloride	SO	µg/g	0.0031
	VOLATILES/SOIL/GCMS	Methylene Chloride	SO	µg/g	0.00616
	VOLATILES/SOIL/GCMS	Bromomethane	SO	µg/g	0.0031
	VOLATILES/SOIL/GCMS	Chloromethane	SO	µg/g	0.035
	VOLATILES/SOIL/GCMS	Bromoform	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Chloroform	SO	µg/g	0.00265
	VOLATILES/SOIL/GCMS	Chlorobenzene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Carbon Disulfide	SO	µg/g	0.014
	VOLATILES/SOIL/GCMS	Dibromochloromethane	SO	µg/g	0.057
	VOLATILES/SOIL/GCMS	Ethylbenzene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Toluene-d8	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Toluene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Methyl Ethyl Ketone	SO	µg/g	0.0025

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
LM33 (Cont.)	VOLATILES/SOIL/GCMS	Methyl Isobutyl Ketone	SO	µg/g	0.0186
	VOLATILES/SOIL/GCMS	2-Hexanone	SO	µg/g	0.018
	VOLATILES/SOIL/GCMS	Styrene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	trans-1,2-Dichloroethene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	trans-1,3-Dichloropropene	SO	µg/g	0.002
	VOLATILES/SOIL/GCMS	Tetrachloroethane	SO	µg/g	0.011
	VOLATILES/SOIL/GCMS	Tetrachloroethene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Trichloroethene	SO	µg/g	0.0025
	VOLATILES/SOIL/GCMS	Xylene, Total Combined	SO	µg/g	0.0075
SW7421		Lead	SO	µg/g	0.7
SW8020	AROMATIC VOLATILES	Benzene	SO	µg/g	0.0042
	AROMATIC VOLATILES	Toluene	SO	µg/g	0.0039
	AROMATIC VOLATILES	Ethylbenzene	SO	µg/g	0.0039
	AROMATIC VOLATILES	Total Xylenes	SO	µg/g	0.0037
SW8290	DIOXINS/FURANS	2,3,7,8-TCDD	SO	ng/kg	1.0
	DIOXINS/FURANS	1,2,3,7,8-Penta-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,4,7,8-Hexa-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,6,7,8-Hexa-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,7,8,9-Hexa-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,4,6,7,8-Hepta-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	Octa-CDD	SO	ng/kg	2.5
	DIOXINS/FURANS	2,3,7,8-TCDF	SO	ng/kg	1.0
	DIOXINS/FURANS	1,2,3,7,8-Penta-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	2,3,4,7,8-Penta-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,4,7,8-Hexa-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,6,7,8-Hexa-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	2,3,4,6,7,8-Hexa-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,7,8,9-Hexa-CDF	SO	ng/kg	2.5

TABLE A-1
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR SOIL

Method Number	Method Name	Test Name	Matrix	Units	CRL
SW8290 (Cont.)	DIOXINS/FURANS	1,2,3,4,6,7,8-Hepta-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	1,2,3,4,7,8,9-Hepta-CDF	SO	ng/kg	2.5
	DIOXINS/FURANS	Octa-CDF	SO	ng/kg	5.0
	DIOXINS/FURANS	Total MonoCDD (2 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total DICDD (10 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total TriCDD (14 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total TetraCDD (22 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total PeCDD (14 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total HxCDD (10 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total HpCDD (2 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total MonoCDF (4 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total DiCDF (16 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total TriCDF (28 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total TetraCDF (38 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total PeCDF (28 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total HxCDF (16 isomers)	SO	ng/kg	5.0
	DIOXINS/FURANS	Total HpCDF (4 isomers)	SO	ng/kg	5.0

TABLE A-2
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR GROUNDWATER

Method Number	Method Name	Test Name	Matrix	Units	CRL
UH21	ORGANIC/WATER/ECD	∝-Benzene Hexachloride	WA	µg/L	0.0434
	ORGANIC/WATER/ECD	∝-Chlordane	WA	µg/L	0.0202
	ORGANIC/WATER/ECD	Endosulfan I	WA	µg/L	0.00856
	ORGANIC/WATER/ECD	Aldrin	WA	µg/L	0.0638
	ORGANIC/WATER/ECD	β-Benzenehexachloride	WA	µg/L	0.0109
	ORGANIC/WATER/ECD	Endosulfan II	WA	µg/L	0.0120
	ORGANIC/WATER/ECD	Decachlorobiphenyl	WA	µg/L	0.0140
	ORGANIC/WATER/ECD	2,4,5,6-Tetrachlorometaxylene	WA	µg/L	0.0767
	ORGANIC/WATER/ECD	∆-Benzenehexachloride	WA	µg/L	0.0488
	ORGANIC/WATER/ECD	Dieldrin	WA	µg/L	0.0321
	ORGANIC/WATER/ECD	Endrin	WA	µg/L	0.0372
	ORGANIC/WATER/ECD	Endrin Aldehyde	WA	µg/L	0.0697
	ORGANIC/WATER/ECD	Endrin Ketone	WA	µg/L	0.0282
	ORGANIC/WATER/ECD	Endosulfan Sulfate	WA	µg/L	0.0200
	ORGANIC/WATER/ECD	∨-Chlordane	WA	µg/L	0.0450
	ORGANIC/WATER/ECD	Heptachlor	WA	µg/L	0.0631
	ORGANIC/WATER/ECD	Heptachlor Epoxide	WA	µg/L	0.006
	ORGANIC/WATER/ECD	Lindane	WA	µg/L	0.0429
	ORGANIC/WATER/ECD	Methoxychlor	WA	µg/L	0.267
	ORGANIC/WATER/ECD	ppDDD	WA	µg/L	0.0848
	ORGANIC/WATER/ECD	2,2-Bis(p-chlorophenyl)-1,1-dichloroethene	WA	µg/L	0.0946
	ORGANIC/WATER/ECD	2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane	WA	µg/L	0.0316
	ORGANIC/WATER/ECD	Toxaphene	WA	µg/L	0.6
	ORGANIC/WATER/ECD	PCB-1016	WA	µg/L	0.859
	ORGANIC/WATER/ECD	PCB-1221	WA	µg/L	0.200
	ORGANIC/WATER/ECD	PCB-1232	WA	µg/L	0.100
	ORGANIC/WATER/ECD	PCB-1242	WA	µg/L	0.100

TABLE A-2
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR GROUNDWATER

Method Number	Method Name	Test Name	Matrix	Units	CRL
UH21 (Cont.)	ORGANIC/WATER/ECD	PCB-1248	WA	µg/L	0.100
	ORGANIC/WATER/ECD	PCB-1254	WA	µg/L	0.100
	ORGANIC/WATER/ECD	PCB-1260	WA	µg/L	0.137
UM06	SEMIVOLATILES/WATER/GCMS	Phenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Bis(2-chloroethyl)ether	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2-Chlorophenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	1,3-Dichlorobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	1,4-Dichlorobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzyl Alcohol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	1,2-Dichlorobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2-Methylphenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Bis(2-chloroisopropyl)ether	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Methylphenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	N-Nitroso-di-n-propylamine	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Hexachloroethane	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Nitrobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Isophorone	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2-Nitrophenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,4-Dimethylphenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzoic Acid	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	Bis(2-chloroethoxy)methane	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,4-Dichlorophenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	1,2,4-Trichlorobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Naphthalene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Chloroaniline	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Hexachlorobutadiene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Chloro-3-methylphenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2-Methylnaphthalene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Hexachlorocyclopentadiene	WA	µg/L	10

TABLE A-2
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR GROUNDWATER

Method Number	Method Name	Test Name	Matrix	Units	CRL
UM06 (Cont.)	SEMIVOLATILES/WATER/GCMS	2,4,6-Trichlorophenol	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,4,5-Trichlorphenol	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	2-Chloronaphthalene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2-Nitroaniline	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	Dimethylphthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Acenaphthylene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	3-Nitroaniline	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	Acenaphthene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,4-Dinitrophenol	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	4-Nitrophenol	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	Dibenzofuran	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,4-Dinitrotoluene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	2,6-Dinitrotoluene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Diethylphthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Chlorphenyl-phenylether	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Fluorene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Nitroaniline	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	4,6-Dinitro-2-methylphenol	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	N-Nitrosodiphenylamine	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	4-Bromophenyl-phenylether	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Hexachlorobenzene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Pentachlorophenol	WA	µg/L	50
	SEMIVOLATILES/WATER/GCMS	Phenanthrene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Anthracene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Di-n-butyl Phthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Fluoranthene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Pyrene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Butylbenzylphthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	3,3'-Dichlorobenzidine	WA	µg/L	20

TABLE A-2
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR GROUNDWATER

Method Number	Method Name	Test Name	Matrix	Units	CRL
UM06 (Cont.)	SEMIVOLATILES/WATER/GCMS	Benzo(a)anthracene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Bis(2-ethylhexyl)phthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Chrysene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Di-n-octylphthalate	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzo(b)fluoroanthene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzo(k)fluoroanthene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzo(a)pyrene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Indene(1,2,3-c,d)pyrene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Dibenz(a,h)anthracene	WA	µg/L	10
	SEMIVOLATILES/WATER/GCMS	Benzo(g,h,i)perylene	WA	µg/L	10
UM05	VOLATILES/WATER/GCMS	1,1,1-Trichloroethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,1,2-Trichloroethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,1-Dichloroethene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,1-Dichloroethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,2-Dichloroethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,2-Dichloropropane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Acetone	WA	µg/L	10
	VOLATILES/WATER/GCMS	Bromodichloromethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	cis-1,2-Dichloroethene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	cis-1,3-Dichloropropene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Vinyl Chloride	WA	µg/L	10
	VOLATILES/WATER/GCMS	Chloroethane	WA	µg/L	10
	VOLATILES/WATER/GCMS	Benzene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Carbon Tetrachloride	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Methylene Chloride	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Bromomethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Chloromethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Bromoform	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Chloroform	WA	µg/L	5.0

TABLE A-2
PACE, INCORPORATED ANALYTICAL METHODS AND CRLS FOR GROUNDWATER

Method Number	Method Name	Test Name	Matrix	Units	CRL
UM05 (Cont.)	VOLATILES/WATER/GCMS	Chlorobenzene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Carbon Disulfide	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Dibromochloroemethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Ethylbenzene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Toluene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	2-Butanone	WA	µg/L	10
	VOLATILES/WATER/GCMS	4-Methyl-2-pentanone	WA	µg/L	10
	VOLATILES/WATER/GCMS	2-Hexanone	WA	µg/L	10
	VOLATILES/WATER/GCMS	Styrene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	trans-1,2-Dichloroethene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	trans-1,3-Dichloropropene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	1,1,2,2-Tetrachloroethane	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Tetrahcloroethene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Trichloroethene	WA	µg/L	5.0
	VOLATILES/WATER/GCMS	Total Xylenes	WA	µg/L	5.0
SW7421		Lead	WA	µg/L	4.0
SW8020	AROMATIC VOLATILES	Benzene	WA	µg/L	0.0042
	AROMATIC VOLATILES	Toluene	WA	µg/L	0.0039
	AROMATIC VOLATILES	Ethylbenzene	WA	µg/L	0.0039
	AROMATIC VOLATILES	Total Xylenes	WA	µg/L	0.0037

APPENDIX B

PACE STANDARD OPERATING PROCEDURES

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COPY

DETERMINATION OF METALS IN SOIL
BY INDUCTIVELY COUPLED ARGON PLASMA EMISSION SPECTROSCOPY (ICP)

I. SUMMARY

Method JS14

A. ANALYTES

This method is applicable to the analysis of the following elements:

ELEMENT	USATHAMA TEST NAME
Aluminum	Al
Arsenic	As
Barium	Ba
Beryllium	Be
Calcium	Ca
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Potassium	K
Magnesium	Mg
Manganese	Mn
Molybdenum	Mo
Sodium	Na
Nickel	Ni
Lead	Pb
Antimony	Sb
Selenium	Se
Thallium	Tl
Vanadium	V
Zinc	Zn

B. MATRIX

This method is applicable to the quantitative determination of the selected metals in environmental soil samples.

C. GENERAL METHOD

This method employs sample digestion using nitric (HNO_3) and hydrochloric (HCL) acid followed by digestate analysis by ICP.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration ranges in standard soil are given in Table 1.

B. SENSITIVITY

The instrument response for each element at the certfied reporting limit is given in Table 1.

C. REPORTING LIMIT

The certified reporting limit (CRL) and the upper certifed reporting limit (UCRL) determined for each element is given in Table 1.

D. INTERFERENCES

ICP interference can be any unwanted radiation that reaches the photomultiplier tubes. Interferences can arise from physical sources or as true spectral interferences. These are compensated for by measuring emission intensity on both sides of each analytical line. The average radiation detected "off-center" is subtracted from the intensity measurement taken at the analytical line. No major interferences were encountered during certification of this method.

TABLE 1. TESTED CONCENTRATION RANGE AND INSTRUMENT SENSITIVITY

Analyte	Tested Concentration Range (ug/g)	CRL (ug/g)	UCRL (ug/g)	Instrument Response at CRL	Wavelength(nm)
[a] Al	1.12 to 4,500	10.7	4500	290	396.152
As	5.00 to 1,000	12.7	1000	560	193.759
Ba	2.00 to 1,000	5.42	1000	350	233.527
Be	0.250 to 1,000	0.250	1000	40	234.861
Ca	50.0 to 5,000	118	5000	2900	422.673
Cd	1.00 to 500	1.00	500	130	228.880
Co	2.50 to 5,000	2.50	5000	60	237.862
Cr	0.250 to 500	0.974	500	60	267.716
Cu	2.00 to 1,000	3.77	1000	340	324.754
[a] Fe	0.250 to 1,000	12.0	1000	7	259.940
K	125.0 to 5,000	142	5000	64	766.491
Mg	50.0 to 5,000	138	5000	640	279.079
[a] Mn	0.0500 to 200	0.511	200	320	257.610
Mo	4.00 to 800	4.00	800	110	202.030
Na	50.0 to 5,000	50.0	5000	440	589.592
Ni	7.50 to 1,500	7.50	1500	170	231.604
Pb	10.0 to 500	10.0	500	130	220.353
Sb	15.0 to 6,000	82.9	6000	820	206.833
Se	18.8 to 7,500	18.8	7500	160	196.090
Tl	10.0 to 4,000	12.5	4000	99	190.864
V	2.00 to 2,000	2.00	2000	91	292.402
Zn	4.00 to 2,000	4.00	2000	910	213.856

[a] These control limits are those for water due to high background concentrations of these analytes in the standard soil.

E. ANALYSIS RATE

The maximum lot size shall be 40 samples. The rate limiting step, ICP analysis, is based on approximately 5 samples being analyzed per hour over an eight hour period.

F. SAFETY INFORMATION

Precautions must be taken due to the corrosive nature of the acid solutions and the potential hazardous nature of environmental samples. Proper laboratory apparel will be worn by all analysts (with safety glasses and lab coats as the minimum). Digestions must be performed in a fume hood.

The laboratory maintains a current file of OSHA regulations regarding the safe handling of chemicals. Material Safety Data Sheets are available to laboratory personnel.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Beakers, (150 mL)
2. Hot Plate
3. Macropipetter with disposable tips
4. Disposable beakers (50 mL)
5. Class A volumetric flasks, as appropriate
6. Class A volumetric pipettes, as appropriate
7. 65 mm watch glass

B. INSTRUMENTATION

ARL 3410 ICP with minitorch (or equivalent). Operating conditions are in accordance with manufacturer's recommendations.

The instrument parameters are initially adjusted to the following settings. Some modifications may be made to optimize analysis conditions.

Incident RF power: 650 Watts

Reflected RF power: 0 Watts

Sample Argon flow rate: 0.8L/minute

Coolant Argon flow rate: 7.5L/minute

C. ANALYTES

The Chemical Abstract Service (CAS) registry numbers and basic physical properties for each element given in Table 2.

D. REAGENTS AND SARMS:

1. Nitric Acid (70.0-71.0%), Baker Instra-Analyzed, or equivalent.

2. Hydrochloric Acid (36.5-38.0%), Baker Instra-Analyzed, or equivalent.

3. ASTM Type I water.

4. Hydrogen peroxide (30%), Mallinckrodt AR, or equivalent.

5. USATHAMA Standard Soil.

6. The primary analytical standard solutions used for certification are given in Tables 3, 4, 5 and 7. All standard solutions used will be NIST traceable and certificates of lot analysis will be maintained in a file.

TABLE 2. CAS REGISTRY NUMBERS AND PHYSICAL PROPERTIES OF TARGET ANALYTES

Analyte	Atomic Weight	CAS Registry Number	M.P.°C
Al	26.98	7429-90-5	660
As	74.92	7440-38-2	817
Ba	137.3	7440-39-3	725
Be	9.01	7440-41-77	1287
Ca	40.08	7440-70-2	845
Cd	112.4	7440-43-9	321
Co	58.93	7440-48-4	1493
Cr	52.0	7440-47-3	1900
Cu	63.54	7440-50-8	1083
Fe	55.8	7339-89-6	1535
K	39.1	7440-09-7	63.7
Mg	24.3	7439-95-4	648
Mn	54.9	7439-96-5	1244
Mo	95.94	7439-98-7	2622
Na	23.0	7440-23-5	97.8
Ni	58.7	7740-02-0	1555
Pb	207.19	7739-92-1	327.4
Sb	121.75	7740-36-0	630.7
Se	78.96	7782-49-2	217
Tl	204.4	7740-28-0	303.5
V	50.9	7740-62-2	1917
Zn	65.37	7740-66-6	419.5

IV. INSTRUMENT CALIBRATION

A. PREPARATION OF STANDARDS

1. The primary stock standards (PSS) are described in Table 3. Primary stock solutions are stored at room temperature in the original bottle and are useable for 1 year.

2. Two instrument calibration standards (ICS), are prepared by adding an appropriate aliquot of each primary stock to a 100-mL volumetric flask and diluting to volume with a 5% nitric acid solution. ICS solutions are stored at room temperature in polyethylene bottles. Instrument calibration standards will be prepared every 3 months, or sooner if warranted by analysis difficulties. The preparation of the ICS solutions is outlined in the table below and final concentrations are listed in Table 3. The elements Ba, Co, Cu, Fe, Mo and V are not present in the commercially prepared primary standard mixes and are added individually to ICS1. ICS3 contains As only.

Standard Prepared	Volume PSS1 (mL)	Volume PSS2 (mL)	Volume PSS3 (mL)	Volume of Individual Element Stock (mL)						
				Ba	Co	Cu	Fe	Mo	V	As
Blank	-	-	-	-	-	-	-	-	-	-
ICS1	10	10	-	0.1	0.1	0.1	0.1	0.1	0.1	-
ICS2	-	-	10	-	-	-	-	-	-	-
ICS3	-	-	-	-	-	-	-	-	-	2.0

3. Multielement stock standards (MSS) are prepared by adding an appropriate volume of 1000-ug/mL individual analyte stock solutions to 1-L volumetric flask and diluting to volume with a 5% nitric acid solution. MSS solutions are stored at room temperature in polyethylene bottles. The preparation of the MSS solutions is outlined in Table 4.

Various aliquots of the MSS solutions are combined and diluted to create two sets of test calibration standards (TCS-A and TCS-B). Two sets are required due to the incompatibility of the elements.

MSS1 and MSS2 are used to prepare TCS-B and MSS3 and MSS4 are used in preparation of TCS-A. The TCS solution concentrations are identified as a factor of the certification target reporting limit, X. The dilution schemes for the preparation of the TCS solutions are given in Table 5 and resulting concentrations are given in Table 6.

4. Calibration check standards (CCS 1 & CCS 2) are prepared from primary stock solutions independent of the test calibration standards. The CCS solutions are prepared in a 5% nitric acid solution. CCS preparation is outlined in Table 7.

B. INITIAL/DAILY INSTRUMENT CALIBRATION

1. Initial calibration consists of a two-point calibration specified in the instrument operation manual. The instrument response produced by a standard and a blank is used to determine a linear calibration equation for each element. The standards analyzed are described in Section IV.A.2. Initial calibration is performed each day prior to sample analysis.

2. Initial calibration is followed by analysis of two calibration check standards, CCS1 and CCS2 (Table 7). Instrument calibration is considered acceptable if the result for at least 75% of the elements in each CCS are within 10% of the actual concentration. The blank and CCS1 will be analyzed after every 15 samples and at the end of the analysis day. CCS2 is analyzed at the beginning and end of each analysis day.

TABLE 3. INITIAL CALIBRATION STANDARD SOLUTIONS (ICS)

	Analyte	Atomic Source	Lot Number	Concentration (mg/L)	Concentration in ICS (mg/L)
ICS1	Al	b	-	200	20.0
	Ba	Spex	2-93-MD	1000	1.00
	Be	a	-	50	5.00
	Ca	b	-	1000	100
	Cd	a	-	150	15.0
	Co	Spex	1-86-MD	1000	1.00
	Cr	b	-	20	2.00
	Cu	Spex	2-122-MD	1000	1.00
	Fe	Spex	2-89-MD	1000	1.00
	K	b	-	400	40.0
	Mn	a	-	100	10.0
	Mo	Spex	2-136-MD	1000	1.00
	Na	b	-	200	20.0
	Ni	b	-	20	2.00
	Pb	a	-	500	50.0
	Se	a	-	200	20.0
	V	Spex	2-142-V	1000	1.00
	Zn	a	-	150	15.0
ICS2	Mg	c	-	1000	100
	Sb	c	-	200	20.0
	Tl	c	-	200	20.0
ICS3	As	Plasma Pure	90-050	1000	20.0

a) Primary Stock Solution 1 (PSS1), Spex Industries, Inc., Lot No. 1-182-TH.
b) Primary Stock Solution 2 (PSS2), Spex Industries, Inc., Lot No. 2-68AS.
c) Primary Stock Solution 3 (PSS3), Spex Industries, Inc., Lot No. 2-155-TH.

TABLE 4. MULTIELEMENT TEST CALIBRATION STANDARD PREPARATION

MSS1

Element	Stock Solution[a]	Volume of Stock Diluted to 1-L (mL)[b]
As	Inorganic Venture F-AS0114	5.00
Ba	Spex 2-93-MD	0.500
Ca	Spex 1-104-CA	50.0
Cd	Spex 1-126-MD	0.250
Cr	Plasma Pure 90-050	0.250
Cu	Spex 2-122-MD	0.500
Mg	Spex 1-105-MG	50.0
Na	Spex 3-42-NA	50.0
Pb	Plasma Pure 90-050	0.250
Zn	Spex 2-37-MD	1.00

MSS3

Element	Stock Solution[a]	Volume of Stock Diluted to 1-L (mL)[b]
Al	Spex 1-83-MD	45.0
Be	Spex 1-79-MD	10.0
Co	Spex 1-86-MD	50.0
Fe	Spex 1-89-MD	10.0
K	Spex 2-49-MD	50.0
Mn	Spex 2-73-MD	2.00
Mo	Spex 2-136-MD	8.00
Ni	Spex 2-69-MD	15.0
Sb	Spex 2-123-MD	60.0
Se	Spex 3-19-SE	75.0
Tl	Spex 3-21-TL	40.0
V	Spex 2-142-V	20.0

MSS2

Element	Stock Solution[a]	Volume of Stock Diluted to 1-L (mL)[b]
Ba	Spex 2-93-MD	10.0
Cd	Spex 1-126-MD	5.00
Cr	Plasma Pure 90-050	5.00
Cu	Spex 2-122-MD	10.0
Pb	Plasma Pure 90-050	5.00
Zn	Spex 2-37-MD	20.0

MSS4

Stock Solution	Volume of Stock Diluted to 1-L (mL)
MSS3	10.0

a All stock solutions are 1000 ug/L

b Volume of stock in mL = final concentration in mg/L

TABLE 5. TEST CALIBRATION STANDARD DILUTIONS

Standard Prepared[a]	Volume of MSS1 (mL)	Volume of MSS2 (mL)	Volume of MSS3 (mL)	Volume of MSS4 (mL)
		TCS-A		
Blank	0.00	0.00	0.00	0.00
0.5X-A	-	-	-	2.50
1X-A	-	-	-	5.00
2X-A	-	-	-	10.0
5X-A	-	-	-	25.0
10X-A	-	-	-	50.0
20X-A	-	-	-	100
50X-A	-	-	2.50	-
100X-A	-	-	5.00	-
200X-A	-	-	10.0	-
500X-A	-	-	25.0	-
1000X-A	-	-	50.0	-
2000X-A	-	-	100	-
		TCS-B		
Blank	0.00	0.00	0.00	0.00
0.5X-B	1.00	-	-	-
1X-B	2.00	-	-	-
2X-B	4.00	-	-	-
5X-B	10.0	-	-	-
10X-B	20.0	-	-	-
20X-B	40.0	-	-	-
50X-B	-	5.00[b]	-	-
100X-B	-	10.0	-	-
200X-B	-	20.0	-	-
500X-B	-	50.0	-	-
1000X-B	-	100	-	-

a) All solutions are prepared in 100-mL volumetric flasks. Each solution was diluted to volume with ASTM Type I water.
b) 5.00-mLs of each 1000-ug/mL stock solution for Ca, Mg, and Na (Table 4) were also added to standard 50X-B.

TABLE 6. ELEMENT CONCENTRATIONS IN TEST CALIBRATION STANDARDS (ug/L)

Element Curve	Standard Identification from Table 5											
	0.5X	1X	2X	5X	10X	20X	50X	100X	200X	500X	1000X	2000X
						TCS-B						
As-B	50	100	200	500	1000	2000	5000	10000	-	-	-	-
Ba-B	5	10	20	50	100	200	500	1000	2000	5000	10000	-
Ca-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Cd-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
Cr-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
Cu-B	5	10	20	50	100	200	500	1000	2000	5000	10000	-
Mg-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Na-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Pb-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
						TCS-A						
Zn-A	10	20	40	100	200	400	1000	2000	4000	10000	20000	-
Al-A	1.25	22.5	45	112.5	225	450	1125	2250	4500	11250	22500	45000
Sb-A	15	30	60	150	300	600	1500	3000	6000	15000	30000	60000
Be-A	2.5	5	10	25	50	100	250	500	1000	2500	5000	10000
Co-A	12.5	25	50	125	250	500	1250	2500	5000	12500	25000	50000
Fe-A	2.5	5	10	25	50	100	250	500	1000	2500	5000	10000
Mn-A	1.5	1	2	5	10	20	50	100	200	500	1000	2000
Mo-A	2	4	8	20	40	80	200	400	800	2000	4000	8000
Ni-A	3.75	7.5	15	37.5	75	150	375	750	1500	3750	7500	15000
K-A	12.5	25	50	125	250	500	1250	2500	12500	25000	50000	-
Se-A	18.75	37.5	75	187.5	375	750	1875	3750	7500	18750	37500	75000
Tl-A	10	20	40	100	200	400	1000	2000	4000	10000	20000	
V-A	5	10	20	50	100	200	500	1000	2000	5000	10000	-

TABLE 6A. ELEMENT CONCENTRATIONS IN TEST CALIBRATION STANDARDS (ug/g)

Standard Identification from Table 5

Element Curve[a]	0.5X	1X	2X	5X	10X	20X	50X	100X	200X	500X	1000X	2000X
						TCS-B						
As-B	5.0	10	20	50	100	200	500	1000	-	-	-	-
Ba-B	0.5	1.0	2.0	5.0	10	20	50	100	200	500	1000	-
Ca-B	50	100	200	500	1000	2000	5000	-	-	-	-	-
Cd-B	0.25	0.5	1.0	2.5	5.0	10	25	50	100	250	500	-
Cr-B	0.25	0.5	1.0	2.5	5.0	10	25	50	100	250	500	-
Cu-B	0.5	1.0	2.0	5.0	10	20	50	100	200	500	1000	-
Mg-B	50	100	200	500	1000	2000	5000	-	-	-	-	-
Na-B	50	100	200	500	1000	2000	5000	-	-	-	-	-
Pb-B	0.25	0.5	1.0	2.5	5.0	10	25	50	100	250	500	-
						TCS-A						
Zn-A	1.0	2.0	4.0	10	20	40	100	200	400	1000	2000	-
Al-A	1.125	2.25	4.5	11.25	22.5	45	112.5	225	450	1125	2250	4500
Sb-A	1.5	3.0	6.0	15	30	60	150	300	600	1500	3000	6000
Be-A	0.25	0.5	1.0	2.5	5.0	10	25	50	100	250	500	1000
Co-A	1.25	2.5	5.0	12.5	25	50	125	250	500	1250	2500	5000
Fe-A	0.25	0.5	1.0	2.5	5.0	10	25	50	100	250	500	1000
Mn-A	0.05	0.01	0.02	0.05	1.0	2.0	5.0	10	20	50	100	200
Mo-A	0.2	0.4	0.8	2.0	4.0	8.0	20	40	80	200	400	800
Ni-A	.375	0.75	1.5	3.75	7.5	15	37.5	75	150	375	750	1500
K-A	1.25	2.5	5.0	12.5	25	50	125	250	1250	2500	5000	-
Se-A	1.875	3.75	7.5	18.75	37.5	75	187.5	375	750	1875	3750	7500
Tl-A	1.0	2.0	4.0	10	20	40	100	200	400	1000	2000	-
V-A	0.5	1.0	2.0	5.0	10	20	50	100	200	500	1000	-

TABLE 7. CALIBRATION CHECK STANDARD PREPARATION

	CCS1			CCS2	
Analyte	Stock Concentration (mg/L)	Stock Volume diluted to 100-mL	Calibration Check Standard Conc. (mg/L)	Volume Stock [g] Solution diluted to 100 mL	Calibration Check Standard Conc. mg/L
As	1000[b]	0.3	3.0	1.00	10.0
Al	100[a]	3.0	3.0	4.00	40.0
Ba	100[a]	3.0	3.0	1.00	10.0
Ca	100[a]	3.0	3.0	4.00	40.0
Cd	100[a]	3.0	3.0	-	-
Co	100[a]	3.0	3.0	4.00	40.0
Cr	100[a]	3.0	3.0	-	-
Cu	100[a]	3.0	3.0	1.00	10.0
Fe	100[a]	3.0	3.0	1.00	10.0
K	100[a]	3.0	3.0	4.00	40.0
Mg	100[a]	3.0	3.0	4.00	40.0
Mn	100[a]	3.0	3.0	-	-
Na	100[a]	3.0	3.0	4.00	40.0
Ni	100[a]	3.0	3.0	1.00	10.0
Pb	100[a]	3.0	3.0	-	-
V	100[a]	3.0	3.0	1.00	10.0
Zn	100[a]	3.0	3.0	1.00	10.0
Mo	1000[c]	0.3	3.0	1.00	10.0
Sb	1000[d]	0.3	3.0	4.00	40.0
Se	1000[e]	0.3	3.0	4.00	40.0
Tl	1000[f]	0.3	3.0	4.00	40.0
Be	100[a]	3.0	3.0	1.00	10.0

a) Inorganic Ventures, Lot. No. F07W6.
b) Plasma Pure No. 90-050
c) Spex, Lot No. 2-136-MD.
d) Spex, Lot No. 2-123-MD.
e) Spex, Lot No. 3-19-SE.
f) Spex, Lot No. 3-21-TL.
g) All stock solutions are 1000-mg/L.

V. CERTIFICATION TESTING

A. CONTROL SPIKES

The recovery of each metal is tested through the complete analytical method including digestion. To facilitate this process, two mutlielement spiking solutions were prepared from a 1,000-ppm reference standard solution of each metal. The certification spike solutions are prepared from separate stock solutions but in the same manner as the TCS in Tables 4 and 5. Concentrations of each element in the certification spike solutions are found in Table 6A.

The certification spike samples were digested and analyzed according to the procedures in Section VII.A.1-6.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURES

Field samples collected for analysis by this method do not require preservation.

B. CONTAINERS

The field samples are to be collected in 250-mL wide-mouth glass or polyethylene bottles for transport to the laboratory.

C. STORAGE CONDITIONS

Sample integrity is maintained during transport to the laboratory by properly preserving the sample with nitric acid and shipping them in coolers packed with blue ice.

D. HOLDING TIME LIMITS

The samples to be analyzed by this method have an analysis holding time of 6 months.

VII. PROCEDURE

A. SAMPLE PREPARATION

1. Transfer a 1-g portion of the soil to a 150-mL beaker.

   To prepare the method blank and control samples, transfer 0.1-g of standard soil to each 150-mL beaker. There is no spike added to the method blank and appropriate volumes of standard are added to control samples as outlined in Table 8. After addition of the spike, wait one hour before continuing digestion procedure.

2. Add 10-mL of (1:1) nitric acid and cover the beaker with a watch glass and heat on a hot plate at 95°C for 10-minutes without boiling. Cool, add 5-mL of concentrated nitric acid and continue to reflux for 30 more minutes. The volume should not be reduced to less than 5-mL and no area of the bottom of the beaker is allowed to go dry.

3. Cool, add 2-mL of Type I water and 3-mL of 30% hydrogen peroxide (H_2O_2). Warm the beaker and ensure that loss of sample doesn't occur due to excessively vigorous effervescence. Heat until effervescence subsides. Continue to add 30% H_2O_2 in 1-mL aliquots with warming until effervescence is minimal or until the sample appearance is unchanged. Add a maximum of 10-mL of H_2O_2.

4. Add 5-mL of (1:1) HCL and 10-mL of Type I water and heat for additional 10 minutes.

5. Wash down the sides of the beakers and the watch glass covers with ASTM Type I water.

Filter the sample through Whatman #41 filter paper (or equivalent). Quantitatively transfer the solution to a 100-mL volumetric flask.

6. Dilute each sample to a final volume of 100-mL with Type I water.

7. To determine % moisture, place a 20-g portion of the soil into a preheated tared aluminum weighing dish. Place in an oven at 103-105°C for a minimum of 4 hours. Remove the sample from the oven and weigh (after cooling in a desiccator). Replace the sample in the drying oven for an additional 2 hours, cool, and weigh. Repeat process as necessary until the weight change is <5%.

$$\% \text{ Moisture} = \frac{\text{weight of wet soil - weight of dry soil}}{\text{weight of wet soil}} \times 100$$

B. CHEMICAL REACTIONS

Non-specific oxidation of organic matter and some ionically bonded species such as carbonates and hydroxides occur.

C. INSTRUMENT ANALYSIS

Perform the procedures for calibration documented in Section IV.B. The daily analytical run will also include analysis of the calibration blank and the CCS1 at a frequency of every 15 samples and at the end of the run. CCS2 will be analyzed after CCS1 at the beginning and end of the run.

VIII. CALCULATIONS

The computer software supplied with the ICP spectrometer provides direct readout of solution concentrations in mg/L. The software performs a calculation based on a linear regression line equation.

The result is then converted to ug/g by applying the appropriate correction factor. If 1 gram of soil is digested and the digestate diluted to 100 mL, this factor is 100.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

Daily quality control samples consist of a standard matrix method blank, a standard matrix spike at approximately two times the CRL and duplicate standard matrix spikes at approximately ten times the CRL. For extended range elements an additional order-of-magnitude control spike shall be prepared. These quality control samples are processed through the entire method with the environmental samples.

The control elements for this method will include Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, Zn. The control samples will be prepared according to Section VII.A and percent recoveries used to maintain accuracy and precision control chart data. Control spike solution preparation and concentration along with the soil matrix control spike concentrations are given in Table 8.

TABLE 8. QUALITY CONTROL SAMPLE PREPARATION

Control Element	Low Spike		High Spike		Extended Spike	
	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/g)	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/g)	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/g)
Ba	10.0	10.0	10.0	100	40.0	800
Cd	2.00	2.00	1.00	10.0	5.0	100
Co	10.0	10.0	10.0	100	50.0	1000
Cr	2.00	2.00	2.00	20.0	10.0	200
Cu	10.0	10.0	5.00	50.0	5.0	100
Mn	1.00	1.00	1.00	10.0	5.0	100
Mo	8.00	8.00	8.00	80.0	32.0	640
Ni	15.0	15.0	15.0	150	50.0	1000
Pb	20.0	20.0	10.0	100	20.0	400
Sb	b	200	b	1000	b	5000
Se	25.0	25.0	25.0	250	125	2500
Tl	25.0	25.0	25.0	250	125	2500
Zn	10.0	10.0	10.0	100	50.0	1000

a) All individual element stock solutions are 1000-mg/L. The volume given (mL) is diluted to 1-L with 5% nitric acid. This volume in mL is equal to the control spike solution concentration in mg/L.

b) Control samples are prepared by spiking the following volumes of control spike solution onto 0.1-g of USATHAMA standard soil and following the procedure in Section VII.A.

Low Spike : 1-mL of the low control spike solution and 0.2-mL of 1000-mg/L Sb.
High Spike: 10-mL of the high control spike solution and 1.0 mL of 1000-mg/L Sb.
Extended Spike: 20-mL of the extended control spike solution and 5.0-mL of 1000-mg/L Sb.

B. CONTROL CHARTS

Control charts will be maintained to monitor variations in precision and accuracy of routine analyses and to detect trends in these variations. The control charting procedure that will be followed is given in the USATHAMA QA Program, January 1990.

Single-Day X-Bar Control Chart
Single-Day R Control Chart
Three-Point Moving Average X-Bar Control Chart
Three-Point Moving Average R Control Chart
Extended Range Three-Point Moving Average X-Bar Control Chart
Extended Range Three-Point Moving Average R Control Chart

X. REFERENCES

A. U.S. Army Toxic and Hazardous Materials Agency, January 1990, Quality Assurance Program. Revision No. 0.

B. United States Environmental Protection Agency. Method 200.7 Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes.

C. United States Environmental Protection Agency, SW-846 Third Edition, Method 6010, Inductively Coupled Plasma Atomic Emission Specroscopy.

XI. DATA

A. STANDARD CHARACTERIZATION

All standards were traceable to NBS/NIST.

B. INSTRUMENT CALIBRATION

The instrument calibration followed Section IV.B.1.

C. STANDARD CERTIFICATION SAMPLE RESULTS

1. Tables and Graphs, LOF and ZI Tests, Precision and Accuracy Data

2. Results of External Calibration Checks

3. Summary of Control Chart Data

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SUMMARY OF CONTROL CHART DATA

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THREE DAY CONTROL CHART DATA FOR ICP METALS SOIL CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AL	119.5	137.9	131.8	107.2	101.1	18.0	46.4	36.9
AS	72.2	100.8	91.3	53.1	43.5	28.0	72.1	57.4
BA	196.3	211.7	206.6	186.1	181.0	15.0	38.6	30.7
BE	93.3	103.6	100.2	86.5	83.1	10.0	25.8	20.5
CA	217.3	243.9	235.1	199.6	190.7	26.0	67.0	53.3
CD	92.0	92.0	92.0	92.0	92.0	0.0	0.0	0.0
CO	112.7	135.2	127.7	97.7	90.2	22.0	56.7	45.1
CR	150.7	195.7	180.7	120.7	105.7	44.0	113.3	90.2
CU	108.0	126.4	120.3	95.7	89.6	18.0	46.4	36.9
FE	118.1	140.4	132.9	103.2	95.8	21.8	56.1	44.7
K	155.9	186.2	176.1	135.7	125.7	29.6	76.2	60.7
MG	136.0	155.4	148.9	123.1	116.7	18.9	48.7	38.7
MN	123.3	138.7	133.6	113.1	108.0	15.0	38.6	30.7
MO	94.0	109.3	104.2	83.7	78.6	15.0	38.6	30.7
NA	113.7	115.7	115.0	112.3	111.6	2.0	5.2	4.1
NI	88.0	101.6	97.1	78.9	74.4	13.3	34.3	27.3
PB	98.0	105.8	103.2	92.8	90.2	7.6	19.6	15.6
SB	57.8	72.2	67.4	48.1	43.3	14.1	36.3	28.9
SE	76.3	85.7	82.6	70.0	66.9	9.2	23.7	18.9
TL	92.8	132.4	119.2	66.3	53.1	38.8	99.8	79.4
V	118.0	125.2	122.8	113.2	110.8	7.0	18.0	14.4
ZN	146.3	160.1	155.5	137.1	132.5	13.5	34.8	27.7

SINGLE DAY CONTROL CHART DATA FOR ICP METALS SOIL CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AS	90.5	93.3	92.4	88.6	87.7	1.5	4.9	3.8
AL	100.9	103.4	102.6	99.2	98.4	1.3	4.4	3.3
BA	100.4	106.3	104.4	96.5	94.5	3.1	10.3	7.9
BE	91.3	101.6	98.1	84.4	80.9	5.5	18.0	13.8
CA	122.0	131.7	128.4	115.5	112.3	5.1	16.8	12.9
CD	92.8	99.3	97.1	88.4	86.2	3.5	11.4	8.8
CO	94.0	110.5	105.0	83.0	77.5	8.8	28.7	22.1
CR	95.8	98.1	97.3	94.3	93.5	1.2	3.9	3.0
CU	94.1	98.6	97.1	91.1	89.6	2.4	7.8	6.0
FE	108.0	115.5	113.0	103.0	100.5	4.0	13.1	10.0
K	100.1	127.2	118.1	82.0	72.9	14.4	47.2	36.3
MG	105.6	113.8	111.1	100.1	97.4	4.4	14.3	11.0
MN	102.3	107.0	105.4	99.1	97.6	2.5	8.2	6.3
MO	90.1	104.6	99.8	80.4	75.5	7.7	25.3	19.5
NA	98.9	101.7	100.8	97.0	96.1	1.5	4.9	3.8
NI	95.2	110.8	105.6	84.8	79.5	8.3	27.2	20.9
PB	92.3	102.8	99.3	85.3	81.7	5.6	18.3	14.1
SB	83.9	108.0	100.0	67.9	59.8	12.8	41.9	32.2
SE	89.6	101.6	97.6	81.6	77.6	6.4	20.9	16.0
TL	96.6	130.9	119.4	73.8	62.3	18.3	59.6	45.8
V	93.1	108.4	103.3	82.9	77.8	8.1	26.6	20.5
ZN	95.7	97.8	97.1	94.3	93.6	1.1	3.6	2.8

EXTENDED RANGE CONTROL CHART DATA FOR ICP METALS SOIL CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AL	99.1	101.0	100.4	97.9	97.2	1.8	4.7	3.8
AS	89.4	103.0	98.5	80.3	75.8	13.3	34.2	27.3
BA	93.7	97.9	96.5	90.9	89.5	4.1	10.6	8.4
BE	87.4	95.7	92.9	81.8	79.0	8.2	21.0	16.7
CA	110.3	114.6	113.2	107.3	105.9	4.3	11.0	8.8
CD	89.8	96.4	94.2	85.4	83.2	6.5	16.6	13.2
CO	91.8	115.9	107.9	75.7	67.6	23.6	60.8	48.4
CR	92.6	96.1	94.9	90.3	89.1	3.4	8.8	7.0
CU	96.0	100.5	99.0	93.0	91.5	4.4	11.4	9.1
FE	100.9	103.1	102.4	99.4	98.6	2.2	5.7	4.5
K	98.1	120.4	113.0	83.2	75.7	21.9	56.3	44.8
MG	98.1	104.0	102.0	94.1	92.2	5.8	14.8	11.8
MN	100.5	104.8	103.3	97.6	96.1	4.3	10.9	8.7
MO	91.3	99.4	96.7	85.9	83.2	7.9	20.4	16.3
NA	98.9	102.3	101.2	96.6	95.5	3.3	8.5	6.8
NI	93.9	103.3	100.2	87.6	84.4	9.2	23.8	18.9
SB	89.4	95.7	93.6	85.2	83.1	6.2	15.9	12.6
SE	87.5	107.9	101.1	74.0	67.2	19.9	51.2	40.8
TL	96.6	110.2	105.7	87.5	83.0	13.3	34.3	27.3
V	94.3	99.5	97.8	90.7	89.0	5.2	13.3	10.6
ZN	91.2	96.2	94.5	87.8	86.1	4.9	12.7	10.1

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MERCURY IN SOIL

Method JB06

I. Summary

A. Analyte: Mercury (Hg)

B. Matrix: This method is applicable to soils and solid wastes

C. General Method: A weighed portion of sample is digested in aqua regia for 2 minutes at 95°c, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique. (EPA #245.5)

II. Application

A. Test Concentration Range

Optimum Range: 0.01 to 0.40 ug/g

B. Sensitivity

Sensitivity is about 0.006 ABS units for 0.01 ug/g mercury

C. Reporting Limits

The certified reporting for mercury is 0.08 ug/g

D. Interferences

Potassium permanganate and potassium persulfate are added during digestion of samples to break down orano-mercury compounds which would otherwise not respond to the cold vapor technique. A heating step is required for methyl mercuric chloride when present in or spiked to a natural system. Possible sulfide interferances are also eliminated by the addition of potassium permanaganate. Concentrations as high as 20 mg/l of sodium sulfide do not interfer with the recovery of added inorganic mercury from distilled water.

E. Analysis Rate

Approximately 120 samples can be analyzed in an 8 hour period.

III. Apparatus and Chemicals

A. Glassware/Hardware

1. Wheaton 300 ml BOD bottles
2. Pyrex 100 ml graduated cylinders
3. GCA/Precision Scientific Water Baths
4. Pyrex Volumatric Class A Pipets, various sizes
5. Pyrex Volumetric Flasks, various sizes, Class A
6. Balance: American Scientific Products Z660
7. Eppendorf Mechanical Pipets, various sizes
8. Glasswool

B. Instrumentation

1. Perkin Elmer Model 603 with manual mercury cold vapor closed cell apparatus. Hitachi Model 561 Strip Recorder
2. Mercury Hollow Cathode Lamp
3. Instrument Operating Parameters for Mercury

a. AA Operating Parameters

1. Lamp current: 6 milliamps
2. Wavelength: 253.1
3. Slit Width: 4
4. Background: off
5. Signal: Abs
6. Mode: Cont
7. Recorder: TC1
8. Oxidant: Air; set air pressure to 25 PSI

b. Chart Recorder Operating Parameters

1. 10 mm/min
2. 5 mv

C. Analytes: Mercury

1. Formula weight: 200.59
2. Density: 13.545
3. CAS Registry number: 7439-97-6
4. Melting Point: -38.842°C
5. Boiling Point: 356.58°C

D. Reagents and Sarms

1. ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

2. Concentrated nitric acid, Baker Instra Analyzed: (HNO_3):

3. Concentrated hydrochloric acid, Baker Instra Analyzed 37% (HCl)

4. Aqua Regia, Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5. Mercury Stock Solution, 1000 mg/l. Dissolve 1.080 g of mercury (II) oxide, HgO, in a minimum volume of 1 + 1 HCl. Dilute to 1 liter with deionized water. Alternatively, a 1000 ppm certified standard was purchased from Ricca Chemical and verified by comparison with an EPA Standard.

6. Mercury Working Standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration range as the samples to be analyzed.

7. Potassium Permanganate, Mallinckrodt ($KMNO_4$), Dissolve 25 g $KMNO_4$ in a minimum volume of water and dilute to 500 ml with deionized water.

8. Potassium Persulfate, Mallinckrodt ($K_2S_2O_8$). Dissolve 40 g $K_2S_2O_8$ in approximately 200 ml deionized water. Heat and stir to dissolve all crystals. Dilute to 500 ml with deionized water.

9. Stannous Chloride, Mallinckrodt ($SnCl_2 \cdot 2H_2O$). Dissolve 50 g $SnCl_2 \cdot 2H_2O$ in 250 ml 1.0 N H_2SO_4. Dilute to 500 ml with deionized water. This solution is a suspension and should be stirred continually during use.

10. Sodium Chloride - Hydroxlamine Sulfate, Kodak, Dissolve 60 g NaCl and 60 g $(NH_2OH)_2 \cdot H_2SO_4$ in deionized water and dilute to 500 ml with deionized water.

11. Magnesium Perchlorate (Anhydrous) Kodak

12. 1.0 N Sulfuric Acid, Add 28 ml concentrated H_2SO_4 to 500 ml deionized water and dilute to 1 liter with deionized water.

13. Air, Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

*NOTE: All reagents should be analyzed to determine levels of impurities. If method blank is less than the MDL, the reagents may be used.

IV. Precertification Calibration

A. Initial Calibration

1. Preparation of Standards

a. Prepare an intermediate stock mercury standard at 1000 ug/l.

Dilute 1 ml of stock mercury standard (1000 mg/L) to 1000 mls with deionized water (equals 1.00 mg/L).

b. Prepare a working stock mercury at 100 ug/l.

Dilute 10 mls of intermediate mercury standard to 100 mls with deionized water (equal 100 ug/l)

c. Using the working stock mercury standard (100 ug/L) prepare the following standards in 100 ml volumetric flasks.

CONCENTRATION OF MERCURY (ug/L)
0.0
0.5
1.0
3.0
5.0
10.0

d. Prepare the above working standards fresh daily and store at room temperature.

2. Instrument Calibration

a. Turn on instrument and set up for the following conditions:

1. Install Mercury Hollow Cathode Lamp

2. Refer to Section III.B.3.a. and III.B.3.b.

b. Allow ½ hour for lamp, instrument warmup

c. Install Mercury cold vapor cell in burner chamber and align with maximum energy through put.

d. Disconnect air line from nebulizer and connect to bubbler. Place bubbler in BOD bottle filled halfway with deionized water. Connect tubing from other end of bubbler to drying column (filled and packed with magnesium perchlorate) and then to left end of cell. Place vent hose from right end of cell in appropriate hood.

e. Place 5.0 ml $NaCl.(NH_2OH)_2$. H_2SO_4 into digested blk and mix. Allow 1 minute for the potassium permarganate to be dispersed.

f. With air running, add 5.0 mls of $SnCl_2$ to blank and quickly place bubbler into blank flask. Record peak height on strip chart.

g. If blank is uncontaminated, run standards in the same manner. When the standards have been analyzed, their values and concentrations are entered into the linear regression program, which prints a curve on which to base all unknown samples.

h. Analyze EPA checks to ensure standards are correct.

i. Calibration of instrument is complete.

3. Analysis of Calibration Data

Acceptability of calibration data occurs when the following are true:

a. Response of the high standard must be within 10% of the mean response of the same concentration determined from past data. After seven calibrations the response must fall within two standard deviations of the mean response.

b. When linear regression data is similar to previous calibrations.

c. When EPA check values are acceptable based on a 95% confidence level of the true value.

B. Daily Calibration

1. Preparation of Standards

Same as Initial Calibration

2. Instrument Calibration

Analyze the high standard at the beginning and end of each day.

3. Analysis of Calibration Data

The response of the high standards must be within 10% or 2 standard deviations (after seven calibrations) of the mean response as determined be previous data.

4. Calibration Checks

ERA or EPA trace metals for water pollution

V. Certification Testing

A. Preparation Certification Matrix for Soils:

1. Prepare soil standard for analysis per USATHAMA Guidelines.

2. Weigh 1.00 gram portions of prepared soil into specially cleaned BOD bottle. Prepare 7 separate units corresponding to the 7 calibration levels.

3. To each bottle, the following known addition of analyte (mercury) was added corresponding to the 7 calibration levels:

UNIT (BEAKER#)	ANALYTE* ADDITION (mls)	CALIBRATION LEVEL ug/g	TRL MULTIPLIER
1	0.0	0.0	0x
2	0.1	0.01	0.5x
3	0.2	0.02	1x
4	0.4	0.04	2x
5	1.0	0.10	5x
6	2.0	0.20	10x
7	4.0	0.40	20x

* Analyte concentration is equal to 100 ug/L mercury and its addition to achieve the calibration level is based on a digestion ratio of 100 mls/1.00 g.

When the sample units have been weighed and the analyte added, they are ready for digestion.

4. To each sample add 5.0 ml deioized water and 5.0 ml aqua regia.

5. Place in water bath and heat to 95°C ± 2° for 2 minutes.

6. Remove from waterbath and cool to room temperature.

7. Add 50 ml deionized water.

8. Add 15 ml potassium permanganate to each bottle. If the purple color disappears, additional permanganate is added, with the increased volume noted. Allow to stand at least 15 minutes.

9. Add 10 ml potassium persulfate to each bottle.

10. Cover mouth of bottles with plastic wrap and place in hot water bath. Bring temperature ot 95°C and maintain for ½ hour.

11. Cool to room temperature. Samples are now ready for analysis.

VI. Sample Handling/Storage

A. Sampling Procedure

1. All sample containers must be new, used containers should be prewashed with detergents, acids and Type II water. Plastic containers are suitable. See Chapter Three, Section 3.1.3, for further information.

2. Nonaqueous samples shall be refridgerated upon receipt and analyzed as soon as possible.

B. Containers

Plastic containters should be used.

C. Mercury Storage Condition

Refrigerate non aqueous samples.

D. Holding Time Limits

28 days

E. Solution Verification

Solutions will be validated against working standards before their initial use and within seven days before subsequent usage. The recovery of the solution must be greater than the lower warning limit on the X control chart for mercury.

VII. Procedure

A. Separations or Digestions

1. Use BOD bottles which have been rinsed with 1:1 nitric acid for samples.

2. Mix samples to acheive homogeneity. Weigh 1.00 g ± 0.02 g and place this into BOD bottle. Mark flask number next to sample number on digestion sheet.

3. To each sample add 5.0 ml deionized water and 5.0 ml aqua regia.

4. Place in water bath and heat to 95°C ± 2° for 2 minutes.

5. Remove from waterbath and cool to room temperature.

6. Add 50 ml deionized water.

7. Add 15 ml potassium permanate to each bottle. If the purple color disappears, additional permanganate is added, with the icreased volume noted. Allow to stand at lease 15 minutes.

8. Cover mouth of bottles with plastic wrap and place in hot water bath. Bring temperature to 95°C and maintain for ½ hour. Cool to room temperature. Samples are now ready for analysis.

B. Chemical Reactions

Samples are converted from a solid phase to an aqueous phase for analytical determination.

C. Instrumental Analysis

1. Turn on instrument and set up following conditions:

   a. Install Mercury Hollow Cathode Lamp

   b. Refer to Section III.B.3.a. and III.B.3.b.

2. Allow ½ hour for lamp, instrument warmup

3. Install Mercury cold vapor cell in burner chamber and align with maximum energy through put.

4. Disconnect air line from nebulizer and connect to bubbler. Place bubbler in BOD bottle filled halfway with deionized water. Connect tubing from other end of bubbler to drying column (filled and packed with magnesium perchlorate) and then to left end of cell. Place vent hose from right end of cell in appropriate hood.

5. Place 5.0 ml $NaCl.(NH_2OH)_2$. H_2SO_4 into digested blk and mix. Allow 1 minute for the potassium permarganate to be dispersed.

6. With air running, add 5.0 mls of $SnCl_2$ to blank and quickly place bubbler into blank flask. Record peak height on strip chart.

7. If blank is uncontaminated, run standards in the same manner. When the standards have been analyzed, their values and concentrations are entered into the linear regression program, which prints a curve on which to base all unknown samples.

8. Analyze EPA checks to ensure standards are correct.

9. Calibration of instrument is complete.

10. Analyze samples and checks and record on strip chart. A standard and EPA checks should be analyzed at least once every 15 samples to ensure proper analysis.

VIII. Calculations

A. (A)(B)/(C)(10) = Mercury in ug/g

Where:

A = Concentration of mercury in ug/l (from linear regression curve drawn)

B =any dilution factor used during analysis to adjust the sample concentration to within the standard range.

C = Weight of sample in gms.

B. For samples which required addtional potassium permanganate during the digestion, calculates as follows:

$$(A)(B)/(C)(10)\ \frac{133 + \text{additional ml}}{100} = \text{mercury in ug/g}$$

Where:

A,B,C, = Same as above.

IX. Daily Quality Control

A. Control Samples

1. Method Blank

For each lot of samples processed, method blanks (water and reagents) are carried throughout the entire sample preparation and analytical process. These blanks are useful in determining if samples are being contaminated.

2. Precision Analysis (reguired for PACE Laboratories, Inc.)

Duplicate samples are processed on a routine basis. Duplicate samples will be used to determine precision. The sample lot size will dictate the frequency but at least one of every ten samples for each matrix will be duplicated.

3. Accuracy Analysis

Spiked samples or standard reference materials are employed to determine accuracy. The following spiked samples will be included in each lot:

a. Certified Soil Spikes

1. One low level spike, 0.20 ug/g mercury

2. Two high level spikes, 0.30 ug/g mercury

3. These are prepared per instructions in Section V.A. Note: Spikes need to be in contact with the soil for at lease one hour before processing continues.

b. Sample Matrix Spike, (Required by PACE Laboratories, Inc.)

1. Prepared and spiked in the same manner as certified soil high levels spikes (0.40 ug/g mercury).

2. Spike one for every ten samples to be analyzed

B. Spiking Solution Control

Dilute working spike solutions will be validated against working standards before initial use and within seven days before subsequent usage.

C. Control Charts

As part of the QC program for this project, single-day and three-point moving average X-R control charts will be generated using either the software provided by USATHAMA or a manual method.

Initial Single-Day X-R Control Limits

Parameter	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Hg	119.8	114.4	93.2	87.8	27.8	21.3

Initial Three-Day X-R Control Limits

Parameter	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Hg	165.9	144.5	58.5	37.1	162.2	129.1

X. References

A. EPA Method 245.1 (Manual Cold Vapor Technique)

B. Perkin Elmer Atomic Absorption Spectrophotometer Operation and Method Manual.

COPY #2

Section No. I
Revision No. 1
Date 03/17/88
Page 1 of 1
Doc. No. WPPMTHUI93

TOTAL CYANIDE IN SOILS Method #KY04

I. Summary

A. Analyte: Total Cyanide

B. Matrix: Soil, Sediments and Solid Waste

C. General Method: The cyanide as Hydrocyanic Acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing Sodium Hydroxide solution. The cyanide is then determined colorimetrically where it is converted to cyanogen chloride CNCl, by the reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on addition of pyridine-barbituric acid reagent. Absorbance is read at 578 nm and is proportional to cyanide concentration. (EPA# 335.2)

II. Application

A. Tested Concentration Range: 0.50 to 20 ug/g

B. Sensitivity: .005 Absorbance units for 0.08 ug/g

C. Certified Reporting Limit: 1.22 ug/g

D. Interferences

1. Sulfides convert CN- to CNS-. Test for S^2 with lead acetate paper, precipitate with $Cd(NO_3)_2$ $4H_2O$ to form CdS and filter.

2. Oxidizing agents such as chlorine decompose cyanide. Test with KI starch paper, treat sample with ascorbic acid.

3. Thiocyanate, (CNS-) can mask cyanide determination; add Magnesium chloride soln. before distillation (20 mls/500 mls of sample)

4. Aldehydes, and ketones, convert cyanide to cyanohydrin, add 2 mls of Ethylene diamine solution per 100 mls of sample.

5. Nitrite, may react with organic contaminants to form HCN resulting in a positive interference add 2 grams of Sulfamic acid per 500 mls of sample prior to the addition of H_2SO_4 in the distillation step.

6. Carbonate causes excessive gasing during distillation procedure, add hydrated lime for stabilization.

E. Analysis Rate

The maximum number of samples that can be analyzed by this method in an 8-hour shift after instrument calibration is 24 samples.

F. Safety Information

Care should be used while handling cyanide samples because of toxicity. Samples should be processed in a hood; avoiding contact, inhalation, or ingestion.

III. Apparatus and Chemicals

A. Glassware/Hardware:

1. 500 ml flat bottomed boiling flask T 24/40 Pyrex
2. Connecting Arm 3-Way T 24/40 Pyrex #9040
3. Thistle Tube Pyrex #
4. Rubber Stopper 1 Hole #4
5. Allihn Condensor T 24/40 12"
6. Connecting tube
7. Gas Absorber 250 ml Pyrex
8. Gas dispersion tube with medium-porosity fritted outlet
9. Vacuum Flask Kimax No. 27060 1,000 ml
10. Vacuum Pump
11. Heating mantel Glas-Col #0402
12. Cordtrol Power Control Glas-Col PL112
13. Tygon tubing
14. Screw Clamp
15. Neoprene tubing
16. Volumetric flasks and pipets, Class A Pyrex Various Sizes
17. Nessler Tubes 100 ml Exax No. 45315
18. Rubber Stopper #3 Solid
19. Cuvette 1 cm pathlength Milton Roy Company #33-17-80
20. Boiling Chips

B. Instrumentation:

Spectrometer - Turner Model 350

a) Wavelength range 400-680 nm

b) Sensitivity .005 Absorbance units for 0.08 ug/g

c) Wavelength 578 nm

C. Analytes: CN or HCN

1. Formula Weight: 27.06

2. Density: 0.901 g/l

3. Melting Point: -13.24°C

4. Boiling Point: 25.70°C

5. CAS #151-50-8

D. Reagents and SARMS

1. Chemical List

a)	NaOH Pellets AR	98.3% pure	Mallinckrodt
b)	Concentrated H_2SO_4 AR	96.4%	Mallinckrodt
c)	$NaH_2PO_4.H_2O$ AR	100.97%	Mallinckrodt
d)	KCN AR	98.4%	Baker
e)	KOH pellets AR min.	86%	Mallinckrodt
f)	Chloramine T		Kodak
g)	Barbituric Acid	98%	Mallinckrodt
h)	Pyridine AR	99%	Baker
i)	HCl-concentrated AR		Mallinckrodt
j)	$MgCl_2.6H_2O$.AR	99.54%	Mallinckrodt
k)	Cadmium carbonate		ICN Pharmaceuticals
l)	Ascorbic acid AR		Kodak
m)	Ethylene diamine AR	98% min.	Kodak

2. Working Reagents

a) 0.25N NaOH: dissolve 100 g NaOH in DI water and dilute to 10 liters.

b) 1.5N sodium dihydrogen phosphate: Dissolve 207 g $NaH_2PO_4.H_2O$ in DI water and dilute to one liter (keep refrigerated).

c) Stock cyanide solution (1 ml = 1 mg): Dissolve 2.51 g KCN and 2 g KOH in DI water and dilute to one liter (keep refrigerated).

d) Chloramine T solution: Dissolve 1.0 g of white, water soluble chloramine T in 100 ml of DI water (make fresh weekly and keep refrigerated).

e) Magnesium chloride solution: Dissolve 510 g of $MgCl_2.6H_2O$ in DI H_2O and dilute to one liter.

f) Pyridine - Barbituric Acid Reagent: Place 15 g barbituric acid in a 250-mL volumetric flask and add just enough water to wash sides of flask and wet barbituric acid. Add 75 mL pyridine and mix. Add 15 mL conc. hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to mark with water and mix. This reagent is stable for up to 1 month: discard if a precipitate develops.

IV. Calibration

A. Initial Calibration

1. Preparation of Standards

a) Prepare a working stock CN standard at 10 mg/L

Dilute 10 mls of stock CN standard (1000 mg/L) to 1,000 mls with deionized water.

b) Using the working stock CN standard (10 mg/L), prepare the following standards in the appropriate size volumetric flasks.

CYANIDE CONCENTRATION (ug/L)	mls OF WORKING STANDARD(10 mg/L)	FINAL VOLUME (ml)
0.00	0	250
2.25	0.225	1,000
5.00	1.000	2,000
10.00	1.000	1,000
25.00	5.000	2,000
50.00	5.000	1,000
100.00	5.000	500
275.00	55.000	2,000

c) The working stock standard and the working standards are prepared daily and stored at room temperature.

d) 250 mls of each standard is used for the cyanide determination.

2. Instrument Calibration

a) Turn on instrument and adjust wavelength to 578 nm.

b) Allow 20 minutes for instrument warmup.

c) Zero instrument with reagent blank consisting of 50 ml 0.25N NaOH, 15ml NaH_2PO_4, 2 ml chloramine T and 5ml Pyridine-barbituric Acid, diluted to 100 ml with deionized water.

d) Analyze standards and EPA checks to ensure proper instrument calibration.

3. Analysis of Calibration Data

Acceptability of calibration data occurs when the following are true.

a) Absorbance of the high standard is within 10% or 2 standard deviations (after seven calibrations) of the mean response determined from past data.

b) Linear regression data is similar to previous calibrations.

c) EPA check values are acceptable based on a 95% confidence level of the true value.

B. Daily Calibration

1. Preparation of Standards

Prepare 250 ug/L standard only.

2. Instrument Calibration

Analyze 250 ug/L standard only.

3. Analysis of Calibration Data

The absorbance for the high standard must be within 10% or two standard deviations (after seven calibrations) of the mean response for the same concentration as determined from previous calibrations.

4. Calibration Checks

EPA check standards are employed as certified calibration check standards.

V. Certification Testing

A. Preparation Certification Matrix for Soils.

1. Prepare soil standard for analysis per USATHAMA guidelines.

2. Weigh 5 gram portions of prepared soil into 500 ml boiling flasks. Prepare 9 separate units corresponding to the 9 calibration levels.

3. To each unit, the following known addition of analyte (CN-) was added corresponding to the 9 calibration levels. Analyte solution: Dilute 10 mls of stock cyanide solution to 1000 mls with deionized water, equals 10 mg/L cyanide.

UNIT (FLASK #)	ANALYTE ADDITION (ml analyte @ 10 mg/L)	CALIBRATION LEVEL (ug/g)	TRL MULTIPLIER
1	0	0	0x
2	0.25	0.50	0.5x
3	0.50	1.0	1x
4	1.0	2.0	2x
5	2.50	5.0	5x
6	5.0	10.0	10x
7	10.0	20.0	20x

VI. Sample Handling/Storage

A. Sampling Procedure

Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

B. Containers

Samples are to be collected in one liter plastic or glass bottles.

C. Storage Conditions

Samples should be stored at 4°C until time of analysis.

D. Holding Time Limits

Maximum holding time is 14 days.

E. Solution Verification

Dilute working spike solutions will be validated against working standards before initial use and within seven days before subsequent usage.

VII. Procedure

A. Separation or Distillation

1. Weigh out 5.0 g of sample and place in a 500 ml boiling flask along with 6-8 boiling chips.

2. Add 250 mls of deionized water to the boiling flask.

3. Pour 100 ml of 0.25N NaOH solution into a 250 ml gas absorber, making sure that the fritted glass end of the dispersion tube is below the surface of the NaOH solution.

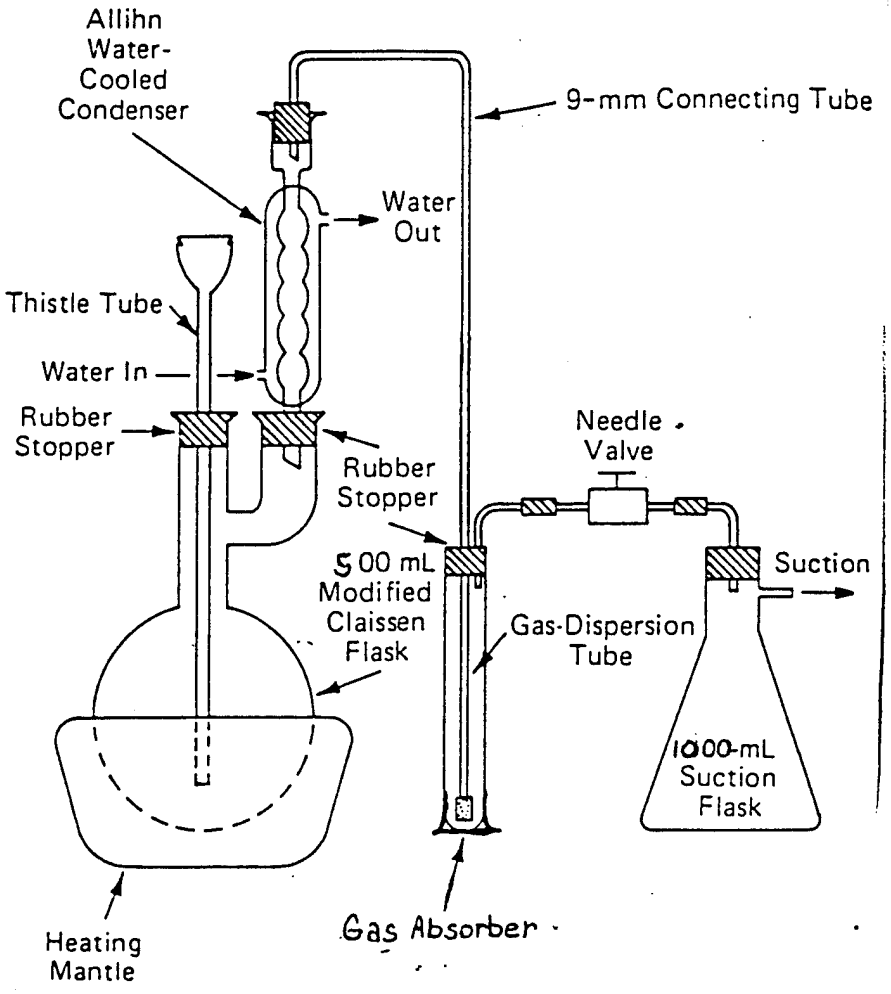
4. Assemble the distillation apparatus as illustrated below. (fig. a)

   a) Place the connecting arm onto the boiling flask with one side connected to the condensor and the other side stoppered with a thistle tube such that the end of the thistle tube projects below the surface of the sample.

   b) Place one end of the connecting tube at the top of the condensor and connect the other end to the gas dispersion tube.

   c) Attach the vacuum source to the gas absorber.

fig. a



5. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

   CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

6. Slowly add 25 ml conc. Sulfuric acid through the thistle tube. Allow the airflow to mix the flask contents for 30 minutes, or until acid is mixed. Increase airflow to speed mixing. Pour 10 ml of Magnesium chloride into the air inlet and wash down with a stream of water.

7. Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Vapors should not rise more than halfway into condenser. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source. Distillation is now complete and the samples are now ready for instrumental analysis.

B. Chemical Reactions

1. The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2. In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed upon the addition of pyridine-barbituric acid reagent.

C. Instrumental Analysis

1. Withdraw 50 ml or less of the absorbing solution from the flask and transfer to a 100 ml nessler tube. If less than 50 ml is taken, dilute to 50 ml with 0.25 N Sodium hydroxide solution. Add 10.0 ml of Sodium phosphate solution and mix.

2. Pyridine - Barbituric acid method: Add 2ml of chloramine T and mix. After 1 to 2 minutes, add 5 ml of pyridine - Barbituric acid solution and mix. Dilute to 100 ml mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes. NOTE: Zero the spectrophotometer with a freshly prepared reagent blank.

VIII. Calculations

A. Absorbance is read on the instrument and the number of ug present is determined based on the linear regression formulated by the standards used during calibration.

B. Solid Samples

CN^-,(ug/g) = A x 50/(BxC)

A = ug CN from calibration curve

B = grams of original sample used

C = mls of distillate used for color development

IX. Daily Quality Control

A. Control Samples

1. Method Blank

For each lot of samples processed, method blanks (Deionized water and reagents) should be carried throughout the entire sample preparation, distillation, and analytical process. These blanks are useful in determining if samples are being contaminated.

2. Precision Analysis (Required by PACE QC Program)

Duplicate samples are processed on a routine basis. Duplicate samples are used to determine precision. The sample load will dictate the frequency, but at least one of every ten samples for each matrix will be duplicated. Duplicates should be carried throughout the entire sample preparation, distillation, and analytical process.

3. Accuracy Analysis

Spiked samples or standard reference materials are employed to determine accuracy. The following spiked samples will be included in each lot:

a. Certified Soil Spikes

1. Two high level spikes, 12 ug/g cyanide

2. One low level spike, 2.4 ug/g cyanide

3. These are prepared per instructions in Section V. A. Note: Spikes need to be in contact with the soil for at least one hour before processing continues.

b. Sample Matrix Spike (Required by PACE QC Program)

1. Prepared and spiked in the same manner as certified soil high level spikes (12.0 ug/g cyanide)

2. Spike one for every ten samples to be analyzed

B. Control Charts

As part of the QC program for this project, single day and three-point moving average X-R control charts will be generated using either the software provided by USATHAMA or a manual method.

Initial Single-Day X-R Control Limits

	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Cyn	123.6	116.0	86.0	78.4	39.2	30.1

Initial Three-Day X-R Control Limits

	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Cyn	103.7	97.7	73.9	67.9	45.1	35.9

X. References

A. American Public Health Association and Others, 1976, Standard Methods for Examination of Water and Waste Waters (15th edition): New York, American Public Health Association, Incorporated, p. 312.

B. American Society for Testing and Materials, 1984, Annual Book of ASTM Standards, Section 11, Water: Philadelphia, American Society for Testing Materials Method D 2036-82, p. 110.

C. United States Environmental Protection Agency, 1979, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020

Environmental Monitoring and Support Laboratory, Cincinnati, Method 335.2.

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#2

ANALYSIS OF ORGANOCHLORINE PESTICIDES (OCP) AND POLYCHLORINATED BIPHENYLS (PCB) IN ENVIRONMENTAL SOIL/SEDIMENT SAMPLES BY GAS CHROMATOGRAPHY (GC)

METHOD LH19

I. SUMMARY

A. ANALYTES

The following analytes can be determined by this method:

USATHAMA DESIGNATION	COMPOUND
CL4XYL	Tetrachloro-m-xylene (surrogate)
CL10BP	Decachlorobiphenyl (surrogate)
ABHC	alpha-BHC
BBHC	beta-BHC
DBHC	delta-BHC
LIN	gamma-BHC
HPCL	Heptachlor
ALDRN	Aldrin
HPCLE	Heptachlor epoxide
AENSLF	alpha-Endosulfan
DLDRN	Dieldrin
PPDDE	4,4'-DDE
ENDRN	Endrin
BENSLF	beta-Endosulfan
PPDDD	4,4'-DDD
ESFSO4	Endosulfan sulfate
PPDDT	4,4'-DDT
MEXCLR	Methoxychlor
ENDRNK	Endrin ketone
ENDRNA	Endrin aldehyde
ACLDAN	alpha-Chlordane
GCLDAN	gamma-Chlordane
TXPHEN	Toxaphene
PCB016	Aroclor 1016
PCB221	Aroclor 1221
PCB232	Aroclor 1232
PCB242	Aroclor 1242
PCB248	Aroclor 1248
PCB254	Aroclor 1254
PCB260	Aroclor 1260

B. MATRIX

This method is applicable to the quantitative determination of the selected OCP/PCB compounds in environmental soil/sediment samples.

C. GENERAL METHOD

A measured weight of soil, nominally 10-grams, is sonicated in dichloromethane (DCM). The DCM extract is filtered and concentrated, solvent exchanged to hexane, then passed through a Florisil column to remove potential interferences. The extract is then analyzed by capillary GC using an electron capture detector (ECD). Dual column analysis allows for simultaneous identification, quantitation, and confirmation of target compounds. Sample results are calculated by an external standard method.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration range in standard soil samples is given in Table 1.

B. SENSITIVITY

The instrument response for each analyte at the calculated reporting limit is given in Table 1.

C. REPORTING LIMITS

The certified reporting limit (CRL) calculated for each target analyte according to the USATHAMA reporting limit software is given in Table 1.

TABLE 1. TESTED MATRIX CONCENTRATION, CERTIFIED REPORTING LIMIT, AND INSTRUMENT SENSITIVITY.

ANALYTE	TEST CONCENTRATION RANGE (UG/G)	CRL (UG/G)	UCRL (UG/G)	AREA COUNTS AT CRL
CL4XYL	0.0025 to 0.125	0.00714	0.125	7,880
CL10BP	0.0025 to 0.125	0.00691	0.125	1,350
ABHC	0.0025 to 0.125	0.0225	0.125	8,630
BBHC	0.0025 to 0.125	0.00539	0.125	5,740
DBHC	0.0025 to 0.125	0.0228	0.125	25,600
LIN	0.0025 to 0.125	0.0200	0.125	16,400
HPCL	0.0025 to 0.125	0.00961	0.125	8,770
ALDRN	0.0025 to 0.125	0.0130	0.125	19,800
HPCLE	0.0025 to 0.125	0.00386	0.125	17,100
AENSLF	0.0025 to 0.125	0.00474	0.125	6,130
DLDRN	0.005 to 0.250	0.00785	0.250	307
PPDDE	0.005 to 0.250	0.0142	0.250	3,150
ENDRN	0.005 to 0.250	0.0111	0.250	13,100
BENSLF	0.005 to 0.250	0.00711	0.250	11,100
PPDDD	0.005 to 0.250	0.0112	0.250	11,300
ESFSO4	0.005 to 0.250	0.0130	0.250	3,540
PPDDT	0.005 to 0.250	0.00964	0.250	9,630
MEXCLR	0.025 to 1.25	0.211	1.25	145,000
ENDRNK	0.005 to 0.250	0.00608	0.250	8,622
ENDRNA	0.005 to 0.250	0.0276	0.250	49,800
ACLDAN	0.0025 to 0.125	0.00398	0.125	13,800
GCLDAN	0.0025 to 0.125	0.0214	0.125	16,800
TXPHEN	0.250 to 12.5	0.250	12.5	12,100
PCB016	0.050 to 2.50	0.050	2.50	12,100
PCB221	0.050 to 2.50	0.050	2.50	6,110
PCB232	0.050 to 2.50	0.050	2.50	5,810
PCB242	0.050 to 2.50	0.050	2.50	9,700
PCB248	0.050 to 2.50	0.050	2.50	6,240
PCB254	0.050 to 2.50	0.050	2.50	9,360
PCB260	0.050 to 2.50	0.050	2.50	8,700

D. INTERFERENCES

Method interferences may be caused by solvents, reagents, glassware, and other sample processing equipment. These interferences may yield artifacts and/or elevated baselines in chromatograms. All sample processing materials will be routinely monitored for potential interferences by analyzing reagent and laboratory blanks. Extra caution must be taken to avoid phthalate contamination from plastic and latex. Phthalates interfere with chlorinated pesticide analysis by GC/ECD. Laboratory personnel must eliminate any contact between sample extracts and latex gloves, tubing, polyethylene bottles, etc.

E. ANALYSIS RATE

The lot size shall not exceed 14 samples plus control samples per 24 hour period.

F. SAFETY

The compounds of interest are toxic and potentially carcinogenic. All chemicals and samples should be handled as potential health hazards. Only personnel trained in the safe handling of such materials will be allowed to work on this procedure. At a minimum laboratory personnel will wear lab coats, safety glasses, and latex gloves when handling samples or standards. Cartridge respirators and other special protective equipment is available if needed.

The laboratory maintains a current file of OSHA regulations regarding the safe handling of chemicals. Material Safety Data Sheets are also available to laboratory personnel.

III. APPARATUS AND CHEMICALS

A. HARDWARE/GLASSWARE

1. Sonic cell disruptor with 3/4 inch tip, Heat Systems Model W-385 or equivalent

2. Amber screw-cap vials with Teflon®-lined septa, as appropriate

3. Chromatographic columns [30 cm x 11 mm inside diameter (ID) and 250 ml reservoir]

4. Disposable volumetric pipettes

5. Class A volumetric flasks, as appropriate

6. Class A volumetric pipettes, as appropriate

7. Pasteur pipettes (disposable)

8. Crimp-top 2-mL amber autosampler vials, Hewlett-Packard or equivalent

9. Gas-tight microliter syringes, as appropriate

10. Wide range pH paper

11. Analytical balance (0.0001-g and 0.01-g sensitivity), American Scientific Products or equivalent

12. Florisil cartridges, 1-g with teflon frit, Analytichem, or equivalent

13. Solid Phase Extraction (SPE) Manifold (Analytichem International, Vac-Elut, or equivalent)

14. Kuderna-Danish Apparatus; including 10-mL graduated concentrator tubes, 500-mL evaporative flask, 3-ball macro Snyder column, and 3-ball micro Snyder column

15. Heated water bath with temperature control

16. Organomation Associates N-Evap nitrogen blowdown apparatus, or equivalent

17. Class A 400-mL beakers

18. Glass culture tubes, 16 x 100 mm, Baxter Healthcare Corporation or equivalent

B. INSTRUMENTATION

A Hewlett-Packard 5890 gas chromatograph (or equivalent) equipped with dual electron capture detectors and an autosampler. Integration is performed using VG Minichrome or Nelson Analytical 2600 chromatography data system (or equivalent, capable of integrating peak heights and areas and recording retention times).

1. ANALYTICAL CONDITIONS - PRIMARY COLUMN

Column: DB-608 (J & W Scientific or equivalent) fused silica capillary (fscc), 30-m length, 0.53-mm ID with a 0.83-um film
Temperature Program: 150°C-170°C for 3-5-min, then 5°C/min to 270°C with a 15-25 min final hold
Injector Temperature: 210°C-230°C
Detector Temperature: 300°C
Carrier Gas: Helium at 3.5-4 mLs/minute
Make-up Gas: 5% Methane/Argon at 60 mLs/minute
Injection Volume: 5-ul

2. ANALYTICAL CONDITIONS - CONFIRMATION COLUMN

Column: DB-1701 (J&W Scientific or equivalent) fscc, 30-m length, 0.53mm ID with a 1-um film
Other conditions: same as primary column

3. RETENTION TIMES

Absolute analyte retention times are given in Section XI. Retention time windows (RTW) are set at ± 0.04 minute. Daily retention time adjustments are based on the retention time from the daily standard +/- the retention time window obtained during certification.

C. ANALYTES

The target analyte CAS numbers and physical properties are given in Table 2.

D. REAGENTS AND STANDARD MATERIALS

Standard materials and reagents are identified in Table 2 along with source, purity, concentration, and preparation information.

TABLE 2. STANDARD MATERIALS AND REAGENTS IDENTIFICATION

COMPOUND	CAS NUMBER	MW	SOURCE/PURITY
CL4XYL	877-09-8	244	Supelco/LA25453
CL10BP	1336-36-3	498.5	Supelco/LA25453
ABHC	319-84-6	290.8	a
BBHC	319-85-7	290.8	b
DBHC	319-86-8	290.8	b
LIN	58-89-9	290.8	a
HPCL	76-44-8	373	a
ALDRN	309-00-2	365	b
HPCLE	1024-57-3	389	b
AENSLF	959-98-8	407	a
DLDRN	60-57-1	381	a
PPDDE	72-55-9	318	b
ENDRN	72-20-8	381	a
BENSLF	33213-65-9	407	b
PPDDD	72-54-8	320	a
ESFSO4	1031-07-8	423	b
PPDDT	50-29-3	354.5	a
MEXCLR	72-43-5	345.7	a
ENDRNK	53494-70-5	381	b
ENDRNA	7421-36-3	382	b
ACLDAN	5103-71-9	410	Velsicol Chemical/82075
GCLDAN	5103-74-2	410	Velsicol Chemical/51983
TXPHEN	9001-35-2	413.8	Restek/A000038
PCB016	12674-11-2	NA	Restek/A000041
PCB221	11104-28-2	NA	Restek/A000043
PCB232	11141-16-5	NA	Restek/A000044
PCB242	53469-21-9	NA	Restek/A000046
PCB248	12672-29-6	NA	Restek/A000048
PCB254	11097-69-1	NA	Restek/A000051
PCB260	11096-82-5	NA	Restek/A000032
Dichloromethane	75-09-2	84	Burdick & Jackson [c]
Hexane	100-54-3	86	Burdick & Jackson [c]
Acetone	67-64-1	58	Burdick & Jackson [c]
Methanol	67-56-1	32	Burdick & Jackson [c]
Toluene	108-88-3	92	Burdick & Jackson [c]
Trimethylpentane	540-84-1	114	Burdick & Jackson [c]
NaOH	1310-73-2	40	Mallinckrodt [d]
H_2SO_4	7664-93-9	98	Mallinckrodt [d]
Florisil Cartridges	-	-	Analytichem International
Sodium Sulfate	-	-	J. T. Baker

a) Supelco Standard Pesticide Mix, LA 24691.
b) Supelco Standard Pesticide Mix, LA 24711.
c) Pesticide grade, distilled in glass solvents or equivalent.
d) Analytical grade.

IV. CALIBRATION

A. STANDARD PREPARATION

1. Individual stock standard solutions are useable for 12 months and mixed working standards are useable for 6 months unless analysis difficulties warrant sooner replacement. All pesticide standard dilutions are in hexane. All standards will be stored at 4°C in amber glass vials with teflon lined caps.

2. Mixed analyte stock solutions obtained commercially are used to prepare the calibration standards. The commercially obtained standard mixes are characterized by direct comparison with USATHAMA SARMs or EPA repository standards. Concentration agreement within ±30% is considered acceptable. Individual surrogate stock solutions at 200 ug/mL are used. The surrogate compounds are tetrachloro-m-xylene and decachlorobiphenyl. Target analytes and concentrations in the pesticide mix are as follows:

PESTICIDE STOCK STANDARD SOLUTION (PSSS)

COMPOUND	CONCENTRATION (ug/mL)	COMPOUND	CONCENTRATION (ug/mL)
ABHC	15.0	ENDRIN	30.0
BBHC	15.0	BENSLF	30.0
DBHC	15.0	PPDDD	30.0
LIN	15.0	ESFSO4	30.0
HPCL	15.0	PPDDT	30.0
ALDRN	15.0	MEXCLR	150
HPCLE	15.0	ENDRNK	30.0
AENSLF	15.0	ENDRNA	30.0
DLNRN	30.0	ACLDAN	15.0
PPDDE	30.0	GCLDAN	15.0

3. An intermediate pesticide calibration standard is prepared from the PSSS in Section IV.A.2 as follows:

Compound	CMC. Stock Conc.	Aliquot	Dilution	Final Conc.
ABHC	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
LIN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
HPCL	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
AENSLF	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
DLDRN	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRN	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDD	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDT	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
MEXCLR	150 ug/mL	1.25 mL	50 mL	3.75 ug/mL
BENSLF	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
DBHC	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
ALDRN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
GCLDAN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
ACLDAN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
BENSLF	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRNA	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ESFSO4	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRNK	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDE	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
CL4XYL	200 ug/mL	0.100 mL	50 mL	0.400 ug/mL
CL10BP	200 ug/mL	0.100 mL	50 mL	0.400 ug/mL

Calibration standards are diluted down from this intermediate in the following way:

Volume Diluted	Final Volume	Standard #
0.10 mL	7.5 mL	WCSP5
1.0 mL	10 mL	WCSP4
2.0 mL	10 mL	WCSP3
4.0 mL	10 mL	WCSP2
8.8 mL	12 mL	WCSP1
0.0 mL	10 mL	Blank

4. The concentrations of the pesticides are found in Table 3.

TABLE 3. CONCENTRATION OF PESTICIDES AT VARIOUS CALIBRATION LEVELS (UG/ML)

TEST NAME	BLANK	WCSP5	WCSP4	WCSP3	WCSP2	WCSP1
ABHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
BBHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
DBHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
LIN	0.00	0.00500	0.0375	0.0750	0.150	0.275
HPCL	0.00	0.00500	0.0375	0.0750	0.150	0.275
ALDRN	0.00	0.00500	0.0375	0.0750	0.150	0.275
HPCLE	0.00	0.00500	0.0375	0.0750	0.150	0.275
AENSLF	0.00	0.00500	0.0375	0.0750	0.150	0.275
DLDRN	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDE	0.00	0.0100	0.0750	0.150	0.300	0.550
ENDRIN	0.00	0.0100	0.0750	0.150	0.300	0.550
BENSLF	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDD	0.00	0.0100	0.0750	0.150	0.300	0.550
ESFSO4	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDT	0.00	0.0100	0.0750	0.150	0.300	0.550
MEXCLR	0.00	0.0500	0.375	0.750	1.50	2.75
ENDRNK	0.00	0.01	0.0750	0.150	0.300	0.550
ENDRNA	0.00	0.01	0.0750	0.150	0.300	0.550
ACLDAN	0.00	0.005	0.0375	0.0750	0.150	0.275
GCLDAN	0.00	0.005	0.0375	0.0750	0.150	0.275
CL4XYL	0.00	0.00530	0.0400	0.0800	0.160	0.293
CL10BP	0.00	0.00530	0.0400	0.0800	0.160	0.293

5. A 1-level calibration is analyzed for Aroclor 1016, Aroclor 1260, and toxaphene prior to sample analysis. If positive results for PCBs or toxaphene are detected in a sample; the sample will be reanalyzed and quantitated against a 1-level calibration of the detected aroclor.

6. An external calibration check standard (CCS) is analyzed to verify each initial calibration. The CCS is prepared from separate stock solutions from the calibration standards and contains as many target analytes as possible at a concentration near the middle of the calibration curve. A CCS prepared from SARM or EPA traceable materials will serve as a concentration verification for available premixed standard solutions where the comparison results are within 30% of the expected value. Example external check standard concentrations are listed below:

COMPOUND	CONCENTRATION (ug/mL)	COMPOUND	CONCENTRATION (ug/mL)
ABHC	0.125	ENDRIN	0.250
BBHC	0.125	BENSLF	0.125
DBHC	0.125	PPDDD	0.250
LIN	0.150	ESF504	0.300
HPCL	0.250	PPDDT	0.301
ALDRN	0.250	MEXCLR	0.250
HPCLE	0.125	ENDRNK	0.308
AENSLF	0.125	ACLDAN	0.177
DLNRN	0.300	GCLDAN	0.163
PPDDE	0.250		

NOTE: As new stocks are made, concentrations will vary slightly.

7. The low level control spike solution is prepared by combining and diluting individual stock solutions for each control analyte in a 100-mL volumetric flask and diluting to volume with acetone. Preparation and final analyte concentrations in the mixed analyte control spike solution are as follows:

Control Analyte	Stock Solution Concentration (ug/mL)	Volume of Stock Diluted to 100-mL (uL)	Control Spike Solution Concentration (ug/mL)
ALDRN	5,000	4.0	0.200
DLDRN	1,000	20.0	0.200
ENDRN	5,000	4.0	0.200
PPDDT	6,010	3.2	0.192
HPCL	5,000	4.0	0.200
LIN	5,000	8.0	0.400
GCLDAN	3,550	11.0	0.391
AENSLF	1,000	20.0	0.200
BENSLF	1,000	20.0	0.200
MEXCLR	5,870	68.0	3.99

Note: Concentrations will vary slightly, as new stocks are made.

8. The high level control spike solution is prepared by combining and diluting individual stock solutions, in a 50-mL volumetric flask and diluting to volume with acetone. Preparation and final analyte concentrations in the mixed analyte control spike solution are as follows:

Control Analyte	Stock Solution Concentration (ug/mL)	In Acetone Volume of Stock Diluted to 50-mLs (uL)	Control Spike Solution Concentration (ug/mL)
AENSLF	1,000	50.0	1.0
ALDRN	5,000	10.0	1.0
GCLDAN	3,550	14.0	0.99
HPCL	5,000	10.0	1.0
LIN	5,000	10.0	1.0
BENSLF	1,000	100	2.0
DLDRN	5,000	20.0	2.0
ENDRN	5,000	20.0	2.0
PPDDT	6,010	17.0	2.0
MEXCLR	5,870	85.0	9.98

Control spike solutions must be prepared from separate stock solutions as those used for calibration standards. Control spike solutions require concentration verification before use and weekly during continued usage.

Note: Concentrations will vary slightly as new stocks are made.

B. INSTRUMENT CALIBRATION

1. INITIAL INSTRUMENT CALIBRATION

a. Initial calibration requires the analysis of a solvent blank and five calibration standards bracketing the certification test range. The nominal standard concentrations analyzed during initial calibration are at 0, 5.00, 37.5, 75.0, 150, and 275-ng/mL.

b. The responses for the five standard levels are plotted versus concentration for each compound and the linear regression equation is calculated. This linear regression equation creates an external standard method for quantitation of the target analytes in environmental samples.

c. Following each calibration curve, an external calibration check standard is analyzed. The results calculated from the linear regression equation generated from the initial calibration curve must be within ±30% of the true value.

d. If samples are analyzed on the same day as initial calibration is performed. The highest concentration standard is then analyzed after sample analyses are completed. The response for each compound must agree within ±25% of the response for the same standard concentration in the initial calibration curve.

2. DAILY INSTRUMENT CALIBRATION

a. Calibration standards are analyzed each day to verify that instrument response has not changed from previous calibration.

b. Before sample analysis each day, the highest concentration standard is analyzed. The response must fall within ±25% of the highest concentrated standard in after seven daily calibrations, analyte responses must agree within 2 standard deviations of the mean response determined from the current initial calibration and seven daily calibrations. If the response fails this check, the daily standard is reanalyzed. If the response from the reanalysis does not meet the acceptable criteria, then initial calibration is repeated before samples are analyzed.

c. After sample analyses are completed each day, the highest concentration standard is reanalyzed. If the response is not within ±25% of the highest concentration standard from the initial calibration, the daily standard is reanalyzed. If the response from the second analysis is not acceptable, the system is considered to have failed calibration. In this case, initial calibration is performed and all samples analyzed since the last acceptable calibration are reanalyzed.

C. ANALYSIS OF CALIBRATION DATA

Initial calibration acceptability is based on:

1) the baseline instrumental detector signal (blank)
2) the linearity of each analyte over the calibration range
3) accurate quantitation of an external standard (CCS).

Once analysis of a solvent blank exhibits acceptable instrument signal to noise ratio (baseline), the five point initial calibration curve is analyzed. The response vs. concentration data for each analyte is plotted and the resulting linear regression data is evaluated. If the linear regression fit coefficient for at least 67% of the target analytes is 0.995 or greater, the initial calibration shows acceptable linearity.

Once linearity is acceptable the CCS standards are quantitated using the external standard linear regression equations. If the calculated CCS values are within 30% of the actual concentration, the initial calibration is considered acceptable and sample analysis may proceed.

V. CERTIFICATION TESTING

Certification samples are prepared and analyzed to determine the certified reporting limits for each target analyte. For pesticides in soil samples, the nominal target reporting limit (TRL) is 0.0025 ug/g. Spikes are prepared at 0, 0.5, 1, 2, 5 10, and 20 times the TRL. Certification spikes are prepared according to Table 4. Separate individual stock standards must be used to prepare certification spike solutions and calibration standards.

10-gram aliquots of standard soil are spiked as outlined in Table 4 (in the beaker) then sonicated, cleaned up, and analyzed according to this method. Target versus found concentration data are entered into the IRDMS IRPQAP program for certified reporting limit calculation.

TABLE 4. PESTICIDE CERTIFICATION SPIKE PREPARATION AND NOMINAL CONCENTRATIONS

Composite Spike Solution	Spike Solution Concentration (ug/mL)	Volume Spiked (mL)	Certification Concentration (ug/g)
CSS1	1.25	1.00	0.125
CSS1	1.25	0.400	0.0500
CSS1	1.25	0.200	0.0250
CSS2	0.100	1.00	0.0100
CSS2	0.100	0.500	0.00500
CSS2	0.100	0.250	0.00250
Blank	0.00	0.500	0.00

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE. Sampling procedures will be performed according to the Sampling Design Plan, Site Specific Quality Assurance Plans, and the USATHAMA QA Program, January 1990.

B. SAMPLE HANDLING. Samples must be received in the laboratory as soon as possible after field sampling. Samples received at the laboratory are checked in by the designated sample custodian.

C. SAMPLE HOLDING TIMES. The holding time is 7 days from the date sampled until the sample is solvent-extracted. After extraction, sample extracts must be analyzed within 40 days.

D. SPIKE SOLUTION VERIFICATION. The control and surrogate spike solutions are verified by GC/ECD every 7 days during use. Verification acceptability is determined according to the USATHAMA QA Program, January 1990.

VII. PROCEDURE

A. GLASSWARE CLEANING

1. Wash glassware with an appropriate brush in hot, soapy water. Use a micro-cleaning solution such as Alconox, or an equivalent detergent.

2. Rinse the washed glassware three times with hot water followed by three rinses with deionized water.

3. Rinse the glassware well with reagent grade acetone; cover the open ends with aluminum foil and store as appropriate. (If glassware is to be used immediately after washing, use high-purity acetone rather than reagent grade.) Immediately prior to use all glassware is triple rinsed with high-purity methylene chloride.

4. Prior to using stored glassware, remove the aluminum foil from the glassware, and rinse all surfaces three times with high-purity acetone followed by rinsing three times with high-purity methylene chloride.

B. SEPARATIONS

The initial separation involves a solvent extraction of the target analytes from the soil into methylene chloride. Chromatographic separation is utilized in the florisil cleanup. The florisil adsorbent retains more polar compounds which may interfere with analyte detection and quantitation by GC/ECD. Selective compound affinity is the basis for analyte separation in the fused-silica capillary column(fscc). The stationary phase in each fscc provides analyte resolution and unique retention times for identification and confirmation.

C. CHEMICAL REACTIONS

There are no chemical reactions occurring in the performance of this method.

D. SAMPLE EXTRACTION, CONCENTRATION, AND CLEANUP

1. Mix samples thoroughly and discard any foreign objects such as sticks, leaves and rocks. Also, decant and discard any standing aqueous phase.

2. Percent Moisture Determination - Weigh 10-15 g of the sediment (to the nearest 0.01 g) into a tared aluminum weighing pan. Determine the moisture by drying overnight at 105°C. After the sample is dry, remove the sample and allow to cool before weighing. Calculate the percent moisture according to the equation below.

$$\text{Percent Moisture} = \frac{\text{Wt of Wet Sample} - \text{Wt of Dry Sample}}{\text{Wt of Wet Sample}} \times 100$$

3. Weigh approximately 10 g of sample (to the nearest 0.1 g) into a beaker and add 20 g of anhydrous sodium sulfate. Also weigh 4 aliquots (10 g) of standard soil to serve as lot control samples. Section IX describes control sample requirements.

4. Add 2.0 mL of the 0.200 ug/mL surrogate solution to all control and environmental soil samples. The surrogate compounds are at 0.040 ug/g. Mix well (the sample and sodium sulfate should be a homogeneous, granular mixture at this point).

5. Allow 1 hour for equilibration. Then add 50 mLs of 1:1 methylene chloride acetone to the sample.

6. Place the bottom surface of the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

   Sonicate for 3 minutes using a 3/4 inch horn at full power (output control knob at 10) with pulse on and percent duty cycle knob set at 50 percent. Do not use a microtip

   NOTE: These settings refer to the Model W-385, refer to the instructions provided by the manufacturer for appropriate output settings.

7. The extracted sample can then be filtered by using gravity or vacuum filtration.

   7.2.8.1 For gravity filtration, prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10-cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with anhydrous sodium sulfate (80-100 g). Decant the extract through the packed funnel and collect it in a 500-mL evaporation (K-D) flask.

   7.2.8.2 For vacuum filtration, use Whatman No. 41 paper in the Buchner funnel. Pre-wet the paper with methylene chloride/acetone before decanting the solvent.

8. Repeat the extraction two more times with additional 50-mL portions of the 1:1 methylene chloride/acetone. Before each extraction, thoroughly mix the solid residue, and make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a

clean spatula. Decant and filter the extraction solvent after each sonication by using the same funnel described in paragraph 6.2.8. After the final sonication, pour the entire sample into the funnel and rinse the beaker and funnel with 60 mLs of 1:1 methylene chloride/acetone.

9. Add one or two clean boiling chips to the K-D evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60° - 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the K-D apparatus so the concentration is complete in 15 to 30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10. The sample extracts are solvent exchanged to hexane by K-D concentration. This is done by concentrating the methylene chloride extracts to near 5-mLs removing the extracts from the water bath and adding 50-mL of hexane to the K-D and continuing concentration to near 5 mL again. Remove the K-D apparatus from the water bath and allow to cool.

11. Remove the Snyder column; using 1 to 2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Place the concentrator tube in a heated bath (30 to 35°C) and evaporate the solvent to near 2 mL by blowing a gentle stream of clean, dry nitrogen onto the solvent. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

12. Attach a vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 1 and 5 pounds of vacuum. Place one Florisil cartridge into the vacuum manifold for each sample extract.

13. Prior to cleanup of samples, the florisil cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge in the vacuum manifold, pulling a vacuum, and passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

14. After the cartridges in the manifold are washed, the vacuum is released, and a rack containing labeled culture tubes is placed inside the manifold. Vacuum to the manifold is restored, and the extract from each sample, blank, or control spike is transferred to the top frit of the appropriate Florisil cartridge.

15. The pesticides/Aroclors in the extract concentrates are then eluted through the column with 9 mL of hexane/acetone (90:10) and are collected into culture tubes held in the rack inside the vacuum manifold.

16. Concentrate the extract to 4.0 mL using nitrogen blowdown. The final volume is measured with a syringe, volumetric pipet or calibrated concentrator tube.

E. INSTRUMENTAL ANALYSIS

Instrumental analysis is performed by injecting 5-uL of the blank, standards, controls, and samples into the GC. The instrument parameters, analytical conditions, standard preparation, and sample preparation described within this method allow for separation, identification, and quantitation of each target compound.

Run sequence has been defined as the following:

1. Non-target list pesticide as the following:
2. Toxaphene and Aroclor 1016/1260 standard
3. Hexane blank
4. Calibration standards 1-5
5. External Check
6. 8 samples, blanks, qc
7. Calibration std. #5
8. 10 samples, blanks qc
9. Calibration std #5

DB608 is the primary channel. Except in cases of matrix interferences, all results will be taken from this channel, calibration criteria only applies to the quantitiation channel.

F. CONFIRMATION ANALYSIS

The gas chromatograph is equipped with a dual-column system. A single injection volume is split immediately after the injection port into two fscc allowing for simultaneous analyte identification, quantitation, and confirmation. Evaluation of the calibration acceptability will be performed on both columns and analyte quantitation may be performed from either column.

VIII. CALCULATIONS

A. INITIAL CALIBRATION

The initial calibration linear regression equation determined for each analyte is used to calculate sample concentrations. The instrument response is plotted on the ordinate and the concentration on the abscissa. The regression equation for each analyte is then calculated as:

$y = mx + b$ where: y = response (area)
m = slope of the line
x = concentration (ug/mL)
b = intercept

B. SAMPLE QUANTITATION

Analyte concentration is determined by translating the above regression equation to:

$A = (y - b)/m$ where: A = calculated amount of material in the sample extract, within the calibration range (ug/mL)

and $\frac{(A)\ (1.0\ mL\ final\ volume)\ (2\ (for\ GPC\ split))}{sample\ weight\ (10\ g)}$ = found concentration (ug/g)

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

Daily control requirements include extraction and analysis of a method blank and three standard matrix spikes. Each analytical lot contains the method blank to check for background contamination and three matrix spikes to monitor method accuracy and precision through percent recoveries.

The method blank contains the surrogate compounds at 0.040 ug/g. The method blank should not contain any confirmed target analytes above the CRL.

The control spiking solutions are prepared as described in Section IV.A.7 and IV.A.8. The control samples are spiked according to Table 6. Percent recovery results for each analyte are determined by quantitation of the found amount of each analyte from the current acceptable initial calibration.

Control results are to be calculated and plotted on control charts to monitor method accuracy and precision. Control charting is conducted according to the USATHAMA QA plan using computer software provided by USATHAMA.

The control spiking solution concentration must be verified weekly against working calibration standards. Dilute the spiking solution with hexane and analyze using GC/ECD. Using the current acceptable calibration regression equation, calculate the found amount of each control analyte. Recovery must be above the current lower warning control limit on the single-day XBAR control chart.

TABLE 6. PREPARATION OF SAMPLE LOT CONTROL SPIKES

Daily Control Spike Sample	Volume of Control Spiking Solution Added (mL)	Volume of 0.200 ug/mL Surrogate Added (mL)
Blank	0.0	2.0
Low Spike	1.0	2.0
High Spike	1.0	2.0
High Spike Dup	1.0	2.0

CONCENTRATION OF CONTROL ANALYTES

Compound	Concentration of Blank (ug/L)	Low Spike Concentration (ug/g)	High Spike Concentration (ug/g)
CL4XYL	0.000	0.040	0.040
CL10BP	0.000	0.040	0.040
AENSLF	0.000	0.020	0.100
ALDRN	0.000	0.020	0.100
BENSLF	0.000	0.020	0.200
DLDRN	0.000	0.020	0.200
ENDRN	0.000	0.020	0.200
GCLDAN	0.000	0.0391	0.099
HPCL	0.000	0.020	0.100
LIN	0.000	0.040	0.100
MEXCLR	0.000	0.399	0.998
PPDDT	0.000	0.0192	0.200

Note: Concentrations will vary slightly as new stocks are made.

B. CONTROL CHARTS

Control charts will be maintained to monitor variations for each control analyte in precision and accuracy during routine analyses and to detect trends in these variations. The control charting procedure that will be followed is given in Section 7.0 of the USATHAMA QA Program, January 1990. The reports will include:

Single-Day XBAR Control Data and Chart
Single-Day RBAR Control Data and Chart

B. CONTROL CHARTS

Control charts will be maintained to monitor variations for each control analyte in precision and accuracy during routine analyses and to detect trends in these variations. The control charting procedure that will be followed is given in Section 7.0 of the USATHAMA QA Program, January 1990. The reports will include:

Single-Day XBAR Control Data and Chart
Single-Day RBAR Control Data and Chart

Three-Day Average XBAR Control Data and Chart

Three-Day Moving Average RBAR Control Data and Chart

X. REFERENCES

1. U.S. Environmental Protection Agency (EPA). 1982. Method 608 -- Test Method for Organochlorine Pesticides and PCBs. In: Compendium of Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA-600/4-82-057.

2. U.S. Environmental Protection Agency (EPA). May, 1990. Statement of Work for Organic Analysis. USEPA Contract Laboratory Program.

3. USATHAMA Quality Assurance Program, January, 1990, USATHAMA PAM 11-41.

XI. DATA

A. ANALYTICAL STANDARD CHARACTERIZATION

B. INITIAL CALIBRATION

C. DAILY CALIBRATION

D. STANDARD CERTIFICATION DATA

COPY #1

LM05 = LM33

STANDARD OPERATING PROCEDURE

Volatile Compounds in Soil by Gas Chromatography/Mass Spectrometry Low Level Method

SOP NUMBER	MN-O-423-ATH
AUTHOR	Steven P. Sanders
EFFECTIVE DATE	November 22, 1991
SUPERSEDES	WPPMNSOP82

APPROVAL

Kent R Lindstrom
Section Supervisor

12-05-91
Date

Susan Shanahan
Organic Laboratory Manager

12-5-91
Date

William H. Scott
Quality Assurance Officer

12-5-91
Date

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I. SUMMARY

A. ANALYTES

1. This method is applicable for the determination of volatile organics. This generally includes compounds that have a boiling point less than 200° C and are insoluble or slightly soluble in water. The analytes certified by this method are given in Table I.

B. MATRIX

1. This is a purge & trap gas chromatograph/mass spectrometer (GC/MS) method applicable to the determination of the target analytes in environmental soil and sediment samples.

C. GENERAL METHOD

1. An inert gas, helium, is swept through a specially-designed purging chamber containing a soil sample in the presence of reagent water at 40° C. The purgeables are efficiently transferred from the solid to the aqueous phase and then to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are removed. After purging is complete, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

1. The tested concentration range is from 0.0025-µg/g to 0.125-µg/g for the analytes listed in Table I. The instrument calibration range is from 2.0 µg/L to 150 µg/L.

2. See Table I for list of targets and surrogates.

B. SENSITIVITY

1. The instrumental response for an absolute quantity of analyte varies with the compound. The response calculated at the certified reporting limit for each compound can be found in Table II.

C. CERTIFIED REPORTING LIMIT (CRL)

1. The certified reporting limit (CRL) and upper certified reporting limit (UCRL) as determined by method certification are given in Table II.

D. INTERFERENCES

1. Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

2. Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3. Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses. The trap and other parts of the system are also subject to contamination. Therefore, frequent bakeout and purging of the entire system may be required.

E. ANALYSIS RATE

1. The analysis rate shall not exceed 20 samples (including lot control samples) per 24 hour period.

F. SAFETY INFORMATION

1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Bottle, wide-mouth, 120-mL capacity, equipped with a teflon-lined screw cap. Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

2. Syringes--5-mL, gas tight, glass hypodermic with Luerlok end.

3. Micro syringes--10-uL, 25-uL, 50-uL, 100-uL, and 250-uL, 1.0-mL, 0.006 in. ID needle.

4. Vial--15-mL, crimp-cap, with Teflon cap liner.

5. Balances--Analytical, capable of accurately weighing 0.0001g. Top loading, capable of accurately weighing 0.01g.

6. 5-mL, 10-mL, 25-mL, 50-mL and 100-mL volumetric flasks - class A, with ground-glass stoppers.

7. Spatula--stainless steel

B. INSTRUMENTATION

1. A Tekmar ALS 2016 autosampler equipped with needle spargers and sample pocket heaters is used to heat and purge the sample. The autosampler is connected via a heated transfer line to a LSC 2000 concentrator equipped with a moisture control module and containing a 25-cm, 1/8" O.D. trap packed with activated charcoal, silica gel, and tenax (Tekmar #3 trap). This trap is rapidly heated to 180° C and desorbed via a six port valve onto the GC analytical column for analysis. A Tekmar cryofocusing module interfaces the concentrator to the GC.

2. A Varian 3400 gas chromatograph with Tekmar capillary interface which is temperature programmable and fit with a capillary column is used to separate the target analytes.

3. A DB-624 capillary column (0.32 mm ID, 30 m, 1.8 um film thickness) is used (J & W Scientific or equivalent). The capillary column elutes directly into the source of the mass spectrometer.

4. Extrel Model ELQ400 Mass spectrometer--Capable of scanning from 35 to 260 amu every 0.5 seconds or less, utilizing 70V (nominal), electron energy in the electron impact ionization mode.

5. Data system--A Digital Equipment PDP11/03 computer system is interfaced to the mass spectrometer allowing continuous acquisition and storage of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching any GC/MS data file for specific m/z (mass/charge ratio) and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software also allows integrating the abundance in any EICP between specified time or scan number limits.

6. Hewlett-Packard 5890 Gas Chromatograph equipped with a flame-ionization detector.

7. Hewlett-Packard 19395A headspace sampler unit.

8. Hewlett-Packard 3396A integrator.

C. ANALYTES

1. Chemical Abstract Service Registry numbers for the target analytes are given in Table III.

D. REAGENTS AND SARMS

1. PACE utilizes deionized water (DI) which is treated with ultraviolet light using an Organic pure system manufactured by Barnstead, Inc.

2. Trap materials: PACE purchases #3 traps from Tekmar Corporation. These are packed with Tenax, silica gel, and charcoal.

3. Methanol--Purge and Trap grade. Burdick & Jackson.

4. Quality Assurance Materials Bank Artificial Soil Blank, Lot No. 014 Sample No. 66 G8280363, or equivalent.

5. PACE utilizes vendor certified (Restek Corp or equivalent) standard mixes for target compounds, internal standards, surrogate standards, and matrix spike solutions. Corresponding data packages are supplied showing GC/FID data, weights, and mass spectra. Vendor standards are checked against EPA or NSI standard mixes after each initial calibration.

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Standard Solution Preparation

a. Prepare a primary mix stock solution of the standard compounds in methanol at a concentration of 100-µg/ml, as

given in Table IV and V. Prepare standards in methanol at 2.0, 10, 20, 50 and 150-μg/L.

b. Store all stock solutions at -10° C (or colder) in Teflon septum capped containers. The working calibration solutions must be replaced each month, or sooner, if comparison with quality control check samples indicate a problem.

c. All standards prepared for use throughout the laboratory are assigned a code number. The standard code number is entered in the standard notebook with all information regarding the preparation of that standard, i.e., date, analyst, name of each compound, amount used, and final volume. All standard containers are labelled with the standard's code, date, concentration and analyst's initials.

d. The instrument response obtained for each compound in a newly prepared standard is compared to the response obtained from the previously prepared standard. Corrective actions such as checking calculations, remaking the standard, and instrument maintenance will be employed if response is not comparable.

2. Instrument Calibration

a. The GC/MS system must be tuned to meet mass calibration through the analysis of bromofluorobenzene (BFB). Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for BFB given in Table VI.

b. A working standard solution of 12DCD4, MEC6D8, and 4BFB surrogate compounds is prepared for addition to each environmental and control sample. This surrogate standard spiking solution is prepared from stock standards at a concentration of 25-μg/mL in methanol (See Table IV). The addition of 10-uL of the 25-μg/mL solution to 5-mL of sample or standard is equivalent to a concentration of 50 μg/L for each surrogate standard. Spiking solutions are prepared every two weeks or as needed based on performance.

c. A working standard solution of BCM, 14DFB, and CLBD5 internal standards is prepared by diluting the stock solution to a final concentration of 25-µg/mL in methanol (See Table IV). The addition of 10-uL of the 25-µg/mL solution to 5-mL of sample or standard is equivalent to a concentration of 50-µg/L of each internal standard. Spiking solutions are prepared every two weeks or as needed based on performance.

d. Using the 25-µg/mL stock standard for surrogates and a 100-µg/mL standard for target analytes, prepare calibration standards (see Table IV and V). The following table lists the initial calibration levels of certified analytes:

Surrogates (µg/L)	2.0	10	20	50	150
Target Analytes (µg/L)	2.0	10	20	50	150

10-uL of internal standard (25-µg/mL) is added to each 5-mL calibration standard. Tabulate the area response of the characteristic ion against concentration for each compound and internal standard and calculate response factors (RF) for each compound using the equation provided in Section VIII. Calculations.

e. Analyze each standard and blank. The relative response factor (RRF) is calculated for each analyte of interest from the initial calibration standards. The relative standard deviation for at least 67% of the target compounds must be <35%.

f. The selected internal standard for quantitation of each target analyte (Table VII) permit most components of interest in a chromatogram to have relative retention times of 0.80 to 1.20. The width of the retention time window used to make identifications is 30 seconds. Daily adjustments to the retention time window will be made based on the relative retention time of each analyte in the daily calibration standard. The primary

ion for quantitation is listed in Table VIII. If interferences are present, the secondary ion (also listed in Table VIII) is used. Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be inspected for malfunctions and corrections made as required. If the extracted ion current profile (EICP) area of any internal standard changes by more than a factor of two (-50% to +100%), from the latest continuing calibration standard, the mass spectrometric system must be inspected for malfunction, corrections made as appropriate, and explanation given for affected samples.

3. Analysis of Calibration Data

a. An initial calibration is acceptable if the relative response factor (RRF) for at least 67% of the analytes is less than 35% relative standard deviation (RSD) over the initial calibration curve. Initial calibration is verified by utilizing USEPA traceable check standards, SARMS, or second-vendor sources.

B. DAILY CALIBRATION

1. Preparation of Standards

a. See Section IV.A.1.

2. Instrument Calibration

a. The GC/MS system must be hardware tuned by injection of BFB to meet the criterion listed in Table VI. BFB tuning criteria must be met every 12 hours during sample analysis.

b. A continuing calibration standard at 50-µg/L for each target analyte will be run before sample analysis..every 12 hours

during sample analysis, and at the end of each day's analysis. In the event the continuing calibration standard run in the middle of a 24-hour lot analysis sequence fails, yet the end of the day standard meets the acceptance criteria, the samples will be reviewed for problems and either reanalyzed or submitted with technical justification.

c. The initial calibration curve as established in Section IV.A.2., is utilized to determine continuing calibration acceptability. The initial calibration curve RRF for each target analyte must be verified on each working day by the measurement of a continuing calibration standard at 50-µg/L for each target analyte.

C. ANALYSIS OF CALIBRATION DATA

1. The daily calibration is considered acceptable if the RRF for at least 67% of the analytes is within 25% of the average RRF from the current acceptable initial calibration curve. If the daily standard fails, it is reanalyzed. If daily calibration fails twice, initial calibration must be performed prior to continuing sample analysis. At the end of each day of sample analysis the daily standard must be analyzed and meet the RRF criteria. If the standard fails, it is reanalyzed. If the end of day standard fails twice, initial calibration must be performed and all samples analyzed since the last acceptable calibration must be reanalyzed.

V. CERTIFICATION TESTING

A. Certification samples are prepared and analyzed to determine the certified reporting limits for each target analyte. For the target volatile compounds in soil samples, the target reporting limit (TRL) is 0.005-µg/g. Spikes are prepared at 0, 0.5, 2, 4, 10 and 25 times the TRL. Separate individual stock standards must be used to prepare certification spike solutions and calibration standards. Certification standard preparation is described in Table IX.

B. PREPARATION OF CERTIFICATION SAMPLES

1. Prepare certification spiking solutions of the target compounds according to Table IX.

2. Weigh out 5.0-g aliquots of standard soil into tared 25-mL needle sparge vessels.

3. Standard certification samples are spiked in duplicate as follows:

CERT SAMPLE	SOIL WEIGHT	CERT SPIKE SOLTN CONC., µg/mL	VOLUME SPIKE SOLTN ADDED TO CERT SAMPLE	CERT SAMPLE CONCENTRATION, (µg/g)
Blank	5.0 g	0.0	5.0-mL	0.0
0.5x TRL	5.0 g	0.0025	5.0-mL	0.0025
2x TRL	5.0 g	0.010	5.0-mL	0.010
4x TRL	5.0 g	0.020	5.0-mL	0.020
10x TRL	5.0 g	0.050	5.0-mL	0.050
25x TRL	5.0 g	0.125	5.0-mL	0.125

C. All samples are processed through the procedure detailed in Section VII.

D. Target versus found concentration data are entered into IRDMS IRPQAP program for certified reporting limit calculation.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE

1. Environmental soil samples are collected according to the Sampling Design Plan, Site Specific Quality Assurance Plan, and the USATHAMA QA Program, January 1990.

B. CONTAINERS

1. Samples are collected in 120-mL glass containers prepared according to the USATHAMA QA program, January 1990, Appendix F. Sample containers should be filled to leave minimum headspace. Containers are sealed tight until the time of analysis.

C. STORAGE CONDITIONS

1. All samples and extracts are stored in a secured area in refrigerators at 4° C.

D. HOLDING TIME LIMITS

1. Holding times are 14 days from date of collection to sample analysis.

E. SOLUTION VERIFICATION

1. All calibration standard solutions are double-checked against the previous preparation of that solution through analysis of a common external check standard containing as many target compounds as accessible.

2. The control spike solution is validated against working calibration standards before initial use and weekly during sample preparation. Calculated concentration from this verification must fall within the current control chart limits.

VII. PROCEDURE

A. SEPARATIONS

1. Not applicable to this procedure.

B. CHEMICAL REACTIONS

1. Not applicable to this procedure.

C. SAMPLE SCREENING

1. Not all samples will be screened. The decision on whether to screen will be made by the analyst based on historical information, sample matrix and/or odor.

2. Screening Procedure

   a. 5 grams of sample is weighed into 10mls of reagent water saturated with sodium sulfate.

   b. The surrogate spike Flourobenzene will be added to each sample to monitor the headspace injection.

   c. A 1-level calibration will be used.

   d. A ratio of the area from the standard peak and the corresponding sample peak area will be calculated to determine the necessary dilution or the need to use LMO5 (the certified medium level method).

D. INSTRUMENTAL ANALYSIS

1. Following acceptable instrument tuning and calibration, sample analysis may proceed.

2. Sample Purging and Gas Chromatography

a. Allow each sample to come to ambient temperature prior to weighing. Add 5.O-g of soil to a tared 25-mL needle sparge. Then quickly attach the sparge to the ALS 2016 and place a pocket heater on the sparge. Add 10 uL of the 25-μg/mL internal standard solution plus 10-uL of the 25-μg/mL surrogate spiking solution to 5-mL of reagent water. Introduce the 5-mL of water with standards added to the soil through the sample valve and sample/purge needle.

b. The following are Tekmar purge and trap conditions:

Stand by: 25° C - 30° C
Sample temperature: 40° C
Sample Preheat: 5 minutes
Purge: 11.0 minutes
Desorb Preheat: 175° C
Bake 12-18 minutes at 225° C
Moisture Control Module: Heat to 90° C
Moisture Control Module: Cool down to 8-10° C
Capillary Interface: -150° to -180° C
Tekmar lines: 100° C
Tekmar Valves: 100° C
GC Column Flow: Helium at 3-mL/minutes
GC Temperature Program: -10° C for 1 min., then 10° C/min to 100° C, then 6° C/min to 140° C, then 20° C/min to 170° C and hold for 10 minutes

VIII. CALCULATIONS

A. Calculate the concentration in the sample using the following equations:

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)} \qquad \text{Equation 1:}$$

where:

- RF = Response Factor.
- A_x = Area of the characteristic ion for the compound to be measured.
- A_{is} = Area of the characteristic ion for the internal standard.
- C_{is} = Concentration of the internal standard. (μg/mL)
- C_x = Concentration of the compound to be measured (μg/mL)

$$\text{Sample Concentration in } (\mu g/g) = \frac{(A_x)(C_s)(V_w)}{(A_{is})(RF)(W)} \qquad \text{Equation 2:}$$

- A_x = Area of the characteristic ion for the compound to be measured
- A_{is} = Area of the characteristic ion for the internal standard
- C_s = Concentration of internal standard in (μg/mL).
- V_w = Volume of water sparged (mL).
- RF = Response factor as determined in the continuing calibration (beginning of 12-hour period).
- W = Sample weight in grams.

B. GC/MS UNCERTIFIED (NONTARGET) COMPOUNDS

1. Conduct a mass spectral library search (EPA/NBS/NIH or equivalent) to tentatively identify all the nontarget peaks which are present in excess of 10 percent of the total area of the nearest internal standard peak. These compounds will also be semiquantitated according to calculations in Section VIII. Hard-copy mass spectra and library search results of all unknowns will be provided with the report. Unknown peaks will be designated by a six-character alpha-numeric code. The first three characters are UNK and the last three are reported as 100 times the RRT (relative to bromochloromethane).

2. The calculations to determine the concentration of compounds for which method certification has not been performed are the same calculations described for certified compounds as described above, except the RF shall be equal to 1.00 and the area of the parameter to be measured shall be the total ion current for that peak.

3. Estimates of concentrations of these uncertified compounds will be reported to only one significant figure.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

1. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control samples and calibration standards that the operation of the measurement system is in control. Each day of sample analysis the analyst must analyze a lot control sample which serves as the method blank and standard matrix spike. Accuracy and precision data from these control samples are used to maintain control charts.

2. The laboratory spikes all samples with surrogate compounds to monitor laboratory performance through percent recovery. Control charts and performance records included in the data package document the quality of data that is generated.

3. The daily lot control spike levels are given below:

Compound	Control Spike Level (µg/g)
MEC6D8	0.050
4BFB	0.050
12DCD4	0.050

4. The control sample consists of a 5.0-g aliquot of standard soil. After spiking, it is processed as a sample with the environmental samples according to Section VII.

5. The control spiking solutions require concentration verification weekly against working calibration standards using the current acceptable calibration regression equation. Recoveries must be above the lower control limit on the X-bar control charts.

B. CONTROL CHARTS

1. Daily control requirements include the analysis of a method blank spiked with the three surrogate compounds. Each analytical lot contains the method blank to check for background contamination and to monitor method efficiency through percent recoveries of the surrogate compounds.

2. Control charts will be maintained to monitor variation in precision and accuracy for each control analyte during routine sample analysis. The control charting procedure that will be followed is given in Section 11.0 of the USATHAMA QA Program, January 1990. The reports will include:

   a. Three-Day Moving Average X-Bar Control Chart

   b. Three-Day Moving Average R-Bar Control Chart

X. REFERENCES

A. EPA Test Methods for Evaluating Solid Waste. Physical/Chemical Methods SW-846. Method 5030. Method 3810. Method 8260. Sept. 1986.

B. USEPA Contract Laboratory Program Statement of Work for Organic Analysis. February. 1988. and June. 1990.

XI. DATA

A. Standard Materials Characterization

B. Initial Calibration Data

C. Daily Calibration Data

D. Standard Certification Sample Data

E. Certification Sample Chromatograms

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TABLE I

IRDMS	TARGET ANALYTE
BRCLM	Bromochloromethane (IS)
14DFB	1,4-Difluorobenzene (IS)
CLC6D5	Chlorobenzene-D5 (IS)
CH3CL	Chloromethane
CH3BR	Bromomethane
C2H3CL	Vinyl Chloride
C2H5CL	Chloroethane
CH2CL2	Methylene Chloride
ACET	Acetone
CS2	Carbon Disulfide
11DCE	1,1-Dichloroethene
11DCLE	1,1-Dichloroethane
C12DCE	cis-1,2-Dichloroethene
CHCL3	Chloroform
12DCLE	1,2-Dichloroethane
MEK	2-Butanone
111TCE	1,1,1-Trichloroethane
CCL4	Carbon Tetrachloride
BRDCLM	Bromodichloromethane
12DCLP	1,2-Dichloropropane
C13DCP	cis-1,3-Dichloropropene
TRCLE	Trichloroethene
DBRCLM	Dibromochloromethane
112TCE	1,1,2-Trichloroethane
C6H6	Benzene
T13DCP	trans-1,3-Dichloropropene
CHBR3	Bromoform
MIBK	4-Methyl-2-Pentanone
MNBK	2-Hexanone
TCLEE	Tetrachloroethene

TABLE 1 (CON'T.)

IRDMS	TARGET ANALYTE
TCLEA	1,1,2,2-Tetrachloroethane
MEC6H5	Toluene
CLC6H5	Chlorobenzene
ETC6H5	Ethylbenzene
STYR	Styrene
TXYLEN	Xylene (total)
T12DCE	trans-1,2-Dichloroethene
MEC6D8	Toluene-d8 (SS)
4BFB	Bromofluorobenzene (SS)
12DCD4	1,2-Dichloroethane-d4 (SS)

TABLE II

IRDMS DESIGNATION	CRL (µg/g)	UCRL (µg/g)	INSTRUMENT RESPONSE AT CRL
MEC6D8	0.0025	0.125	25000
4BFB	0.0025	0.125	7300
12DCD4	0.0025	0.125	9100
CH3CL	0.035	0.125	750
CH3BR	0.0031	0.125	6900
C2H3CL	0.0038	0.125	8700
C2H5CL	0.0029	0.125	5700
CH2CL2	0.0062	0.125	20000
ACET	0.044	0.125	200000
CS2	0.014	0.125	100000
11DCE	0.032	0.125	5000
11DCLE	0.0025	0.125	16000
C12DCE	0.0025	0.125	7400
CHCL3	0.0026	0.125	13000
12DCLE	0.0027	0.125	12000
MEK	0.0025	0.125	17000
111TCE	0.0025	0.125	9200
CCL4	0.0031	0.125	7400
BRDCLM	0.0025	0.125	10000
12DCLP	0.0025	0.125	11000
C13DCP	0.0030	0.132	16000
TRCLE	0.0025	0.125	7000
DBRCLM	0.057	0.125	8200
112TCE	0.0025	0.125	7600
C6H6	0.0025	0.125	32000
T13DCP	0.0023	0.115	11000
~~CHBR3~~ CH_2Br_2	0.0025	0.125	6600

TABLE II (CON'T.)

IRDMS DESIGNATION	CRL (µg/g)	UCRL (µg/g)	INSTRUMENT RESPONSE AT CRL
MIBK	0.019	0.125	150000
MNBK	0.018	0.125	120000
TCLEE	0.0025	0.125	5500
TCLEA	0.011	0.125	16000
MEC6H5	0.0025	0.125	18000
CLC6H5	0.0025	0.125	19000
ETC6H5	0.0025	0.125	10000
STYR	0.0025	0.125	21000
TXYLEN	0.0075	0.125	26000
T12DCE	0.0025	0.125	6100

TABLE III

Name		CAS Number
1.	Chloromethane	74-87-3
2.	Bromomethane	74-83-9
3.	Vinyl Chloride	75-01-4
4.	Chloroethane	75-00-3
5.	Methylene Chloride	75-09-2
6.	1,1-Dichloroethene	75-35-4
7.	1,1-Dichloroethane	75-34-3
8.	Chloroform	67-66-3
9.	1,2-Dichloroethane	107-06-2
10.	1,1,1-Trichloroethane	71-55-6
11.	Carbon Tetrachloride	56-23-5
12.	Bromodichloromethane	75-27-4
13.	1,2-Dichloropropane	78-87-5
14.	cis-1,3-Dichloropropene	10061-01-5
15.	Trichloroethene	79-01-6
16.	Dibromochloromethane	124-48-1
17.	1,1,2-Trichloroethane	79-00-5
18.	Benzene	71-43-2
19.	trans-1,3-Dichloropropene	10061-02-6
20.	Bromoform	75-25-2
21.	Tetrachloroethene	127-18-4
22.	1,1,2,2-Tetrachloroethane	79-34-5
23.	Toluene	108-88-3
24.	Chlorobenzene	108-90-7
25.	Ethyl Benzene	100-41-4

TABLE III (CON'T.)

Name		CAS Number
26.	trans-1,2-Dichloroethene	544-59-0
37.	Acetone	67-64-1
28.	Carbon Disulfide	75-15-0
29.	2-Butanone	78-93-3
30.	2-Hexanone	591-78-6
31.	4-Methyl-2-pentanone	108-10-1
32.	Styrene	100-42-5
33.	Xylenes (total)	1330-20-7

TABLE IV

PREPARATION OF STANDARDS

1. Working Standard Preparation

Compound	Stock Solution Conc. (µg/mL)	Aliquot Vol (mL)	Dilution Vol (mL)	Final Conc (µg/mL)
VOA INT. STD. MIX	2500	0.100	10.0	25
VOA SURR. SPIKE MIX	2500	0.100	10.0	25
VOA MIX #1	5000	0.100	5.0	100
VOA MIX #2	2000	0.250	5.0	100
VOA MIX #3	2000	0.250	5.0	100
VOA MIX #4	2000	0.250	5.0	100
VOA MIX #5	2000	0.250	5.0	100
m-Xylene	2000	0.250	5.0	100

See Table V for a list of compounds in each mixture.

Mixes #1-4 and m-Xylene are combined into one solution called VOA 3/90 mix and Mix #5 is kept as a single mix containing the permanent gases. The internal standard and surrogate spike are also separate solutions.

TABLE IV (CON'T.)

PREPARATION OF STANDARDS

2. Final Standard Preparation* - Targets

	Working Std. Conc. (µg/mL)	Aliq. of Working Std.(mL)	Dilution Vol Water (mL)	Final Conc. (µg/L)
	100	0.0020	100	2.0
	100	0.0010	10	10
	100	0.0020	10	20
	100	0.0050	10	50
	100	0.015	10	150
Surrogates				
	25	0.0004	5.0	2.0
	25	0.0020	5.0	10
	25	0.0040	5.0	20
	25	0.010	5.0	50
	25	0.030	5.0	150

10-uL of internal standard mix at 25-µg/mL is added to every 5.0 mL standard and blank injection to yield a concentration of 50-µg/L for each internal standard compound.

TABLE V

COMPOUND LISTS

VOA INTERNAL STANDARD MIX

This mixture contains 2500 µg/mL of each of the following components in purge and trap grade methanol:

Bromochloromethane
1,4-Difluorobenzene
Chlorobenzene-D5

VOA SURROGATE SPIKE MIX

This mixture contains 2500 µg/mL of each of the following components in purge and trap grade methanol:

1,2-Dichloroethane-D4
Toluene-D8
4-Bromofluorobenzene

VOA MIX #1

This mixture contains 5000 µg/mL of each of the following components in purge and trap grade methanol:

Acetone
2-Butanone
4-Methyl-2-pentanone
2-Hexanone

VOA MIX #2

This mixture contains 2000 µg/mL of each of the following components in purge and trap grade methanol:

Carbon disulfide
Benzene
Ethyl benzene
o-Xylene
Vinyl acetate
Toluene
p-Xylene

TABLE V (CON'T.)

COMPOUND LISTS

VOA MIX #3

This mixture contains 2000 µg/mL of each of the following components in purge and trap grade methanol:

1,1-Dichloroethene	1,1,2-Trichloroethene
1,2-Dichloropropane	1,1,2-Trichloroethane
Chlorobenzene	Methylene chloride
1,1-Dichloroethane	Chloroform
Carbon tetrachloride	

VOA MIX #4

This mixture contains 2000 µg/mL of each of the following components in purge and trap grade methanol:

trans-1,2-Dichloroethene	cis-1,2-Dichloroethene
1,1,1-Trichloroethane	1,2-Dichloroethane
bromodichloromethane	cis-1,3-Dichloropropene
trans-1,3-Dichloropropene	Tetrachloroethene
Dibromochloromethane	Styrene
Bromoform	1,1,2,2-Tetrachloroethane

VOA Mix #5

This mixture contains 2000 µg/mL of each of the following components in purge and trap grade methanol:

Chloromethane
Vinyl chloride
Bromomethane
Chloroethane

TABLE VI

BFB KEY M/Z ABUNDANCE CRITERIA

Mass	a/z Abundance Criteria
50	8.0 to 40.0% of mass 95.
75	30.0 to 66.0% of mass 95.
95	Base Peak, 100% Relative Abundance.
96	5.0 to 9.0% of mass 95.
173	<2.0% of mass 174.
174	50.0% to 120.0% of mass 95.
175	4.0 to 9.0% of mass 174.
176	93.0% - 101.0% of mass 174.
177	5.0 - 9.0% of mass 176.

TABLE VII

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SYSTEM MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon Tetrachloride	4-Methyl-2-Pentanone
Vinyl Chloride	Bromodichloromethane	Tetrachloroethene
Chloroethane	1,2-Dichloropropane	1,1,2,2-Tetrachloroethane
Methylene Chloride	trans-1,3-Dichloropropene	Toluene
Acetone	Trichloroethene	Chlorobenzene
Carbon Disulfide	Dibromochloromethane	Ethylbenzene
1,1-Dichloroethene	1,1,2-Trichloroethane	Styrene
1,1-Dichloroethane	Benzene	Xylene(total)
1,2-Dichloroethene(tot.)	cis-1,3-Dichloropropene	Bromofluorobenzene(smc)
Chloroform	Bromoform	Toluene-d_8(smc)
1,2-Dichloroethane		
2-Butanone		
1,2-Dichloroethane-d_4 (smc)		

(smc) - system monitoring compound

TABLE VIII

CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS

Analyte	Primary Ion*	Secondary Ion
SURROGATE COMPOUNDS		
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d4	65	102
Toluene-d8	98	70, 100
INTERNAL STANDARDS		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d5	117	82, 119
TARGET COMPOUNDS		
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	43**	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Bromodichloromethane	83	85

TABLE VIII (CON'T.)

CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS

Analyte	Primary Ion*	Secondary Ion
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	-
cis-1,3-Dichloropropene	75	77
Bromoform	173	171,175,250,252,254,256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	91	92
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91

* The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

** m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

TABLE IX

CERTIFICATION STANDARDS

1. Standards used were as follows (see Table V for list of compounds in each mix):

Standard Mix	Vendor(a) Lot #	Original Concentration µg/mL	Working Std Conc. (µg/mL)	PACE Std #
VOA Internal Standard	A000470	2500	25	GCMS 310
VOA Surrogate Spike	A000361	2500	25	GCMS 311
VOA Calibration Mix #1	A000362	5000	100	GCMS 312
VOA Calibration Mix #2	A000533	2000	100	GCMS 312
VOA Calibration Mix #3	A000288	2000	100	GCMS 312
VOA Calibration Mix #4	A000535	2000	100	GCMS 312
VOA Calibration Mix #5	A000608	2000	100	GCMS 313
m-Xylene	A000163	2000	100	GCMS 312

(a) Restek Corporation

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#1

STANDARD OPERATING PROCEDURE

The Determination of Extractable Base/Neutral and Acid Compounds in Soil by Gas Chromatography/Mass Spectrometry

(LM30)

SOP NUMBER	MN-O-416-ATH
AUTHOR	Gabriel J. LeBrun
EFFECTIVE DATE	October 25, 1991
SUPERSEDES	WPPTHU01

APPROVAL

Gabriel J. LeBrun — 10-28-91
Section Supervisor — Date

Lysa Shanahan — 10-30-91
Organic Laboratory Manager — Date

William D. Swartz — 10-31-91
Quality Assurance Officer — Date

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I. SUMMARY

A. ANALYTES

1. This method is applicable for the determination of extractable organics. The parameters certified by this method are given in Table I.

B. MATRIX

1. This method involves the determination of the compounds given in Table I in soil and sediment.

C. GENERAL METHOD

1. A 30-gram portion of sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. A portion of this dilute extract is concentrated fivefold and is screened by GC/FID or GC/MS. If peaks are present at greater than 20-ug/g, the extract is diluted to reduce the major peaks to the mid portion of the calibration range. If no peaks are present at greater than 20-ug/g, the extract is concentrated to 1-mL and analyzed by capillary column gas chromatography/mass spectrometry.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

1. The tested concentration range is from 0.168-ug/g to 4.67-ug/g for the analytes listed in Table I. The calibration range is from 4.0-ug/mL to 160-ug/mL.

B. SENSITIVITY

1. The instrumental response for an absolute quantity of analyte varies with the compound. The response calculated at the certified reporting limit for each compound can be found in Table II.

C. CERTIFIED REPORTING LIMIT (CRL)

1. The certified reporting limit (CRL) and upper certified reporting limit (UCRL) as determined by method certification are given in Table II.

D. INTERFERENCES

1. Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles.

2. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

E. ANALYSIS RATE

1. The analysis rate shall not exceed 20 samples (including lot control samples) per 24 hour period.

F. SAFETY

1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Ultrasonic cell disruptor, Heat Systems-Ultrasonics, Inc. Model 385 sonicator with 3/4 inch disruptor horn.

2. Sonabox - acoustic enclosure.

3. Concentrator tubes - Kuderna-Danish, 10-mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

4. Evaporation flasks - Kuderna-Danish, 500-mL. Attach to concentrator tube with springs.

5. Snyder columns - Kuderna-Danish, Three-ball macro.

6. Snyder columns - Kuderna-Danish, Two-ball macro.

7. Vials - Disposable glass, 2-mL capacity with Teflon-lined screw cap, or crimp-top caps.

8. Water bath - Heated with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

9. Balance - Top-Loading, capable of accurately weighing 0.01-g.

10. Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C.

11. Drying oven.

12. Desiccator.

13. 400-mL beakers.

14. Vacuum pump - Precision Laboratory Equipment, Model DD50.

15. Hirsch funnel.

16. Filter paper, Whatman No. 41

17. Balance - Analytical, capable of accurately weighing 0.0001-g

18. Syringe, 10-mL with Luer - Lok fitting.

19. Syringe, filter holder and filters - stainless steel and TFE, Gelman 4310.

B. INSTRUMENTATION

1. Three separate GC/MS systems configured with a Hewlett Packard Model 5995 Gas Chromatograph - Mass Spectrometer and a Hewlett Packard Auto Sampler Model 7673. The computer is a Hewlett Packard Model 7936 with additional memory, a HP Model 7974 Magnetic Type Storage device and a Rugged Writer printer (or equivalent).

2. Column - 30-m x (0.25-0.32)mm ID with film thickness of 0.25 - micron bonded-phase silicone-coated fused-silica capillary column (fscc). (J & W Scientific DB-5 or equivalent).

3. Operating parameters:

a. HP-3:

Initial column temperature: 45°C for 4 minutes
Temperature ramp rate: 8°C/minute
Final column temperature: 290°C for 10 minutes
Temperature ramp rate: 4°C/minute
Final column temperature: 292°C
Injector temperature: 270°C
Transfer line temperature: 295°C
Source temperature: 220°C
Injector: Grob-type, splitless
Sample injection volume: 1-uL
Carrier gas: Helium at 2-mL/minute

b. HP-2:

Initial column temperature: 45°C for 4 minutes
Temperature ramp rate: 8°C/minute
Final column temperature: 270°C for 4 minutes
Temperature ramp rate: 5°C/minute
Final column temperature: 290°C
Injector temperature: 270°C
Transfer line temperature: 290°C
Source temperature: 220°C
Injector: Grob-type, splitless
Sample injection volume: 1-uL
Carrier gas: Helium at 2-mL/minute

c. HP-4:

Initial column temperature: 45°C for 4 minutes
Temperature ramp rate: 9°C/minute
Final column temperature: 290°C for 10 minutes
Temperature ramp rate: 4°C/minute
Final column temperature: 292°C
Injector temperature: 250°C
Transfer line temperature: 290°C
Source temperature: 250°C
Injector: Grob-type, splitless
Sample injection volume: 1-uL
Carrier gas: Helium at 2-mL/minute

d. The following initial parameters are required for all performance tests and for all sample analyses:

Electron Energy:	70 volts (nominal)
Mass Range:	35 to 500 amu
Scan Time:	$\leq$ 1 second/scan

4. Retention Time and Retention Time Windows

a. The mixed internal standard solution is added to all calibration standards and sample extracts just prior to analysis by GC/MS. The internal standard to be used for each target compound is identified in Table VII. The retention times are listed in Table VIII. The width of the retention time window used to make identifications is ± 30 seconds. This is determined from the mean relative retention time obtained during certification ± three standard deviations. Daily adjustments to the retention time window will be based on the relative retention time of each analyte in the daily calibration standard. The selected internal standards permit most of the semivolatile target compounds to have a relative retention time from 0.8 to 1.20 minutes to its associated internal standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT will be assigned by using extracted ion current profiles for ions unique to the component of interest.

5. GC/FID screening instrument complete with a temperature programmable gas chromatograph and splitless injection port for capillary column and a flame ionization detector.

C. ANALYTES

1. Chemical Abstract Service Registry numbers and basic physical properties for the target analytes are given in Table III.

D. REAGENTS AND SARMS

1. Reagents and standard materials for the target analytes identified in Table III were commercially obtained.

   Concentration and preparation information differ depending on the compound. This information is given in Section IV.A.1.

2. A combined internal standard solution (IS) containing 2000-ug/mL of each of the following:

   1,4-Dichlorobenzene-D4
   Naphthalene-D8
   Acenapthene-D10
   Phenanthrene-D10
   Chrysene-D12
   Perylene-D12

   Purchased from Supelco, Inc.

   a. A 20-uL portion of this solution should be added to 1-mL of each sample extract yielding concentration of 40-ug/mL of each IS.

3. Standard soil - Supplied by USATHAMA.

4. Acetone, methanol, methylene chloride - Pesticide quality. Burdick & Jackson.

5. Sodium sulfate - Powdered, anhydrous - Purify by heating at 400°C for four hours in a shallow tray, or soxhlet extract using methylene chloride to remove impurities. Mallinckrodt.

6. All off-the-shelf materials will be positively identified by mass spectrometry.

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Standard Solution Preparation

a. Prepare primary mix stock solution of the standard compounds in methylene chloride at a concentration of 160-ug/mL as given in Table IV. Prepare in methylene chloride standards at 4.0, 20, 50, 80, 120 and 160-ug/mL. The working standards are serially diluted from the 160-ug/mL stock standard according to the scheme in Table V, and placed in limited volume vials.

b. Store all stock solutions at 4°C (±2°C) in Teflon-Sealed Containers. The working calibration solutions must be replaced after 6 months, or sooner, if comparison with quality control check samples indicate a problem.

c. All standards prepared for use throughout the laboratory are assigned a code number. The standard code number is entered in the standard notebook with all information regarding the preparation of that standard, i.e., date, analyst, name of each compound, amount used, and final volume. All standard containers are labeled with the standard's code, date and analyst's initials.

d. The instrument response obtained for each compound in a newly prepared standard is compared to the response obtained from the previously prepared standard. Corrective actions such as checking calculations, remaking the standard, and instrument maintenance will be employed if response is not comparable.

2. Instrument Calibration

a. The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as FC-43 or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution decafluorotriphenylphosphine (DFTPP).

b. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for DFTPP given in Table VI. The analysis of the DFTPP solution is performed by injecting 1-uL of a 50-ug/mL solution of DFTPP and/or by adding of DFTPP to the mid-level calibration standard to achieve a final concentration of 50-ug/mL.

c. Analyze 1-uL of each standard and blank by direct injection into the fused silica capillary column. GC/MS operating conditions to be used are given in Section B. The mean response factor (RRF) is calculated for each analyte of interest from the initial calibration standards at 4.0, 20, 50, 80, 120 and 160-ug/mL. The relative standard deviation for at least 67% of the target compounds must be <35%.

d. The selected internal standards permit most components of interest in a chromatogram to have relative retention times of 0.80 to 1.20.

The base peak ion from the specific internal standard is used as the primary ion for quantification. If interferences are noted, a secondary ion is used according to Table VII. Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be inspected for malfunctions and corrections made as required. If the extracted ion current profile (EICP) area of any internal standard changes by more than a factor of two (-50% to +100%), from the latest continuing calibration standard, the mass spectrometric system must be inspected for malfunction, corrections made as appropriate, and explanation given for affected samples.

3. Analysis of Calibration Data

a. An initial calibration is acceptable if the relative response factor (RRF) for at least 67% of the analytes is less than 35% relative standard deviation (RSD) over the 6-point calibration curve. Initial calibration is verified by utilizing USEPA traceable check standards, SARMS, or second-vendor sources.

B. DAILY CALIBRATION

1. PREPARATION OF STANDARDS

See Section IV.A.1.

2. Instrument Calibration

a. The GC/MS system must be hardware tuned by injection of DFTPP to meet the criterion listed in Table VI. DFTPP tuning criteria must be met every 12 hours during sample analysis.

b. A continuing calibration standard at 50-ug/mL for each target analyte will be run before sample analysis, every 12 hours during sample analysis, and at the end of each day's analysis. In the event the continuing calibration standard run in the middle of a 24-hour lot analysis sequence fails, yet the end of the day standard meets the acceptance criteria, the samples will be reviewed for problems and either reanalyzed or submitted with technical justificafion. The acceptance criteria are given in Section IV.B.3.

c. The initial calibration curve as established in Section IV.A.2., is utilized to determine continuing calibration acceptability. The initial calibration curve RRF for each target analyte must be verified on each working day by the measurement of a continuing calibration standard at 50-ug/mL for each target analyte.

3. ANALYSIS OF CALIBRATION DATA

a. The daily calibration is considered acceptable if the RRF for at least 67% of the analytes is within 25% of the average RRF from the current acceptable initial calibration curve (20 to 160-ug/mL standards). If the daily standard fails, it is reanalyzed. If daily calibration fails twice, initial calibration must be performed prior to continuing

analysis. At the end of each day of sample analysis the daily standard must be analyzed and meet the RRF criteria. If the standard fails it is reanalyzed. If the end of day standard fails twice, initial calibration must be performed and all samples analyzed since the last acceptable calibration must be reanalyzed.

V. CERTIFICATION TESTING

A. Certification samples are prepared and analyzed to determine the certified reporting limits for each target analyte. For extractable compounds in soil samples, the target reporting limit (TRL) is 0.33-ug/g. Spikes are prepared at 0, 0.5, 2, 10, and 15 times the TRL. Separate individual stock standards must be used to prepare certification spike solutions and calibration standards.

B. PREPARATION OF CERTIFICATION SAMPLES

1. Prepare a primary mixed stock solution of the target compounds in methylene chloride at a concentration of 140-ug/mL.

2. Weigh out 30-g aliquots of standard soil.

3. Standard certification samples are spiked in duplicate as follows:

CERT SAMPLE	SOIL WEIGHT	CERT SPIKE SOLTN CONC. ug/mL	VOLUME SPIKE SOLTN ADDED TO CERT SAMPLE	CERT SAMPLE CONCENTRATION (ug/g)
Blank	30-g	0.0	0.0-mL	0.0
0.5x TRL	30-g	140	0.036-mL	0.168
2x TRL	30-g	140	0.14-mL	0.653
10x TRL	30-g	140	0.70-mL	3.27
15x TRL	30-g	140	1.0-mL	4.67

C. All samples are processed through the procedure defined in Section VII.

D. Target versus found concentration data are entered into the IRDMS IRPQAP program for certified reporting limit calculation.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE

1. Environmental soil samples are collected according to the Sampling Design Plan, Site Specific Quality Assurance Plan, and the USATHAMA QA Program, January 1990.

B. CONTAINERS

1. Samples are collected in amber glass bottles prepared according to the USATHAMA QA program, January 1990, Appendix F.

C. STORAGE CONDITIONS

1. All samples and extracts are stored in locked refrigerators at 4°C.

D. HOLDING TIME LIMITS

1. Holding times are seven days from date of collection for sample extraction, and 40 days from extraction for sample analysis.

E. SOLUTION VERIFICATION

1. All calibration standard solutions are double-checked to the previous preparation of that solution. There should be no more than 25% difference between each preparation as determined from GC/MS analysis.

2. The control spike solution is validated against working calibration standards before initial use and weekly during sample preparation. Calculated concentration from this verification must fall within the current control chart limits.

VII. PROCEDURE

A. SEPARATIONS

1. Weigh approximately 30-g of sample into a 400-mL beaker and record the weight to the nearest 0.1 g. Add 60-g of anhydrous sodium sulfate and mix the sample well. The sample should be free-flowing at this point. Spike the field samples and associated control samples with surrogate compounds and allow to sit 1-hr. for equilibration. Slowly add 100-mL of 1:1 methylene chloride: acetone to each beaker of soil.

   a. Determination of percent moisture: A portion of the samples should be weighed out at the same time as the portion used for analytical determination.

   b. Immediately after weighing the sample for extraction, weigh 10.0-15.0 g of the sample into a tared aluminum foil weighing boat. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of wet sample} - \text{g of dry sample}}{\text{g of wet sample}} \times 100 = \% \text{ moisture}$$

c. Determination of pH (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

2. Place the bottom surface of the tip of the #207 3/4" disruptor horn about 1/2" below the surface of the solvent, but above the sediment layer. Sonicate for 1.5 minute with output control knob set at 5 and with mode switch on Pulse and percent-duty cycle knob set at 50%.

3. Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

4. Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Hirsch funnel and rinse with extraction solvent.

5. Extract Screening

a. The solvent extracts of soil/sediment samples are screened on a gas chromatograph/flame ionization detector (GC/FID).

b. For soil samples, the results of the screen may be used to determine an appropriate dilution factor for the GC/MS analysis of the sample extract.

c. 1 to 5-uL of a screening standard containing phenol, phenanthrene and di-n-octylphthalate (50-ug/mL) is injected into the GC/FID every 12 hours. The GC must be standardized for half scale response from 50-ng of phenanthrene, adequate separation of phenol from the solvent front, and a minimum quarter scale response of di-n-octylphthalate using the following operating conditions:

- Initial Column Temperature Hold - 50°C for 4 minutes.
- Column Temperature Program - 50-280°C at 8 degrees/min.
- Final Column Temperature Hold - 280°C for 8 minutes.
- Injector - Grob-type, splitless
- Sample Volume - 1-5 uL.
- Carrier Gas - Helium at 15 to 30-mL/min.

d. Inject the GC calibration standard and ensure the criteria specified above are met before injecting samples. Estimate the response for 10 ng of phenanthrene.

6. If high levels are expected in the extract, samples are screened by taking 5.0-mL from the 300-mL (approximate) total extract and concentrating to 1.0-mL. 1-uL of this solution is injected into the GC/FID. If there is greater than 10% full scale deflection the extract can be assumed to have concentration >20-ug/g and the extract should be diluted to the upper region of the calibration curve.

7. Upon evaluation of the screening information, recombine the screening extract with the original extraction solvent. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Add one

or two clean boiling chips to the evaporative flask and attach a three-ball macro-Snyder column. Prewet the macro-Snyder column by adding about 1-mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1-mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

8. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride. Further concentration is performed using nitrogen blowdown.

9. When the liquid reaches an apparent volume of less than 1.0-mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 min. Adjust the final volume to 1.0-mL.

10. Internal Standards - 1,4-dichlorobenzene-D4, napthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12. A 20-uL portion of this solution should be added to each 1-mL aliquot of sample extract prior to analysis. This will give a concentration of 40-ug/mL of each constituent.

11. Transfer the concentrated extract to a clean screw-cap or crimp-top vial. Seal the vial with a Teflon-lined lid. Label with the sample number and store in the dark at less than 0°C.

B. CHEMICAL REACTIONS

Not applicable to this procedure.

C. INSTRUMENTAL ANALYSIS

1. Analyze 1-uL of each sample extract by direct injection onto the GC/MS system.

VIII. CALCULATIONS

A. Calculate response factors (RF) for each standard compound using Equation 1.

$$\text{Equation 1: } RF = \frac{(A_x) \times (C_{is})}{(A_{is}) \times (C_x)} \quad \text{and} \quad \overline{RF} = \left(\sum_{i=1}^{N} (RF) \right) / N$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the internal standard (ug/mL).

C_x = Concentration of the compound to be measured (ug/mL).

$\overline{RF}$ = Average response factor

N = Number of calibration levels

B. Calculate the concentration in the sample using the following equation:

$$\text{Concentration} \quad \text{ug/g} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected in micrograms (ug)

V_o = Weight of soil extracted in grams (g)

V_i = Volume of extract injected (uL)

V_t = Volume of total extract (uL)

RF = Response factor from the beginning of the day continuing calibration standard.

C. GC/MS UNCERTIFIED (NONTARGET) COMPOUNDS

1. Conduct a mass spectral library search (EPA/NBS/NIH or equivalent) to tentatively identify all the nontarget peaks which are present in excess of 10 percent of the total area of the D_{10}-phenanthrene internal standard peak. These compounds will also be semiquantitated according to calculations in Section VIII. Hard-copy mass spectra and library search results of all unknowns will be provided with the report.

   Unknown peaks will be designated by a six-character alpha-numeric code. The first three characters are UNK and the last three are reported as 100 times the RRT plus 500.

2. The calculations to determine the concentration of compounds for which method certification has not been performed are the same calculations described for certified compounds as described above, except the RF shall be equal to 1.00 and the area of the parameter to be measured shall be the total ion current area for that peak.

3. Estimates of concentrations of these uncertified compounds will be reported to only one significant figure.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

1. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control samples and calibration standards that the operation of the measurement system is in control. Each day of sample analysis the analyst must analyze a lot control sample which serves as the method blank and standard matrix spike. Accuracy and precision data from these control samples is used to maintain control charts.

2. The laboratory spikes all samples with surrogate compounds to monitor laboratory performance through percent recovery. Control charts and performance records included in the data package document the quality of data that is generated.

3. The daily lot control spike levels are given below:

Compound	Control Spike Level (ug/g)
2FP	3.3
PHEND6	3.3
NBD5	1.7
2FBP	1.7
246TBP	3.3
TRPD14	1.7

5. The control samples consist of a 30-g aliquot of USATHAMA standard soil. After spiking, the method blank is processed as a sample with the environmental samples according to Section VII.

6. The control spiking solutions require concentration verification weekly against working calibration standards using the current acceptable calibration regression equation. Recoveries must be above the lower control limit on the X-bar. control charts.

B. CONTROL CHARTS

1. Daily control requirements include the extraction and analysis of a method blank spiked with the six surrogate compounds. Each analytical lot contains the method blank to check for background contamination and to monitor method efficiency through percent recoveries of the surrogate compounds.

2. Control charts will be maintained to monitor variation in precision and accuracy for each control analyte during routine sample analysis. The control charting procedure that will be followed is given in Section 11.0 of the USATHAMA QA Program, January 1990. The reports will include:

   a. Three-Day Moving Average X-Bar Control Chart

   b. Three-Day Moving Average R-Bar Control Chart

3. Control limits initiated from certification data are given in Section XI.A.

X. REFERENCES

A. EPA Test Methods for Evaluating Solid Waste. Physical/Chemical Methods SW-846, Method 3550, Method 3640, Method 8270, Sept. 1986.

B. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, February, 1988.

C. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, May, 1990.

XI. DATA

A. INSTRUMENT CALIBRATION DATA

B. RESPONSE VERSUS CONCENTRATION DATA, GRAPHS, LACK OF FIT, AND ZERO INTERCEPT TESTS

C. CHROMATOGRAMS

TABLE I

IRDMS	TARGET ANALYTE
124TCB	1,2,4-Trichlorobenzene
12DCLB	1,2-Dichlorobenzene
13DCLB	1,3-Dichlorobenzene
14DCLB	1,4-Dichlorobenzene
245TCP	2,4,5-Trichlorophenol
246TBP	2,4,6-Tribromophenol (surrogate)
246TCP	2,4,6-Trichlorophenol
24DCLP	2,4-Dichlorophenol
24DMPN	2,4-Dimethylphenol
24DNP	2,4-Dinitrophenol
24DNT	2,4-Dinitrotoluene
26DNT	2,6-Dinitrotoluene
2CLP	2-Chlorophenol
2CNAP	2-Chloronaphthalene
2FBP	2-Fluorobiphenyl (surrogate)
2FP	2-Fluorophenol (surrogate)
2MNAP	2-Methylnaphthalene
2MP	2-Methylphenol
2NANIL	2-Nitroaniline
2NP	2-Nitrophenol
33DCBD	3,3'-Dichlorobenzidine
46DN2C	4,6-Dinitro-2-methylphenol
4BRPPE	4-Bromophenyl-phenylether
4CL3C	4-Chloro-3-methylphenol
4CLPPE	4-Chlorophenyl-phenylether
4MP	4-Methylphenol
4NANIL	4-Nitroaniline
4NP	4-Nitrophenol
ANAPNE	Acenaphthene
ANAPYL	Acenaphtylene
ANTRC	Anthracene
B2CEXM	bis(2-chloroethoxy)methane
B2CIPE	bis(2-chloroisopropyl)ether
B2CLEE	bis(2-chloroethyl)ether
B2EHP	bis(2-Ethylhexyl)phthalate
BAANTR	Benzo(a)anthracene
BAPYR	Benzo(a)pyrene
BBFANT	Benzo(b)fluoranthene
BBZP	Butylbenzylphthalate

TABLE I Continued

IRDMS	TARGET ANALYTE
BENZOA	Benzoic acid
BGHIPY	Benzo(g,h,i)perylene
BKFANT	Benzo(k)fluoranthene
BZALC	Benzyl alcohol
CHRY	Chrysene
CL6BZ	Hexachlorobenzene
CL6CP	Hexachlorocyclopentadiene
CL6ET	Hexachloroethane
DBAHA	Dibenz(a,h)anthracene
DBZFUR	Dibenzofuran
DEP	Diethylphthalaate
DMP	Dimethylphthalate
DNBP	Di-n-butylphthalate
DNOP	Di-n-octylphthalate
FANT	Fluoranthene
FLRENE	Fluorene
HCBD	Hexachlorobutadiene
ICDPYR	Indeno(1,2,3-cd)pyrene
ISOPHR	Isophorone
NAP	Naphthalene
NB	Nitrobenzene
NBD5	Nitrobenzene-D5 (surrogate)
NNDNPA	N-Nitroso-di-n-propylamine
NNDPA	N-Nitrosodiphenylamine
PCP	Pentachlorophenol
PHANTR	Phenanthrene
PHEND5	Phenol-D5 (surrogate)
PHENOL	Phenol
PYR	Pyrene
TRPD14	Terphenyl-D14 (surrogate)

TABLE II

IRDMS Designation	CRL (ug/g)	UCRL (ug/g)	Instrument Response At CRL
2FP (surrogate)	0.35	4.7	4560
PHEND5 (surrogate)	0.17	4.7	5300
NBD5 (surrogate)	0.17	4.7	4090
2FBP (surrogate)	0.18	4.7	6220
246TBP (surrogate)	0.35	4.7	740
TRPD14 (surrogate)	0.74	4.7	3490
PHENOL	0.17	4.7	6100
B2CLEE	1.60	4.7	5970
2CLP	0.17	4.7	4931
13DCLB	0.58	4.7	4800
14DCLB	0.17	4.7	5770
BZALC	0.17	4.7	2960
12DCLB	0.32	4.7	5100
2MP	0.17	4.7	3860
B2CIPE	0.17	4.7	6710
4MP	0.18	4.7	3860
NNDNPA	1.10	4.7	2620
CL6ET	0.17	4.7	2160
NB	0.19	4.7	4300
ISOPHR	0.32	4.7	9250
2NP	0.26	4.7	2660
24DMPN	0.34	4.7	3970

TABLE II (Continued)

IRDMS Designation	CRL (ug/g)	UCRL (ug/g)	Instrument Response At CRL
BENZOA	0.92	4.7	2440
B2CEXM	0.17	4.7	5720
24DCLP	0.28	4.7	3330
124TCB	0.29	4.7	3490
NAP	0.17	4.7	11600
HCBD	0.28	4.7	1750
4CL3C	0.23	4.7	3460
2MNAP	0.14	4.7	6820
CL6CP	1.80	4.7	1130
246TCP	0.29	4.7	1730
245TCP	0.24	4.7	1810
2CNAP	0.33	4.7	5940
2NANIL	0.36	4.7	2150
DMP	0.17	4.7	6850
ANAPYL	0.27	4.7	9530
ANAPNE	0.27	4.7	5940
24DNP	3.10	4.7	656
4NP	2.40	4.7	440
DBZFUR	0.17	4.7	7280
24DNT	0.31	4.7	2073
26DNT	0.20	4.7	1760

TABLE II (Continued)

IRDMS Designation	CRL (ug/g)	UCRL (ug/g)	Instrument Response At CRL
DEP	0.35	4.7	6700
4CLPPE	0.20	4.7	2550
FLRENE	0.17	4.7	5650
4NANIL	2.60	4.7	627
46DN2C	0.84	4.7	937
NNDPA	0.13	4.7	3490
4BRPPE	0.13	4.7	1180
CL6BZ	0.26	4.7	1430
PCP	0.48	4.7	753
PHANTR	0.17	4.7	8030
ANTRC	0.17	4.7	6520
DNBP	0.52	4.7	10800
FANT	0.60	4.7	5800
PYR	0.97	4.7	5780
BBZP	0.20	4.7	3860
33DCBD	3.60	4.7	529
BAANTR	0.12	4.7	3600
B2EHP	0.19	4.7	5030
CHRY	0.26	4.7	3490
DNOP	0.22	4.7	7460
BBFANT	0.73	4.7	2670
BKFANT	0.40	4.7	2670
BAPYR	0.24	4.7	2590
ICDPYR	0.15	4.7	2150
DABAHA	0.27	4.7	2310
BGHIPY	0.25	4.7	2260

TABLE III

STANDARD MATERIALS AND REAGENTS IDENTIFICATION

USATHAMA DESIGNATION	CAS NUMBER	MW	MOLECULAR FORMULA
246TBP	118-77-6	330	C6H3BR30
2FBP	321-60-8	172	C12H9F
2FP	367-12-4	112	C6H5FO
NBD5	4165-60-0	128	C6D5NO2
PHEND5	4165-62-2	99	C6HD5O
TRPD14	1718-51-0	244	C18D14
124TCB	120-82-1	181	C6H3CL3
12DCLB	95-50-1	147	C6H4CL2
13DCLB	541-73-1	147	C6H4CL2
14DCLB	106-46-7	147	C6H4CL2
245TCP	95-95-4	197	C6H3CL30
246TCP	88-06-2	197	C6H3CL30
24DCLP	120-83-2	163	C6H4CL20
24DMPN	105-67-9	122	C8H10O
24DNP	51-28-5	184	C6H4N205
24DNT	121-14-2	182	C7H6N204
26DNT	606-20-2	182	C7H6N204
2CLP	95-57-8	129	C6H5CLO
2CNAP	91-58-7	163	C10H7CL
2MNAP	91-57-6	142	C11H10
2MP	95-48-7	108	C7H8O
2NANIL	88-74-4	138	C6H6N2O2
2NP	88-75-5	139	C6H5NO3

TABLE III (Continued)

STANDARD MATERIALS AND REAGENTS IDENTIFICATION

USATHAMA DESIGNATION	CAS NUMBER	MW	MOLECULAR FORMULA
33DCBD	91-94-1	253	C12H10CL2N2
46DN2C	534-52-1	198	C7H6N2O5
4BRPPE	101-55-3	249	C12H9BRO
4CL3C	59-50-7	143	C7H7CLO
4CLPPE	7005-72-3	205	C12H9CLO
4MP	106-44-5	108	C7H8O
4NANIL	100-01-6	138	C6H6N2O2
4NP	100-02-7	139	C6H5NO3
ANAPNE	83-32-9	154	C12H10
ANAPYL	208-96-8	152	C12H8
ANTRC	120-12-7	178	C14H10
B2CEXM	111-91-1	173	C5H10CL2O2
B2CIPE	108-60-1	171	C6H12CL2O
B2CLEE	111-44-4	143	C4H8CL2O
B2EHP	117-81-7	391	C24H38O4
BAANTR	56-55-3	228	C18H12
BAPYR	50-32-8	252	C20H12
BBFANT	205-99-2	252	C20H12
BBZP	85-68-7	312	C19H20O4
BENZOA	65-85-0	122	C7H6O2
BGHIPY	191-24-2	276	C22H12
BKFANT	207-08-9	252	C20H12
BZALC	100-51-6	108	C7H8O

TABLE III (Continued)

STANDARD MATERIALS AND REAGENTS IDENTIFICATION

USATHAMA DESIGNATION	CAS NUMBER	MW	MOLECULAR FORMULA
CHRY	218-01-9	228	C18H12
CL6BZ	118-74-1	285	C6CL6
CL6CP	77-47-4	273	C5CL6
CL6ET	67-72-1	237	C2CL6
DBAHA	53-70-3	278	C22H14
DBZFUR	132-64-9	168	C12H80
DEP	84-66-2	222	C12H1404
DMP	131-11-3	194	C10H1004
DNBP	84-74-2	278	C16H2204
DNOP	117-84-0	391	C24H3804
FANT	206-44-0	202	C16H10
FLRENE	86-73-7	166	C13H10
HCBD	87-68-3	261	C4CL6
ICDPYR	193-39-5	276	C22H12
ISOPHR	78-59-1	138	C9H140
NAP	91-20-3	128	C10H8
NB	98-95-3	123	C6H5NO2
NNDNPA	621-64-7	130	C6H14N20
NNDPA	86-30-6	198	C12H10N20
PCP	87-86-5	266	C6HCL50
PHANTR	85-01-8	178	C14H10
PHENOL	108-95-2	94	C6H60
PYR	129-00-0	202	C16H10

TABLE IV

PREPARATION OF INITIAL CALIBRATION STANDARD

Compound	Parent Sol.* Number	Conc. of Parent Sol. ug/mL	Allq. Vol. mL	Mixture** Number	Final Con./Sol. ug/mL
BNA MIX2	LA20923	2000	0.120	1	160
BNA MIX1	LA20813	2000	0.120	2	160
HAZMIX1	LA20554	2000	0.120	3	160
HAZMIX2	LA23090	2000	0.120	4	160
Phenol	LA21356	2000	0.120	5	160
PAH	LA21181	2000	0.120	6	160
Benzidines	LA20272	2000	0.120	7	160
Acid Surr.	LA24266	2000	0.120	8	160
Base Surr.	LA22975	1000	0.240	9	160
IS	LA23103	2000	0.030	10	40
MeCL	NA	--	0.102	--	--
DFTPP	902	5000	0.048	--	160

* Refers to Lot# of Solution

** Refers to the contents of the mixture (see below)

TABLE IV (Continued)

PREPARATION OF INITIAL CALIBRATION STANDARD

Mixture 1: Base Neutals Mix 2

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Azobenzene	2-Chloronaphthalene
1,2-Dichlorobenzene	1,3-Dichlorobenzene
1,4-Dichlorobenzene	2,4-Dinitrotoluene
2,6-Dinitortoluene	Hexachlorobenzene
Hexachlorobutadiene	Hexachlorocyclopentadiene
Hexachloroethane	Isophorone
Nitrobenzene	1,2,4-Trichlorobenzene

Mixture 2: Base Neutals Mix 1

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Bis(2-chloroethoxy)methane	Bis(2-chloroethyl)ether
Bis(2-ethylhexyl)phthalate	Bis(2-chloroisopropyl)ether
4-Bromophenylphenyl ether	Butyl benzyl phthalate
4-Chlorophenylphenyl ether	Diethyl phthalate
Dimethyl phthalate	Di-n-butyl phthalate
Di-n-octyl phthalate	N-Nitrosodimethylamine
N-Nitrosodi-n-propylamine	N-Nitrosodiphenylamine

Mixture 3: Hazardous Substances Mix 1

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Benzoic acid	2-Methylphenol
4-Methylphenol	2,4,5-Trichlorophenol

TABLE IV (Continued)

PREPARATION OF INITIAL CALIBRATION STANDARD

Mixture 4: Hazardous Substances Mix 2

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Aniline	Benzyl alcohol
4-Chloroaniline	Dibenzofuran
2-Methylnaphthalene	2-Nitroaniline
3-Nitroaniline	4-Nitroaniline

Mixture 5: Phenols Mix

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

4-Chloro-3-methylphenol	2-Chlorophenol
2,4-Dichlorophenol	2,4-Dimethylphenol
2,4-Dinitrophenol	2-Methyl-4,6-dinitrophenol
2-Nitrophenol	4-Nitrophenol
Pentachlorophenol	Phenol
2,4,6-Trichlorophenol	

TABLE IV (Continued)

PREPARATION OF INITIAL CALIBRATION STANDARD

Mixture 6: Polynuclear Aromatic Hydrocarbons Mix

This mixture contains 2000 ug/mL of each of the following components in methylene chloride: benzene (50:50):

Acenaphthene	Acenaphthylene
Anthracene	Benzo(a)anthracene
Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(ghi)perylene	Benzo(k)fluoranthene
Chrysene	Dibenzo(a,h)anthracene
Fluoranthene	Fluorene
Indeno(1,2,3-cd)pyrene	Naphthalene
Phenanthrene	Pyrene

Mixture 7: Benzidines Mix

This mixture contains 2000 ug/mL of each of benzidine and 3,3'dichlorobenzidine in methanol:

Mixture 8: Acids Surrogate Standard Mix

This mixture contains 2000 ug/mL of each of the following components in methanol:

2-Fluorophenol	Phenol-D_6
2,4,6-Tribromophenol	2-Chlorophenol-D_4

Mixture 9: Base-Neutrals Surrogate Standard Mix

This mixture contains 1000 ug/mL of each of the following components in methylene chloride:

Nitrobenzene-D_5	2-Fluorobiphenyl
4-Terphenyl-D_{14}	1,2-Dichlorobenzene-D_4

TABLE IV (Continued)

PREPARATION OF INITIAL CALIBRATION STANDARD

Mixture 10: Internal Standards Mix

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Acenaphthene-d_{10}	Chrysene-d_{12}
1,4-Dichlorobenzene-d_4	Naphthalene-d_8
Perylene-d_{12}	Phenanthrene-d_{10}

TABLE V

Primary Stock Concentration	Volume of Primary Stock	Volume of Methylene Chloride	Final Conc. ug/mL
160-ug/mL	80-uL	0-uL	160
160-ug/mL	60-uL	20-uL	120
160-ug/mL	40-uL	40-uL	80
160-ug/mL	25-uL	55-uL	50
160-ug/mL	10-uL	70-uL	20
160-ug/mL	2.0-uL	78-uL	4.0
Blank	0.0-uL	80-uL	0.0

TABLE VI

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z may be up to 110 percent that of m/z 198.

TABLE VII

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS

Parameter	Internal Standard For Quantitation	Primary Ion	Secondary Ion(s)
Phenol	1	94	65, 66
bis(2-Chloroethyl)ether	1	93	63, 95
2-Chlorophenol	1	128	64, 130
1,3-Dichlorobenzene	1	146	148, 113
1,4-Dichlorobenzene	1	146	148, 113
1,2-Dichlorobenzene	1	146	148, 113
2-Methylphenol	1	108	107
bis(2-chloroisopropyl) ether	1	45	77, 79
4-Methylphenol	1	108	107
N-Nitroso-di-n-propylamine	1	70	42, 101, 130
Hexachloroethane	1	117	201, 199
Nitrobenzene	2	77	123, 65
Isophorone	2	82	95, 138
2-Nitrophenol	2	139	65, 109
2,4-Dimethylphenol	2	107	121, 122
bis(2-Chloroethoxy)methane	2	93	95, 123
2,4-Dichlorophenol	2	162	164, 98
1,2,4-Trichlorobenzene	2	180	182, 145
Naphthalene	2	128	129, 127
Hexachlorobutadiene	2	225	223, 227
4-Chloro-3-methylphenol	2	107	144, 142
2-Methylnaphthalene	2	142	141
Hexachlorocyclopentadiene	3	237	235, 272
2,4,6-Trichlorophenol	3	196	198, 200
2,4,5-Trichlorophenol	3	196	198, 200
2-Chloronaphthalene	3	162	164, 127
2-Nitroaniline	3	65	92, 138
Dimethyl phthalate	3	163	194, 164
Acenaphthylene	3	152	151, 153
Acenaphthene	3	153	152, 154
2,4-Dinitrophenol	3	184	63, 154
4-Nitrophenol	3	109	139, 65
Benzoic Acid	2	122	105, 77
Benzyl Alcohol	1	108	79, 77

TABLE VII (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS

Parameter	Internal Standard For Quantitation	Primary Ion	Secondary Ion(s)
Dibenzofuran	3	168	139
2,4-Dinitrotoluene	3	165	63, 182
2,6-Dinitrotoluene	3	165	89, 121
Diethylphthalate	3	149	177, 150
4-Chlorophenyl-phenylether	3	204	206, 141
Fluorene	3	166	165, 167
4-Nitroaniline	3	138	92, 108
4,6-Dinitro-2-methylphenol	4	198	182, 77
N-Nitrosodiphenylamine	4	169	168, 167
4-Bromophenyl-phenylether	4	248	250, 141
Hexachlorobenzene	4	284	142, 249
Pentachlorophenol	4	266	264, 268
Phenanthrene	4	178	179, 176
Anthracene	4	178	179, 176
Di-n-butylphthalate	4	149	150, 104
Fluoranthene	4	202	101, 100
Pyrene	5	202	101, 100
Butylbenzylphthalate	5	149	91, 206
3,3'-Dichlorobenzidine	5	252	254, 126
Benzo(a)anthracene	5	228	229, 226
bis(2-Ethylhexyl)phthalate	5	149	167, 279
Chrysene	5	228	226, 229
Di-n-octyl phthalate	6	149	-
Benzo(b)fluoranthene	6	252	253, 125
Benzo(k)fluoranthene	6	252	253, 125
Benzo(a)pyrene	6	252	253, 125
Indeno(1,2,3-cd)pyrene	6	276	138, 227
Dibenz(a,h)anthracene	6	278	139, 279
Benzo(g,h,i)perylene	6	276	138, 277
SURROGATES			
Phenol-D_5	1	99	42, 71
2-Fluorophenol	1	112	64
2,4,6-Tribromophenol	3	330	332, 141
Nitrobenzene-D_5	2	82	128, 54
2-Fluorobiphenyl	3	172	171
Terphenyl-D_{14}	5	244	122, 212

TABLE VII (Continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS

Parameter	Internal Standard For Quantitation	Primary Ion	Secondary Ion(s)
INTERNAL STANDARDS			
1,4-Dichlorobenzene-d_4	1	152	115
Naphthalene-d_8	2	136	68
Acenapthene-d_{10}	3	164	162, 160
Phenanthrene-d_{10}	4	188	94, 80
Chrysene-d_{12}	5	240	120, 236
Perylene-d_{12}	6	264	260, 265

TABLE VIII

RETENTION TIMES FOR SEMIVOLATILE ORGANIC TARGET COMPOUNDS, SURROGATES AND INTERNAL STANDARDS

TARGET COMPOUND	IRDMS CODE	RETENTION TIME (MIN)	RELATIVE RETENTION TIME
1,4-Dichlorobenzene-d4 (IS)	14DBD4	11.58	
Naphthalene-d8 (IS)	NAPD8	15.54	
Acenaphthene-d10 (IS)	ACND10	21.19	
Phenanthrene-d10 (IS)	PHAD10	25.82	
Chrysene-d12 (IS)	CYSD12	34.49	
Perylene-d12 (IS)	PYLD12	41.14	
2-Fluorophenol (S)	2FP	8.32	0.718
Phenol-D5 (S)	PHEND5	10.96	0.946
Nitrobenzene-D5 (S)	NBD5	13.43	0.864
2-Fluorobiphenyl (S)	2FBP	19.13	0.903
2,4,6-Tribromophenol (S)	246TBP	23.73	1.120
Terphenyl-D14 (S)	TRPD14	30.98	0.898
Phenol	PHENOL	10.99	0.949
bis(2-Chloroethyl)ether	B2CLEE	11.05	0.954
2-Chlorophenol	2CLP	11.14	0.962
1,3-Dichlorobenzene	13DCLB	11.43	0.987
1,4-Dichlorobenzene	14DCLB	11.64	1.005
Benzyl alcohol	BZALC	12.22	1.055
1,2-Dichlorobenzene	12DCLB	12.19	1.052
2-Methylphenol	2MP	12.69	1.096
bis(2-Chloroisopropyl)ether	B2CIPE	12.67	1.094
4-Methylphenol	4MP	13.17	1.137
N-Nitroso-di-n-propylamine	NNDNPA	13.13	1.134
Hexachloroethane	CL6ET	13.09	1.131
Nitrobenzene	NB	13.47	0.867
Isophorone	ISOPHR	14.24	0.916
2-Nitrophenol	2NP	14.46	0.931
2,4-Dimethylphenol	24DMPN	14.76	0.950
Benzoic acid	BENZOA	15.23	0.980
bis(2-Chloroethoxy)methane	B2CEXM	15.03	0.967
1,2,4-Trichlorobenzene	124TCB	15.44	0.994
2,4-Dichlorophenol	24DCLP	15.26	0.982
Naphthalene	NAP	15.61	1.005
4-Chloraniline	4CANIL	15.95	1.026
Hexachlorobutadiene	HCBD	16.24	1.045
4-Chloro-3-methylphenol	4CL3C	17.61	1.133
2-Methylnaphthalene	2MNAP	17.83	1.147
Hexachlorocyclopentadiene	CL6CP	18.57	0.877

TABLE VIII (CONT)

RETENTION TIMES FOR SEMIVOLATILE ORGANIC TARGET COMPOUNDS, SURROGATES AND INTERNAL STANDARDS

TARGET COMPOUND	IRDMS CODE	RETENTION TIME (MIN)	RELATIVE RETENTION TIME
2,4,3-Trichlorophenol	246TCP	18.89	0.891
2,4,5-Trichlorophenol	245TCP	19.02	0.898
2-Chloronaphthalene	2CNAP	19.37	0.914
2-Nitroaniline	2NANIL	19.90	0.939
Dimethyl phthalate	DMP	20.64	0.974
Acenaphthylene	ANAPYL	20.70	0.977
2,6-Dinitrotoluene	26DNT	20.83	0.983
3-Nitroaniline	3NANIL	21.24	1.002
Acenaphthene	ABAPNE	21.30	1.005
2,4-Dinitrophenol	24DNP	21.57	1.018
4-Nitrophenol	4NP	21.95	1.036
Dibenzofuran	DBZFUR	21.81	1.029
2,4-Dinitrotoluene	24DNT	22.04	1.040
Diethylphthalate	DEP	22.90	1.081
4-Chlorphenyl-phenylether	4CLPPE	22.97	1.084
Fluorene	FLRENE	22.90	1.081
4-Nitroaniline	4NANIL	23.23	1.096
2-Methyl-4,6-Dinitrophenol	46DN2C	23.34	0.904
N-Nitrosodiphenylamine	NNDPA	23.40	0.906
4-Bromophenyl-phenylether	4BRPPE	24.48	0.948
Hexachlorobenzene	CL6BZ	24.89	0.964
Pentachlorophenol	PCP	25.50	0.988
Phenanthrene	PHANTR	25.90	1.003
Anthracene	ANTRC	26.05	1.009
Di-n-butyl phthalate	DNBP	28.03	1.086
Fluoranthene	FANT	29.66	1.149
Pyrene	PYR	30.34	0.880
Butyl benzyl phthalate	BBZP	32.72	0.949
3,3'-Dichlorobenzidine	33DCBD	34.48	1.000
Benzo(a)anthracene	BAANTR	34.43	0.998
Chrysene	CHRY	34.61	1.003
bis(2-Ethylhexyl)phthalate	B2EHP	35.12	1.018
Di-n-octyl phthalate	DNOP	38.11	0.926
Benzo(b)fluoranthene	BBFANT	39.41	0.958
Benzo(k)fluoranthene	BKFANT	39.52	0.961
Benzo(a)pyrene	BAPYR	40.87	0.993
Indeno(1,2,3-c,d)pyrene	ICDPYR	47.44	1.153
Dibenz(a,h)anthracene	DBAHA	47.69	1.159
Benzo(g,h,i)perylene	BGHIPY	47.28	1.198

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STANDARD OPERATING PROCEDURE

The Determination Of Total Petroleum Hydrocarbons By Infrared Spectrophotometry

SOP NUMBER	MN-I-307-BHW
AUTHOR	D. Wright
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APPROVAL

Jane Costello — 10-6-93
Inorganic Supervisor — Date

Mark Engen — 10/6/93
Inorganic Manager — Date

Joseph [illegible] — 10-06-93
Quality Assurance Officer — Date

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THE DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

I. PURPOSE

A. To determine the total petroleum hydrocarbon concentration in waters, liquid wastes, or soils by infrared absorption.

II. SCOPE/APPLICATION

A. The concentration range is 1-1000 mg/L in water samples.

B. The minimum detectable quantity is 1 mg of extractable material in a 10 mm cell. For 1,000 mL of sample, this yields a MDL of 1 mg/L in water samples. For 50 g of solid sample, this yields a MDL of 10 mg/kg in soil.

C. INTERFERENCES

1. Trichlorotrifluoroethane has the ability to dissolve not only fatty matters and hydrocarbons but also other organic substances. Some more polar hydrocarbons such as complex aromatics and hydrocarbons containing chlorine, sulfur or nitrogen may be adsorbed by the silica gel. The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected. Gloves should be worn during handling all materials to limit potential contamination.

THE DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

D. HAZARDS AND PRECAUTIONS

1. Extraction of samples with trichlorotrifluoroethane should be performed in a hood with the analyst wearing safety glasses and latex gloves. Inhalation of high concentrations can produce asphyxiation, while prolonged skin contact will cause defatting and possible dermatitis.

III. SUMMARY OF METHOD

A. Liquid samples are acidified to a low pH (<2) and serially extracted with Freon-113 (Trichlorotrifluoroethane) in a separatory funnel. Solid samples are soxhlet extracted with Freon-113. Silica gel which adsorbs polar materials is added to the extract. Infrared analysis of the extract is performed and concentration determined by direct comparison with standards.

IV. RESPONSIBILITIES

A. PERSONNEL

1. All personnel responsible for adherence to this SOP.
2. Personnel are responsible for ensuring that any deviations of this SOP are reported.
3. Personnel are responsible for reporting to the section supervisor any required changes to the SOP.

B. DEPARTMENT SUPERVISORS/MANAGERS

1. The department supervisors and managers are

responsible for ensuring adherence to this SOP.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Office.

C. QUALITY ASSURANCE OFFICE (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.
2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.
3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

V. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.
B. At the time of review, any required revisions will be incorporated.
C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

VI. DISTRIBUTION

A. This SOP will be issued to the Inorganic Chemistry Manager, the Section Supervisor, Corporate QAO, and any other areas deemed appropriate by Regional QAO.

THE DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

VII. APPARATUS AND CHEMICALS

A. GLASSWARE/EQUIPMENT

1. 500 mL amber soil jars with teflon®-lined caps.
2. 1 L amber bottles with teflon®-lined caps.
3. Separatory funnels; 1,000 mL with glass stoppers and Teflon stopcocks.
4. Gravimetric funnels (glass)
5. Filter paper (Whatman #40 or equivalent)
6. Graduated Cylinders (various class A) for sample measurement.
7. Volumetric flasks; 100 mL Class A
8. Cells, quartz, 10-mm path length
9. Analytical balance
10. Distillation apparatus, (for distillation of freon) all glass, consisting of one liter Claussen flask with ground glass joints fitted to a Graham condenser.
11. Extraction Apparatus, Soxhlet (40 mL capacity)
12. Boiling Flasks, 250 mL, flat bottomed
13. Extraction thimble, cellulose, 33 mm x 94 mm
14. Grease-free muslin
15. Beakers, 150 mL Pyrex

B. INSTRUMENTATION

1. Perkin Elmer 1600 Series FTIR Spectrophotometer or equivalent

THE DETERMINATION OF TOTAL PETROLEUM

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C. REAGENTS

1. Deionized water (DI H_20) ASTM Type II

2. Freon-113 (1,1,2-trichloro-1,2,2-tri-fluoroethane), boiling point 47°C. The solvent may be distilled prior to use so that there is no measurable absorbance at 2930 cm^{-1} relative to a pure solvent blank.

3. Sodium sulfate, Na_2SO_4, anhydrous crystal.

4. 1:1 sulfuric acid: H_20 (50% H_2SO_4): Slowly add 500 mL concentrated H_2SO_4 to 500 mL DI H_2O. Store at room temperature in a glass container.

5. Sodium Chloride, NaCl

6. n-Hexadecane (Cetane), 99% minimum purity

7. Isooctane (2,2,4-trimethylpentane), 99% minimum purity.

8. Hydrochloric acid, HCl concentrated

9. Magnesium sulfate, anhydrous $MgSO_4$

10. Silica gel, 100-200 mesh

VIII. SAMPLE HANDLING AND STORAGE

A. Collect a representative sample in a wide-mouth bottle that has been rinsed with deionized water to remove any detergent film. Acidify water samples in the bottle to a pH<2 with 1:1 sulfuric acid. All samples should be kept at 4°C $\pm$ 2°C analyzed within 28 days of collection.

THE DETERMINATION OF TOTAL PETROLEUM

HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

IX. CALIBRATION

A. PREPARATION OF CALIBRATION STANDARDS

1. A blend of isooctane and hexadecane is used to prepare the calibration standards by pipetting equal amounts, 20 or 25 mL, of each chemical into a glass-stoppered bottle. The contents of the bottle are mixed well and the integrity of the mixture maintained by keeping the container tightly sealed except when a portion is withdrawn for blending.

2. Calibration Solution Blend A - Place a 100 mL Volumetric flask on a balance and tare. To this flask quickly add about 1 mL of the calibration mixture and obtain its exact weight. Fill to the mark with Freon-113, stopper and mix the liquid well by shaking the flask. Calculate the exact concentration of the calibrating material in solution in terms of mg/100 mL. Multiply this calculated concentration (about 730 mg/100 mL) by 1.4. This concentration value (about 1022 mg/100 mL) is to be used for Blend A throughout the remainder of this method.

NOTE: For many years, a mixture of iso-octane, cetane and benzene (ASTM D3921-85, or chlorobenzene by 418.1) was accepted as a standard for calibration. Concern regarding the hazards of exposure to benzene, which acts here only as a diluent having no contribution at 2930 cm^{-1}, has prompted elimination of benzene, and chlorobenzene, as components for calibration. To

maintain relevance between current and future analytical data with those of the past, it is necessary to compensate for differences in concentration and in density between the former and present calibration standards. The factor of 1.4 accomplishes this because the weight ratio of combined iso-octane plus n-hexadecane in the new mix to that in the old mix is 1.000 to 0.714, or 1.40.

3. Calibration Solution Blend B - Dilute 4 mL of Blend A with Freon-113 in a 100 mL volumetric flask. Conc B = (0.04)(Conc A).

4. Calibration Solution Blend C - Dilute 3 mL of Blend A with Freon-113 in a 100 mL volumetric flask. Conc C = (0.03)(Conc A).

5. Calibration Solution Blend D - Dilute 2 mL of Blend A with Freon-113 in a 100 mL volumetric flask. Conc D = (0.02)(Conc A)

6. Calibration Solution Blend E - Dilute 25 mL of Blend C with Freon-113 in a 100 mL volumetric flask. Conc E = (0.25)(Conc C)

7. Calibration solution Blend F - Dilute 10 mL of Blend E with Freon-113 in a 100 mL volumetric flask. Conc F = (0.10)Conc E)

8. Calibration solution Blend G - Distilled Freon-113 that was used for dilution of the previous calibration standards. Conc G = 0 mg

B. INITIAL CALIBRATION

1. Turn on the instrument and allow to warm up for at least 30 minutes.
2. Run reference blank.
3. Run calibration. Standards are to be analyzed in increasing concentrations as listed below. Follow the instrument instructions that are listed on the instrument computer screen. Following completion of the calibration program, print the calibration absorbances, curve plots, and raw spectrum needed to reconstruct the acquired curve.

Calibration Standard	Approximate Concentration mg/L	Approximate Absorbance
G	0	0
F	0.7	0.01
E	7	0.14
D	20	0.38
C	30	0.57
B	40	0.78

4. The calibration curve must have a correlation coefficient of at least 0.995.

5. The instrument is ready to analyze samples.

THE DETERMINATION OF TOTAL PETROLEUM

HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

D. DAILY CALIBRATION

1. Daily calibration is the same as initial calibration.

X. PREPARATION PROCEDURE

A. WATERS

1. Extraction

a. Mark the sample bottle at the water meniscus for later determination of the sample volume. Pour the sample into a separatory funnel.

b. Add approximately 5 g NaCl to the sample.

c. Add ~30 mL of Freon-113 to the sample bottle and rinse the sides. Transfer the solvent into the separatory funnel and extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into a 100 mL volumetric flask through a funnel containing filter paper and approximately 5-10 grams of Na_2SO_4.

d. Repeat the extraction twice more, with additional ~30 mL portions of fresh solvent. Combine all Freon-113 into the 100 mL volumetric flask.

e. Rinse the funnel and filter paper with an additional 10-20 mL of Freon-113 and collect the rinsings in the 100 mL flask.

f. Dilute the sample to 100.0 mL with Freon-113 and cap tightly.

g. Remove and discard about 5-10 mL of the sample extract from the volumetric flask. Add ~3g silica gel and a stirring bar; stopper the volumetric flask; and stir the solution for 5 minutes on a magnetic stirrer.

h. Allow the silica gel to settle before analysis.

B. SOIL AND SEDIMENT

1. Extraction

a. Weigh 50 grams of sample into an extraction thimble.

b. If moisture is evident, weigh sample into a 150 mL beaker, transfer to an extraction thimble and add enough $MgSO_4$ to absorb moisture and stir to a smooth paste.

c. Pour 100 mL of Freon-113 into a 250 mL boiling flask, and assemble a Soxhlet extractor.

d. Extract the sample in the Soxhlet apparatus at a rate of 20 cycles/hour for 4 hours.

e. Quantitatively transfer the extract from the boiling flask into a 100 mL volumetric flask. If any turbidity exists, filter the sample through muslin into the volumetric flask.

f. Dilute to the mark on the flask with fresh Freon-113 and cap tightly.

g. Remove and discard about 5-10 mL of the sample extract from the volumetric flask. Add ~3 g silica gel and a stirring bar; stopper the volumetric flask; and stir the solution for approximately 5 minutes on a magnetic stirrer.

h. Allow the silica gel to settle before analysis.

XI. INSTRUMENTAL ANALYSIS

A. Fill the sample cell with the sample extract and measure the infrared absorbance of the extract in a manner identical to that used for the calibration blends.

B. If the absorbance of the sample is greater than that of the highest standard, dilute the sample with Freon-113 and scan the diluted extract.

THE DETERMINATION OF TOTAL PETROLEUM

HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

XII. CALCULATIONS

A. Calculate the equation of the calibration curve analyzed with the samples. Sample concentrations are calculated by placing the sample absorbance values into the formula of the calibration curve.

$$y = mx + b \quad \text{or} \quad x = \frac{y-b}{m}$$ Equation 1

where:

y = absorbance value of sample
m = slope of calibration curve
x = concentration value of sample mg/L
b = intercept of calibration curve

The concentration of TPH in samples is calculated by the formula:

$$A = \frac{(X)(D)(0.10L)}{[V\ (1-M)]}$$ Equation 2

where:

A = The concentration in the samples in mg/kg (soil) or mg/L (water)
X = Concentration value of the sample mg/L
D = Dilution Factor
V = The original sample extracted in kg or L
M = The % moisture divided by 100 (soils only)

THE DETERMINATION OF TOTAL PETROLEUM

HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

XIII. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

1. Initial Calibration Verification (ICV)

a. The ICV standard is prepared in the same manner as calibration standard D or C but from chemicals obtained from a different source than the calibration standards.

b. After the instrument has been calibrated, the accuracy of the initial calibration shall be verified and documented by the analysis of the ICV solution. When measurements exceed the control limits of ± 10%, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

2. Continuing Calibration Verification (CCV)

a. A CCV standard must be analyzed and reported at a frequency of 10% to ensure calibration accuracy during the analytical run.

b. The concentration in the CCV must be at or near the mid-range levels and be obtained from a different source than the calibration standards. The same solution used as the ICV may be used as the CCV.

c. The CCV standards must be at the same concentration throughout the analytical run. If the deviation of the CCV is greater than the control limit of ±10%, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of all analytical samples analyzed since the last compliant CCV must be performed.

3. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

a. A calibration blank must be analyzed immediately after every ICV and CCV.

b. If the absolute value of the calibration blank exceeds the MDL, terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze all analytical samples analyzed since the last compliant calibration blank.

4. Laboratory Control Sample (LCS)

a. Laboratory Control Samples (LCS) must be analyzed for each batch using the same sample extraction and analytical methods employed for the samples. If the percent recovery falls outside the control limits of 80-120% or limits provided by the manufacturer the

analysis must be terminated, the problem corrected and the samples associated with that LCS reextracted and reanalyzed.

5. Preparation Blank (PB)

a. For each batch of samples extracted, a preparation blank (DI water and reagents) must be carried through the entire sample preparation and analytical process. The muslin can be a source of contamination but if the TPH concentration in the PB is greater than three times the MDL, all samples less than ten times the MDL shall be reextracted and reanalyzed.

6. Matrix Spike/Matrix Spike Duplicate Sample Analyses (MS/MSD)

a. The matrix spike sample analysis is designed to provide information about the effect of the sample matrix on the measurement procedures. The spikes are performed at a minimum frequency of 5%. Samples identified as field blanks cannot be used for matrix spike/matrix spike duplicate sample analyses.

b. The spike is added to the sample before extraction. Use 3 mLs of standard A and spike directly into the sample volume used for extraction.

c. Spike sample recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \qquad \text{Equation 3}$$

Where SSR = Spike sample result, mg/L or mg/kg

SR = Sample result, mg/L or mg/kg

SA = Spike added, mg/L or mg/kg

7. Analytical Spike Sample Analysis (A)

a. The spike sample analysis is designed to provide information about the effect of the sample matrix on the measurement procedures whenever the matrix/matrix spike duplicate sample analyses are not acceptable. The spikes are performed at a minimum frequency of 5%. Samples identified as field blanks cannot be used for spike sample analysis.

b. The spike is added to the sample after extraction. Use 0.1 mL of standard A and 10 mL of sample.

c. Spike sample recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \qquad \text{Equation 3}$$

Where SSR = Spike sample result, mg/L or mg/kg

SR = Sample result, mg/L or mg/kg

SA = Spike added, mg/L or mg/kg

When the sample concentration is less than the instrument detection limit, use SR = 0 for the purpose of calculation spike recovery.

8. Duplicate Sample Analysis (D)

a. Duplicate sample analysis must be performed at a minimum frequency of 5% when sample volume permits. Samples identified as field blanks cannot be used for duplicate sample analysis. Duplicates must be carried through the entire sample extraction and analytical process.

b. The relative percent difference (RPD) is calculated as:

$$RPD = \frac{(2)(|S - D|)}{(S + D)}(100) \qquad \text{Equation 4}$$

Where S = Sample value, mg/L or mg/kg

D = Duplicate sample value, mg/L or mg/kg

THE DETERMINATION OF TOTAL PETROLEUM

HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

XIV. DOCUMENTATION

A. INSTRUMENT LOGBOOK

1. Analyte (TPH)
2. Date of analysis
3. Analyst's initials
4. Results and % recovery for standard reference materials
5. Instrument maintenance
6. Notation of unusual occurrences or observations

B. DATA VALIDATION

After analysis is completed, a second analyst is required to review all data for calculation and data entry errors. Upon completion of the data review, the second analyst shall initial the validation list sheets and raw data sheets in the corresponding locations.

XV. FINAL REPORT

A. The applicable CLP inorganic forms will be modified to report information regarding analysis. Forms 1, 3, 5, 6, 7 and 10 will be modified to report sample results, method blank results, matrix spike results, duplicate results, control spike results and the instrument detection limit, respectively. A quality control chart will also be included with blank control spike results plotted. The

package will be arranged in the following order:

B. QUALITY CONTROL CHARTS

C. FORMS 1, 3, 5, 6, 7 and 10

D. SAMPLE, BLANK AND CALIBRATION RAW DATA

XVI. REFERENCES

A. Standard Methods 16th Edition, Method 503B

B. EPA Method 418.1 (Spectrophotometric Infrared Separatory Funnel Extraction)

C. ASTM Designation D3921-85

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STANDARD OPERATING PROCEDURE

The Determination of Specific Aromatic Compounds and Gasoline Range Organics in Soil

SOP NUMBER	MN-O-487-A
AUTHOR	Dennis Seeger
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APPROVAL

Dennis L Seeger
Section Supervisor — 8/17/94 Date

Melvin D Rozeboom
Department Manager — 8/18/94 Date

Joseph W Hatt
Quality Assurance Officer — 08/18/94 Date

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MN-O-487-A

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I. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to define a purge and trap gas chromatographic method for analysis of 10 individual compounds and total hydrocarbons/gasoline range organics (THC/GRO) in soils and solids.

II. SCOPE/APPLICATION

A. CONCENTRATION RANGES

1. All of the ranges of the compounds start at their particular MDL (as determined by 40 CFR136, Appendix B, July 1, 1987) and a majority end at 500 ppb for individual compounds and 7800 ppb for THC/GRO. The concentration ranges are listed in Table III.

B. METHOD DETECTION LIMITS

1. The method detection limit (MDL) is the minimum concentration of a compound that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects; therefore, quantitation limits have been set. The quantitation limits are higher than MDL and have been chosen to account for contamination from the sample preparation area and for some inherent instrument and matrix effects.

C. INTERFERENCES

1. Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap may cause contamination problems. The analytical system must be demonstrated to be free from contamination by running method blanks under the condition of analysis.

2. Samples can be contaminated by diffusion of volatile organics compounds (i.e., freons and methylene chloride) through the sample vial septum or between the vial and septum interface. A sample blank prepared with organic-free water and carried to the site with the sample vials is used to check for this contamination.

3. Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Rinsing the sample loop or the sample loading syringe twice with organic-free water between samples prevents cross-contamination during sample loading. Analyses of organic free water are used to verify sparge cleanliness following highly contaminated

samples.

D. HAZARDS AND PRECAUTIONS

1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, goggles, and masks). Reference files of OSHA regulations and MSDS's are available to all personnel involved in the analysis. Additional references to laboratory safety have been identified and are available for inspection by the analyst.

2. Benzene has been tentatively classified as known or suspected human or mammalian carcinogen. Primary standards of this toxic compound should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when an analyst handles high concentrations of this toxic compound.

III. RESPONSIBILITY

A. PERSONNEL

1. All personnel are responsible for adherence to the SOP.

2. All personnel are responsible for notifying the section supervisor/manager of any required revisions to the SOP.

B. DEPARTMENT SUPERVISOR/MANAGER

1. Supervisors/Managers are responsible for ensuring adherence to this SOP.

2. Supervisors/Managers are responsible for performing an annual review of the SOP.

C. QUALITY ASSURANCE OFFICER (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revision will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

This SOP will be issued to the Organic Chemistry Manager, the Section Supervisor, Corporate QAO, Regional QAO, and any other areas deemed appropriate by Regional QAO.

VI. SUMMARY OF METHOD

A. ANALYTES

1. The 12 volatile organic compounds are listed in Table I.

2. Gasoline range organics (GRO) or total hydrocarbons (CA LUFT method).

B. MATRIX

1. This method is appropriate for analyzing soils and solids.

C. DESCRIPTION

1. Volatile organic compounds are volatilized by adding an aliquot of an extract to 5 mL of reagent water and bubbling an inert gas through the 5 ml water sample. The vapor is then swept through a sorbent tube where the volatiles are trapped. When the purging is complete, the trap is heated and backflushed with inert gas to desorb the volatiles onto a chromatographic column. A temperature program is used in the gas chromatographic system to separate the volatiles before detection with a photoionization detector and a flame ionization detector connected in series.

VII. APPARATUS AND MATERIALS

A. GLASSWARE AND EQUIPMENT

1. Sampling Equipment: 40-ml vial, Teflon-faced silicone septum, screw cap with hole in center. Detergent wash vial and septum, then rinse with tap and organic-free water, and dry at 105 degrees C before use.

2. Syringes: 5-mL glass hypodermic with Luerlock tip.

3. Microsyringes: 10-μL, 25-μL, 100-uL and 250-μL.

4. Bottle: 15-mL, crimp top, with Teflon cap liner.

5. Balance: analytical, capable of accurately weighing 0.0001 gram.

6. Volumetric flasks: 5, 10, 25 and 50 mL Class A, with ground-glass stoppers.

B. INSTRUMENTS

1. Gas chromatographs

   a. Hewlett Packard 5890 and 5890 Series II GC's are used with temperature programming. VG data systems are used for measuring peak areas.

2. Purge and Trap System:

   a. (System I) O.I. Model MPM-16 (multi purging module) and an O.I. 4460A sample concentrator.

   b. (System II) O.I. 4551 (loop sampling module) and an O.I. 4560A sample concentrator with O.I. SIM (STANDARD INJECTION MODULE) for addition of internal standard.

   c. (System III) Tekmar ALS (10 place autosampler) and LCS-2 sample concentrator.

3. Detectors

   a. System I and II O.I. 4430 PID and HP FID

1) Detector temperature Fid is 250°C, PID is 230°C.

2) Detector ranges and lamp intensity are adjusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

b. System III O.I. 4450 PID/FID Tandem detectors

1) Detector temperature is 250°C.

2) Detector ranges and lamp intensity are adjusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

C. REAGENTS

1. Reagent water: water in which there are no interferents at the MDL of the parameters of interest.

a. A Culligan water pretreatment system is used to deionize tap water. A carbon filter is used to remove organic contamination. This is followed by UV treatment using a Barnstead Organic Pure system in the VOA lab to ensure consistent volatiles removal.

2. Methanol - Purge and trap quality or equivalent.

3. Quality Control Check Sample Concentrate - Available from Macro Scientific or from another external source.

4. Working Standard Solutions

a. Concentrations of mixtures and standards appear in Table II.

5. Internal Standard and Surrogate Standard Solution

a. A stock solution of 1-Chloro-4-fluorobenzene is prepared by filling a 10-mL volumetric flask with about 9 milliliters of methanol, and adding the reference material (50 μL) to the methanol.

b. The flask is diluted to volume, stoppered, and then mixed by inverting three times.

c. The stock standard solution is transferred into an amber bottle. The bottle is sealed with a mininert valve and stored at -10°C.

d. Fluorobenzene is prepared similarly for use as a surrogate standard to be spiked in all analyses (250 μL into 5 mL).

e. System I and II: A working standard solution is prepared by adding the stock internal standard into methanol. The surrogate standard, is added to the same solution and this solution is spiked in all analyses. System II: A working internal standard solution is prepared in the same manner and loaded into the SIM (Standard Injection Module). A separate surrogate standard solution is prepared and spiked into the 40 mL vials before analysis.

6. Matrix Spike Solution

a. A spiking solution that contains the 12 analytes is prepared in methanol, each at 100 μg/mL using the procedures outlined in Section XII.

7. Solution Verification

a. Solutions will be validated against working standards before their initial use and within seven days before subsequent usage. The recovery of the solution must be greater than the lower warning limit on the X control chart for each control analyte.

VIII. SAMPLE HANDLING AND STORAGE

A. Samples are collected in 8 oz. glass sample jars or brass tubes. The jars are sealed with a screw cap and a Teflon-faced septum in a manner that minimizes headspace. The tube ends are covered with a Teflon sheet and sealed with a plastic cap.

B. The samples must be refrigerated at 4 $\pm$ 2 degrees C from the time of collection.

C. Samples must be analyzed within 14 days.

IX. CALIBRATION

A. METHOD START-UP AND VALIDATION

1. To demonstrate the capability of the laboratory to generate valid data, the following steps need to be performed.

a. Calibration standards are analyzed at 5 concentrations.

b. A calibration curve is established for each compound, THC, and GRO.

c. The average % spike recovery (R) and the standard deviation (S) are calculated for the replicates. The calculated R and S values are compared to EPA literature and/or any other literature values available. The upper and lower control limits are calculated at $\pm$ 2 times the standard deviation. The upper and lower control limits and the average % recovery are utilized to construct control charts for the ongoing quality control.

d. The method detection limit is calculated by analyzing seven replicates prepared in blank water at 1 to 5 times higher than the estimated detection limit.

e. Method detection levels are calculated according to 40 CFR 136, Appendix B (July 1, 1987).

f. The data are evaluated and, if acceptable, the method can be utilized on a routine basis. Any changes in laboratory preparation or chromatography that may effect the recovery or detection of the compounds requires that this entire section be repeated.

B. INITIAL CALIBRATION

1. Monthly Standard Preparation (See Section VII-C)

2. Instrument Calibration

a. Initial calibration ideally takes place after new stock standards are made. This may occur at varying frequencies, depending on the compound responses.

b. Using working standards, a 5 point calibration curve for each compound of interest is built from the FID response at the concentrations as listed in Table III.

c. The calibration curve for the individual compounds are constructed utilizing the Internal Standard calculation procedure as shown in Section IX-B-3. Retention time windows must be established as follows:

1) The retention time shift of the internal standards is verified. The retention time shift between the initial and subsequent standards must be less than 2.0%. If this is not met, replicate standards are injected to meet this criterion.

2) The standard deviation of the absolute retention times is calculated for each analyte of interest.

3) The standard deviations determined in IX.B.2.c.2 shall be used to determine the retention time windows for a particular run sequence plus or minus three times the standard deviations in VII.B.2.c.2 is applied to the retention times of each analyte of interest (from the daily calibration check). This range of retention time defines the retention time window for the compound of interest.

4) In cases where the retention time window is less than 0.01 minutes, use +/- 1.0% of the retention time of the daily calibration check standard to define the retention time window.

d. The response factor for each compound is calculated by the data system for each level of calibration. These factors define the calibration curve for each compound of interest.

e. Response factors for GRO and THC are determined from the FID response of the appropriate standards at the concentrations listed in Table V. Response factors are calculated from the total area of the standards over the retention time ranges listed in Table I using the external standard method of quantitation (RF = Area Std/Amt. std). The average RF from the five standard levels is used for quantitation of continuing calibration, QC, and sample analyses.

3. Analysis of Calibration Data

a. Tabulate peak height or area responses against concentration for each compound and internal standard and calculate response factors (RF) for each compound by using this equation:

$$RF = \frac{As(C_{IS})}{A_{IS}(C_S)}$$

Where: A_S = response for parameter of concern
A_{IS} = response for IS (internal standard)

C_S = concentration of parameter of concern
C_{IS} = concentration of IS

b. If the relative standard deviation (RSD) for the response factors is <20%, the RF can be assumed to be invariant and the average RF

can be used for calculations. The results can also be used to plot a calibration curve of response ratios:

$$\frac{As}{A_{IS}} \quad \text{vs.} \quad RF$$

C. DAILY CALIBRATION

1. Standard Preparation

a. System I

Daily standards (midpoint concentrations of the calibration curve) are prepared by carefully adding 12.5 μL of the working standards and 10 μL of the internal standard solution to a 5-mL Leurlock syringe containing 5 mL of organic-free water.

b. System II

Daily standards (midpoint concentrations of the calibration curve) are prepared by carefully adding 21.5μL of the working standards and 10 μL of the surrogate standard solution to a 42-mL sample vial containing organic-free water.

2. Instrument Calibration

a. After the standards have been run and checked for compliance, a laboratory blank is analyzed to check the analytical system for interferences.

b. The blank must contain less than the quantitation level of each analyte of interest before sample analysis can start (See Section XII).

c. After calibration has been completed and the system is free of interferences, sample analysis can start.

3. Calibration Data Analysis

a. 90% of the daily standard recoveries must be between three standard deviations of a mean recovery calculated for each compound over ten or more runs. If the system is not in control, a recalibration is performed at 5 concentration levels for the appropriate compounds.

4. Calibration Check Standards

a. A spiked solution containing the parameters to be tested is prepared in organic free water. The spike solution is made by carefully adding working standards to a 5-mL Leurlock syringe containing 5 mL of organic-free water. The results must fall in the range of 3 times the standard deviation of an average recovery calculated for each compound over ten or more runs. The limits are updated by the PACE QA staff.

X. PROCEDURE

A. SAMPLE PREPARATION (Unpreserved samples)

1. Weigh out 10.0 gram +/-0.5 sample into 15 mL amber vial.

2. Add 10 mL methanol + 100 μL of surrogate working STD solution.

3. Seal with a teflon lined septum and crimp cap.

4. Shake well and equilibrate 1 hour.

5. A methanol blank is prepared with the samples using 10 mL of purge and trap grade methanol plus 10 μL of surrogate working standard in a 15 mL amber vial.

B. SAMPLE PREPARATION (Methanol Preserved Samples)

1. Samples should be collected in tared, wide mouth 60 mL VOC vials containing 25 mls of purge and trap grade methanol.

2. The tared sample vial is weighed to determine the actual weight. If the sample weight is more than 25 gms, then additional methanol is added at a 1:1 ratio (mls methanol to grams sample in excess of 25 gms). If the sample is less than 25 gms, this fact is reported.

3. The sample is shaken for 2 minutes and sonicated for 20 minutes.

4. The sediment is allowed to settle until a layer of methanol is apparent.

C. LOADING SAMPLES

1. Systems I and III: Reagent water is added to a 5 mL syringe and adjusted to 5 mL volume. 50 μL of the methanol extract of the sample is added. For highly contaminated samples, the volume of methanol may be reduced.

   System II: An amber VOA vial is filled with reagent water (42 mL). 420 μL of sample extract is added and the vial is sealed with TFE seal and cap.

2. System I and III: 10 μL of the internal standard solution is injected into the syringe. The internal standard is pulled up into a 25-μL syringe. If no air bubbles are present, the volume is adjusted to exactly 10 μL and the internal standard is injected into the 5-mL Leurlock syringe containing the sample. The Leurlock syringe is secured onto the sample valve. The valve is opened and the sample is loaded into sparging vessel. The sample valve is then closed to reseal the system. Finally, the Leurlock syringe is removed from the valve.

   System II - Internal standard is added automatically by a sample injection module.

3. M-and p-Xylene are not resolved for this analysis. These compounds are footnoted as coeluters when present, or, with approval of the client, total xylenes are reported.

D. TRAP CONDITIONS

1. Purge 11 minutes (40 mL/minute of Helium)
   Desorb 2 minutes at 180°C
   Bake approximately 15:00 minutes at 200°C

E. GAS CHROMATOGRAPHY

1. Detectors

   a. System I O.I. 4450 PID/FID Tandem detectors

      1) Detector temperature is 250°C

      2) Detector ranges and lamp intensity are adjusted to provide

appropriate sensitivity at the MDL and linearity through the calibration range.

b. System II O.I. 4430 PID and HP FID.

1) Detector temperature FID is 250°C. PID is 230°C.

2) Detector ranges and lamp intensity are adjusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

2. Column

a. Restek Rtx-1 fused silica capillary column
30m x 0.53 mm ID, 3.0 um film thickness
Column flow: ~10 mL/minute of Helium
Initial temperature: 40°C; hold for 2 minutes
Rate: 5°C/minute to 100°C
Rate B: 20°C/minute to 220°C
Final Hold: 5 minutes

E. TROUBLESHOOTING

1. Routine maintenance that is performed does not prevent all problems associated with volatile organic analyses. Equipment malfunctions and samples with very high concentrations can cause a variety of problems that are difficult to diagnose. Each problem may require a combination of corrective actions before acceptable data may be generated.

XI. CALCULATIONS

A. Calculations are performed by the internal standard procedure utilizing 1-Chloro-4-fluorobenzene as the internal standard for the individual aromatics analyses.

B. The equations used to calculate the absolute amount of a component (y) are:

1. For a single level calibration the equations are of the form:

$$RRF_{(y)} = \frac{\text{Area (y)} * \text{Amount (I)}}{\text{Amount (y)} * \text{Area (I)}}$$

Where, y = Any calibrant peak or group of peaks
I = An Internal Standard peak

RRF = The relative response factor for peak y.
Area = The peak area of calibrant y or Internal Standard I in the standard.
Amount = The amount of y or I in the standard.

2. Then,

$$\text{Amount (y)} = \frac{\text{Area (y)} * \text{Amount (I)} * \text{Dilution Factor}}{\text{Area (I)} * \text{RRF(y)}} \text{ (Extraction Factor)}$$

Where, Area = The peak area or height of y or I in the sample.
Amount = The amount of I in the sample.
Extraction Factor = Adjustment for methanol extraction. This is nominally 100 when 50 μL of a > 1:1 soil weight to solvent volume extract is added to 5 mL of reagent water for analysis.

3. The actual concentrations of sample components are calculated by the data system using the equations of the best fit of straight line through the points of the initial calibration and zero.

4. The calibration plot for THC/GRO is constructed similarly, using the area sum for all of the components of the THC/GRO standard from the FID. The THC/GRO concentration is a comparison of the total peak area from the sample between the MTBE and naphthalene retention times to the linear plot through zero of the THC/GRO calibration standards. This concentration is calculated by the data system.

XII. QUALITY CONTROL

A. Duplicate spikes are processed approximately one in every twenty samples to monitor the performance of the gas chromatographic system. The spikes are prepared by adding 100 μL of the matrix spike solution to 10 g of sample and 10 mL of methanol in a 15 mL amber vial. Spikes are then analyzed in the same manner as the samples. Spike results are compared to PACE control limits (which are $\pm$ 3 times the standard deviation of an average recovery calculated for each compound over 20 or more runs). Corrective actions are taken if the recoveries fall outside the limits specified.

B. A lab control spike is prepared as the MS/MSD above, but 10 g of a blank soil matrix is used.

C. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that all glassware and reagents are interference free.

D. PRECISION AND ACCURACY DATA REVIEW

1. Replicate spiked samples are analyzed every 20 samples along with a check standard (spiked method blank) to monitor the performance of the gas chromatographic system. The data are evaluated according to the flowchart in Figure IX-3.

   a. Samples and spikes are analyzed and the data are calculated and recorded on the worksheets.

   b. The spike data are in control if 90% of the recoveries are between 3 standard deviations of an average recovery calculated for each compound over about ten runs. If the data are acceptable, QC data are recorded and the sample data are reported.

   c. If the sample spike data are out of control, the check standard is evaluated. If that is within limits, the sample spike data for the compound in question are documented as "sample spike out of control due to matrix effects, check standard is in control." QC with appropriate comments is documented and sample data are reported.

   d. If the check standard data are also out of control, analysis must cease until the problem is corrected and documented. All samples since the last in-control situation are then re-analyzed.

XIII. REFERENCES

A. "Determination of Volatile ORGANICS IN SOIL by Purge and Trap Method", Method 465-D, Minnesota Department of Health.

B. Federal Register, Vol. 44, No. 231, Thursday, Nov. 29, 1979.

C. Federal Register, Vol. 44, No. 233, Monday, Dec. 3, 1979.

D. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," Method 502.1, EPA #600/4-81-059.

E. Federal Register, Vol. 49, No. 209, Friday, Oct. 26, 1984.

F. 40 CFR Part 136, Appendix B, July 1, 1987.

TABLE I

Approximate Retention Times of Analytes of Interest

	RETTIME (MIN) PID	RETTIME (MIN) FID
MTBE	2.04	
Benzene	3.45	
Toluene	6.36	
Ethyl benzene	9.53	
m-xylene (coelute)	9.85	
p-xylene	9.85	
o-xylene	10.59	
1,3,5-Trimethyl benzene	13.23	
1,2,4-Trimethyl benzene	14.04	
Fluorobenzene (surrogate)	3.71	3.73
Naphthalene	17.79	
1-Chloro-4-Fluorobenzene (ISTD)	8.65	8.67
THC	1.25-20.05	
GRO		1.92-17.8

TABLE II

Standard Preparation Concentration

Compound	Initial Conc. µg/mL	Final Conc. µg/mL
BTEX Calibration Check Std. (E)		
Benzene	NEAT d = 0.8787	200
Toluene	NEAT d = 0.866	200
Ethyl benzene	NEAT d = 0.866	200
m-xylene	NEAT d = 0.8684	100
p-xylene	NEAT d = 0.8104	100
o-xylene	NEAT d = 0.8801	200
1,3,5-TMB	NEAT d = 0.8761	100
1,2,4-TMB	NEAT d = 0.8637	100
BTEX Calibration Check Std. (H)		
Benzene	200	50
Toluene	200	50
Ethyl benzene	200	50
m-xylene	100	25
p-xylene	100	25
o-xylene	200	50
1,3,5-TMB	100	25
1,2,4-TMB	100	25
BTEX QC Spike (E)		
MTBE	1000	200
Benzene	1000	200
Toluene	1000	200
Ethyl benzene	1000	200
m,p,o-xylene	1000	200 (ea.)
1,3,5-TMB	1000	200
1,2,4-TMB	1000	200

TABLE II (Continued)

Standard Preparation Concentration

Compound	Initial Conc. µg/mL	Final Conc. µg/mL
BTEX QC Spike (H)		
MTBE	1000	40
Benzene	1000	40
Toluene	1000	40
Ethyl benzene	1000	40
m,p,o-xylene	1000	40 (ea.)
1,3,5-TMB	1000	40
1,2,4-TMB	1000	40
THC Calib/Spike Std. (H)		
Unleaded gas	780,000	780 ug/mL
THC Calib/Spike Std. (E)		
Unleaded gas	780,000	7800

TABLE III

Concentration of Compounds in Calibration Curve $\mu g/L$

	Level 1	Level 2	Level 3	Level 4	Level 5
System I and III					
Benzene	2	50	100	300	500
Toluene	2	50	100	300	500
Ethyl benzene	2	50	100	300	500
m-Xylene	2	50	100	350	500
p-Xylene	2	50	100	350	500
o-Xylene	2	50	100	300	500
1,3,5-Tri-methylbenz	2	50	100		
1,2,4-Tri-methylbenz	2	50	100		
MTBE	2	50	100	300	500
Hexane	16.5	66	132	396	660
System II					
B	2	10	50	100	200
T	2	10	50	100	200
E	2	10	50	100	200
MX	2	10	50	100	200
PX	2	10	50	100	200
OX	2	10	50	100	200
135	2	10	50	100	200
124	2	10	50	100	200
MTBE	2	10	50	100	200
Hexane	2.64	6.6	66	132	264

TABLE IV

Parameter	CAS Number
Benzene	71-43-2
Toluene	108-88-3
Ethyl benzene	100-41-4
m-xylene	108-38-3
p-xylene	106-42-6
o-xylene	95-47-6
MTBE	1634-04-4
1,3,5-TMB	108-67-8
1,2,4-TMB	95-63-6

TABLE V

THC Calibration Curve (μg/L)

	Level 1	Level 2	Level 3	Level 4	Level 5
System I & III	39	195	780	3900	7800
System II	78	780	1950	3900	5620

GRO Calibration Curve (μg/L)

System I & III	20	500	1000	3000	5000
System II	20	100	500	1000	2000

TABLE VI

Method Detection Limits, Quantitation Limits

Parameters	Quantitation Limit in mg/kg
Benzene	0.10
Toluene	0.10
Ethyl benzene	0.10
m-xylene	0.10
p-xylene	0.10
o-xylene	0.10
1,3,5-TMB	0.10
1,2,4-TMB	0.10
MTBE	0.40

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COPY #14

STANDARD OPERATING PROCEDURE

INDUCTIVELY COUPLED PLASMA TRACE ANALYZER ATOMIC EMISSION SPECTROSCOPY (RCRA)

SOP NUMBER	MN-I-457-B
AUTHOR	Scott Engelman
EFFECTIVE DATE	July 25, 1994
SUPERSEDES	MN-I-457-A

APPROVALS

Timothy J. Pr — 8/29/94
Section Supervisor — Date

Melvin D. Rozeboom — 8/26/94
Department Manager — Date

David W. Mr for Jwr — 8/29/94
Quality Assurance Officer — Date

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I. PURPOSE

A. The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the determination of metals by inductively coupled plasma atomic emission spectroscopy.

II. SCOPE/APPLICATION

A. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is utilized for the determination of metals in solution. The method is applicable to a large number of matrices. All matrices, including ground water, aqueous samples, leachates, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

B. Elements for which this method is applicable are listed in Table I.

III. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

1. Overall responsibility for ensuring that the SOP is implemented and followed.

B. INORGANIC LABORATORY MANAGER

1. Responsible for ensuring that analysts perform analysis according to the method described by this SOP.

2. Responsible for notifying the QAO regarding revision to the method to ensure that SOPs are updated as required.

C. ANALYST

1. Responsible for performing the analysis in accordance with the method described in this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Office.

VI. SUMMARY OF METHOD

A. Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods.

B. This method describes the simultaneous multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes.

C. Background correction may be required. Background is measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section VIII should also be recognized and appropriate corrections made as necessary.

VII. SAFETY

A. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current

awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheet should be made available to all personnel involved in the chemical analysis.

B. Concentrated acids are corrosive and should be used in a laboratory hood when possible. Protective clothing and safety glasses should be worn.

VIII. INTERFERENCES

A. SPECTRAL INTERFERENCES are caused by:

1. Overlap of a spectral line from another element;

2. Unresolved overlap of molecular band spectra;

3. Background contribution from continuous or recombination phenomena.

4. Stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line. Interelement correction factors are used on the simultaneous ICP.

B. PHYSICAL INTERFERENCES

1. These are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high levels of dissolved solids or high acid concentrations. If physical interferences are present, they may be reduced by diluting the sample. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which effects aerosol flow rate and causes instrument drift. The problem can be controlled by wetting the argon prior to nebulization, or diluting the sample.

IX. APPARATUS AND MATERIALS

A. INSTRUMENTATION

1. See Appendix I.

2. Liquid argon gas supply.

B. BALANCE

1. Analytical, accurate to at least 10 mg.

C. BEAKERS

1. 150 mL or other appropriate vessel with watchglass covers.

D. FILTER PAPER

1. Whatman No. 41 or equivalent.

E. VOLUMETRIC FLASKS

1. Assorted Class A volumetric flask.

F. PIPETS

1. Assorted Class A.

2. Automatic pipets with disposable tips.

G. HOT PLATES

X. REAGENTS

A. Hydrogen Peroxide, 30%

B. Hydrochloric Acid, conc.

C. Hydrochloric Acid, (1:1). Add 500mL conc. HCl to 400mL DI water and dilute to 1L.

D. Concentrated Nitric Acid (HNO_3), Instra-Analyzed, or equivalent.

E. Nitric Acid (1:1) Add 500mL conc. HNO_3 to 400mL DI water and dilute to 1L.

F. Deionized Water (DI)

1. Water should be monitored for impurities. Prep blanks will provide the necessary data.

G. Standard Stock Solutions, purchased (NIST Traceability must be available) or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure).

1. Mixed Calibration Standard Solutions:

a. Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table II for appropriate concentrations and element compatibility). Add 5 mL concentrated HNO_3 and dilute to 100 mL with Type II water. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Fresh mixed standards should be prepared as needed, or if older than 30 days. Verify calibration standards using a second source standard. Some typical calibration standard combinations are listed in Table II.

2. Spiking Solutions:

a. A suitable spiking solution can be prepared from stock solutions by utilizing specified volumes and concentrations outlined in Table III.

3. Calibration Verification Standard:

a. If the instrument was calibrated using the standards in Table II, a suitable verification standard would contain 3.0 mg/L of all listed constituents.

XI. SAMPLE PRESERVATION AND HOLDING TIMES

A. SAMPLE PRESERVATION

1. Water Sample Preservation

   a. Measurement Parameter: Dissolved metals. Samples are filtered through a 0.45 micron filter immediately on-site by the sampler before adding preservatives.

   b. Container: polyethylene or glass.

   c. Preservation: Sample preservation is performed by the sampler immediately upon sample collection. Use HNO_3 to bring the pH to <2.

2. Soil and Sediment Preparation

   a. Soils/sediment will be maintained at 4° C (± 2) until analysis.

B. HOLDING TIMES FOR WATER AND SOIL/SEDIMENT SAMPLES

1. The maximum sample holding time for metals is 180 days from sample receipt.

XII. SAMPLE PREPARATION

A. DISSOLVED METALS WATER SAMPLE PREPARATION

1. Transfer a 100 mL aliquot of well-mixed sample to a beaker.

2. Add 2 mL of concentrated HNO_3 and 5 mL of concentrated HC1. The sample is covered with a ribbed watchglass and heated on a steam bath or hot plate at 90 to 95° C until the volume has been reduced to 15-20 mL.

CAUTION: Do NOT boil. Antimony is easily lost by volatilization from hydrochloric acid media.

3. Remove the beaker and allow to cool. Wash down the beaker walls and watchglass with DI water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

4. Adjust the final volume to 100 mL with DI water.

B. TOTAL METALS WATER SAMPLE PREPARATION

1. Transfer a 100-mL representative aliquot of the well-mixed sample to a 150 mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watchglass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3 mL portion of concentrated HNO_3. Re-cover beaker with a nonribbed watchglass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

2. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watchglass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL of final solution) and warm the beaker for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

3. Wash down the beaker walls and watchglass with DI water and, when

necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3. Adjust to the final volume of 100 mL with DI water. The sample is now ready for analysis.

C. SOIL/SEDIMENT SAMPLE PREPARATION

1. Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00 g portion of sample.

2. Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watchglass. Heat the sample to 95° C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watchglass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watchglass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

3. After Step 2 has been completed and the sample has cooled, add 2 mL of DI water and 3 mL of 30% H_2O_2. Cover the beaker with a watchglass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

4. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

   NOTE: Do NOT add more than a total of 10 mL H_2O_2.

5. Add 5 mL of concentrated HCl and 10 mL of DI water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to 100 mL with DI water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by

centrifugation, or by allowing the sample to settle.

5.1 Filtration: Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with DI water.

5.2 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

XIII. INSTRUMENTAL ANALYSIS

A. Consult instrument manufacturer's user's manuals for specific operational instructions.

B. See Table IV for an example run sequence.

C. INSTRUMENT CALIBRATION

1. Instrumental calibration is to be performed in accordance with the manufacturer's specifications.

2. Instruments must be calibrated once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

XIV. QA/QC REQUIREMENTS

A. The QA/QC requirements for the analysis are listed below:

1. Instrument Calibration

2. Analysis of Calibration Standards

3. Initial Calibration Verification (ICV) and Continuing Calibration

Verification (CCV)

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB) and Preparation Blank (PB)

5. Interference Check Sample (ICS)

6. Laboratory Control Sample (LCS)

7. Matrix Spike Sample (MS) and Matrix Spike Duplicate (MSD)

8. Interelement Corrections for ICP (IEC)

9. Serial Dilution Analysis (L)

B. ANALYSIS OF CALIBRATION STANDARDS

1. Immediately after calibration, the calibration standards (standard containing each element of interest) must be run to insure calibration accuracy. The result should be ±5% of the expected value. When measurements exceed the ±5% limit, the analysis should be terminated and the problem investigated.

C. INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

1. Initial Calibration Verification (ICV)

   a. The Initial Calibration Verification Solution(s) should be obtained from a different source than the calibration standards.

   b. Immediately after the analysis of calibration standards, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of an Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of ±10% the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified.

D. CONTINUING CALIBRATION VERIFICATION (CCV)

1. To ensure calibration accuracy during each analysis run, a continuing calibration verification must be analyzed for every wavelength used for the analysis of each analyte, at a frequency of 10% during an analytical run. The standard must also be analyzed after the last analytical sample. The analyte concentrations in the continuing calibration standard should be at or near the mid-range levels of the calibration curve. The ICV solution can be utilized as the CCV.

2. If the deviation of the continuing calibration verification is greater than the control limits of $\pm$ 10%, the instrument should be recalibrated and the preceding analytical samples since the last acceptable calibration verification should be reanalyzed.

E. INITIAL CALIBRATION BLANK (ICB), CONTINUING CALIBRATION BLANK (CCB) AND PREPARATION BLANK (PB)

1. Initiate Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

   a. A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10%.

2. Preparation Blank (PB) Analysis

   a. At least one preparation blank (or reagent blank), consisting of deionized water must be prepared and analyzed with each group of samples digested. If the concentration in the PB is greater than 3X the reporting limit samples associated with that PB must be reprepped.

F. INTERFERENCE CHECK SAMPLE (ICS)

1. To verify that interelement and background correction factors are working correctly, an interference check sample must be analyzed at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent.

2. The interference check samples consist of 2 parts: Solution A and Solution AB. Solution A consists of the interferants and Solution AB is a mixture of the interferants and other analytes of concern. An ICS analysis consists of analyzing both solutions consecutively, starting with A.

3. Results for the interferants in A must be within ±20% of their true values, while the elements not present in A must be not detected and within ± the CRDL (AS 10 μg/L , Pb 3 μg/L, Se 5 μg/L and T1 10 μg/L). If there is a positive or negative hit in Solution A for any of these 4 elements greater than the CRDL, the IEC's must be recalculated and these values entered into the software. The instrument is then recalibrated and the analytical run is restarted.

4. Results for the interferants and analytes of interest in Solution AB must be within ±20% of the true values. If not, terminate the analysis, correct the problem, recalibrate the instrument and reanalyze.

ICS Solutions

Interferants	(mg/L) A	Analytes	(mg/L) AB
Al	500	Pb	1.0
Ca	500		
Fe	200		
Mg	500		

G. LABORATORY CONTROL SAMPLE (LCS)

1. Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the samples received. One aqueous LCS must be prepared and analyzed for every batch of samples digested.

2. If the percent recovery for the LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses should be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

H. MATRIX SPIKE SAMPLE (MS)

1. The matrix spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spiked sample must be analyzed for each batch of samples of a similar matrix spike type (i.e., water, soil) at a minimum frequency of 5%. Spiking levels are listed in Table III. The spiked sample recovery is to be within 20% of the actual value.

   The percent recovery of the spike is calculated from the following equation:

$$\% \text{ Recovery} = \frac{(SSR-SR) \times 100}{ST}$$

   Where SSR = Spike sample result, µg/L or mg/kg dry
   SR = Sample result, µg/L or mg/kg dry
   ST = Spike target, µg/L or mg/kg dry

2. When sample concentration is less than the instrument detection limit, let SR = 0 only for calculating percent recovery.

I. MATRIX SPIKE DUPLICATE ANALYSIS (MSD)

1. One matrix spike duplicate sample must be analyzed from each batch of samples of a similar matrix type (i.e., water, soil).

2. This analysis will be performed at a minimum frequency of 5%. The relative percent differences can be calculated as follows:

$$RPD = \frac{(S-D)(100)}{(S+D)/2}$$

   Where, RPD = Relative Percent Difference

   S = Original Spiked Sample Value, µg/L or mg/kg dry

   D = Second Spiked Sample Value, µg/L or mg/kg dry

J. INTERELEMENT CORRECTIONS FOR SIMULTANEOUS ICP

1. Interelement correction factors must be determined annually. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP.

2. If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined.

XV. DOCUMENTATION

A. INSTRUMENT LOG BOOK

1. Record the applicable information (calibration standard no., date, run sequence, etc.) in the instrument log book assigned to the instrument being used for the analysis. Maintenance should also be recorded as performed.

B. STANDARD PREPARATION LOG BOOK

1. Record the necessary information (volumes, manufacturer, lot number, expiration date, etc.) in the standard solution log.

XVI. REFERENCES

A. "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition Final Update 1, Revision 1, July 1992, Method 6010A

TABLE I
TARGET ANALYTE LIST

Element	Wavelength[a] (nm)	MDL[b] (µg/L)
Aluminum	308.215	14
Arsenic	193.696	8
Calcium	317.933	40
Iron	259.940	7
Lead	220.353	2
Magnesium	279.079	20
Selenium	196.026	4
Thallium	190.864	9

Footnotes:

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted when using a sequential instrument if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The method detection limits (MDL) shown are approximate. Actual detection limits are instrument specific and matrix dependent.

TABLE II
CALIBRATION STANDARD CONCENTRATION

	Calibration Standard 1 (S_1), mg/L	Calibration Standard 2 (S2), mg/L	Calibration Standard 3 (S3), mg/L
As	0	1.0	-
Al	0	40.0	-
Ca	0	200.0	-
Fe	0	20.0	-
Pb	0	1.0	-
Mg	0	-	100
Se	0	1.0	-
Tl	0	1.0	-

TABLE III
ICP SPIKING SOLUTION

Element	mLs of 1000 ppm Stock Solution (1)	Conc. of Spiking Solution (ppm)(1)	Spike Target (ppm) (2)
Al	10.0	10.0	1.0
As	1.0	1.0	0.10
Fe	10.0	10.0	1.0
Pb	1.0	1.0	0.10
Se	1.0	1.0	0.10
Tl	1.0	1.0	0.10

(1) Spiking solution is made in a final volume of 1000 mL in 5% conc HNO_3.

(2) Spike targets are the result of adding 10.0 mLs of spiking solution to 100 mLs of sample.

Note: In addition to the spiking solution above, samples are spiked with a purchased mixed standard containing 10,000 mg/L Ca, Mg, K, Na (1.0 mL standard to a final volume of 100 mL, TV = 100 mg/L) and 0.5 mL of a 1000 mg/L Mo standard (also purchased) TV = 5.0 mg/L in 100 mL final volume of sample.

TABLE IV

SAMPLE RUN SEQUENCE

1	Calibration Standard(s)
2	ICV
3	ICB
4	ICSAI
5	ICSABI
6	PB
7	LCS
8	Sample 1
9	Sample 2
10	Sample 2MS
11	Sample 2MSD
12	Sample 3
13	CCV1
14	CCB1
15	Sample 4
16	Sample 4L
17	Sample 5
18	Sample 6
19	Sample 7
20	Sample 8
21	ICSAF
22	ICSABF
23	CCV2
24	CCB2

APPENDIX I - MN

I. INSTRUMENTATION

A. SIMULTANEOUS ICP

1. TJA 61E Trace Analyzer

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COPY
DRAFT #3

STANDARD OPERATING PROCEDURE

ANALYSIS OF POLYCHLORINATED BIPHENYLS IN OIL, SOIL, WATER, WIPE AND AIR MATRIXES

SOP NUMBER	MN-O-432-A
AUTHOR	Daryl K. Peterson
EFFECTIVE DATE	September 28, 1992
SUPERSEDES	First Issue

APPROVAL

Supervisor	Date
Organic Laboratory Manager	Date
Quality Assurance Officer	Date

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I. PURPOSE

A. This method is to define criteria used in the analysis of water, soil, oil, and wipe samples for Polychlorinated Biphenyls. Specifically, the following PCB aroclors may be analyzed by this method.

Aroclor

Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260

Other aroclors may be extracted by this method, including Aroclor 1268.

II. APPLICATION

A. SUMMARY OF METHOD

1. Sample extracts in hexane will be analyzed using capillary column GC with an ECD detector. Sample will be quantitated by external standard using 3-8 peaks per aroclor.

B. INTERFERENCES

1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

2. Interferences by phthalate esters pose a major problem in PCB analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached during laboratory operation. Interferences from phthalates can be best minimized by avoiding the use of plastics. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. Refer to PACE's SOP on Glassware Cleaning.

3. Interferences co-extracted from the samples will vary considerably from source to source. Three optional clean-ups are provided as part of this method.

4. Spiked laboratory replicates should be analyzed to validate the precision and accuracy of the analyses.

C. HAZARDS AND PRECAUTIONS

1. The toxicity or carcinogenicity of each reagent used in this extraction method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, goggles, and dust masks). Reference files to OSHA regulations and MSDS's are available to all personnel involved in the extraction of these samples. Additional references to laboratory safety have been identified and are available for inspection by all personnel.

III. RESPONSIBILITIES

A. ANALYSTS

1. All personnel involved in the analysis are responsible for adherence to this SOP.

2. Personnel are responsible for ensuring that any deviations to this SOP are reported.

3. Personnel are responsible for reporting to the section supervisor any required changes to the SOP.

B. DEPARTMENT SUPERVISORS/MANAGERS

1. The department supervisors and managers are responsible for ensuring that this SOP is understood, implemented, and adhered to by all designated personnel.

2. The department supervisor/manager is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Department.

C. QUALITY ASSURANCE DEPARTMENT (QAD)

1. The QAD is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAD is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAD is responsible for determining distribution of and maintaining document control for this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

VI. SAMPLE COLLECTION, HANDLING AND STORAGE

A. Samples should be collected in a solvent rinsed amber glass container with a Teflon lined cap.

B. Samples must be maintained at a temperature of 2oC to 6oC.

C. Samples must be extracted within 7 days for waters and 14 days for soils, oils and wipes from day of collection.

VII. REAGENT AND STANDARDS

A. SOLVENTS

1. Acetone, pesticide quality

2. Hexane, pesticide quality

B. CALIBRATION STANDARDS

1. Prepare from 200 ug/mL Supelco stocks or equivalent vendor. Surrogates will be added to all calibration standards. Calibration standard concentration are listed below. Depending on criteria, a 3-5 point calibration is prepared that defines the working range of the detector. The low standard (0.1 ug/ml) defines the instrument MDL and must be fully resolved.

Aroclor	TCMZDCBP

C. EXTERNAL CHECK STANDARD

1. External check standards made up from a separate source that the calibration standards. They may be made up from EPA repository or from a commercial vendors standard. There are no surrogates added to the external check standards.

VIII. INSTRUMENTATION

A. GAS CHROMATOGRAPH

1. A Hewlett Packard 5890 or a Varian 3700 gas chromatograph (or equivalent) equipped with an electron capture detector and a Hewlett Packard 7376a Hewlett Packard Autosampler. Integration is performed using V.G. minichrome or Nelson 2600 chromatography data system (or equivalent capable or integrating peak height and areas and recording retention times).

B. COLUMNS

1. DB1701 fused silica capillary column. 30 m X 0.32 or 0.53id with a 1-um film thickness. Duel column confirmation if necessary would use a DB-608 30m x 0.32 or ? with a 0.83 film thickness. Other alternative columns may be used.

C. SUGGESTED INSTRUMENT CONDITIONS

1. Temperature Program: 150o/1 minute - 5o/min. to 270o.
   Hold 30 min.
   Injector Temperature: 220o
   Detector Temperature: 300o
   Carrier Gas: Helium 3 mLs/min.
   Make-up Gas: 5% methane argon at 60 mLs/min.
   Injection Volume: 3-5 uL.

IX. CALIBRATION

A. Establish GC operating conditions equivalent to those indicated in Section VIII. C. Calibrate the chromatographic system for one aroclor, usually 1016 or 1260 using the external standard procedure with a minimum of three points. Calibration exceptance criteria can be distinguished two ways depending on client needs.

1. To calculate linear curves with zero intercepts using linear regression. $r^2 Z 0.995$ If 67% of the correlation co-efficients from the linear curves for each calibrated peak are greater than or equal to 0.995, then the calibration is considered acceptable and the linear regression equation will be used to calculate sample concentration.

   If the curve fails to meet this criteria, corrective action is required.

2. To calculate % relative standard deviation updated with an average response factor, % RSD must be $\leq$ 20% to meet crtieria. For the aroclor, choose 3-8 peaks.

B. After the initial calibration, an external check is run in order to test the accuracy of the calibration curve. The response must agree within $\pm$ 25%.

C. Once the initial calibration and external check standard have been analyzed, sample analysis begins. After the analysis of samples has begun every 12 hours, an aroclor standard is analyzed. This standard can either be part of a

continuing curve of a different aroclor, or a continuing calibration check. A continuing calibration check is a mid-level calibration standard. The continuing check is compared to the calibration curve, and if the response varies by more than 25% of the true value, the calibration is considered out of control and all samples ran since the last good check must be re-analyzed under a new curve.

D. Retention windows are not calculated for PCB analysis because pattern-matching is used as a means of determining the presence of the aroclors in the samples.

X. SAMPLE QUANTITATION

A. ANALYSIS SEQUENCE IS DEFINED AS THE FOLLOWING

1. Aroclor low std.
2. Aroclor mid. std.
3. Aroclor high std.
4. Aroclor external std.
5. 12 hours of samples
6. Aroclor low std. or continuing check
7. 12 hours of samples
8. Aroclor std. or continuing check

B. Examine the sample's chromatogram to identify any aroclors present in the samples. Weathered samples and mixtures of aroclors cam be make quantitation difficult. In such cases, the best possible aroclor match is used to calculate the PCB concentration.

C. Calculate the concentration of any aroclor present using the average of the concentration determined for each calibrated peak.

XI. QUALITY CONTROL

A. Calculate the surrogate recovery for all samples, blanks and spikes. Surrogates are used to show extraction efficiency. After 20 replicates, limits are established.

B. A lab control spike and lab control spike duplicate will be extracted with every 20 samples. Recovery and precision will be calculated for all LCS/LCS dups. After 20, replicates, limits are established. Limits will be updated on a yearly basis.

C. With every extraction set, or 20 samples, which every is more frequent, a method blank will be extracted and analyzed. The method blank must be free of all aroclors.

XII. MDLs BY MATRIX

XIII. REFERENCES

A. EPA 390CLP Statement of Work

B. Method 608

COPY

#2

DETERMINATION OF METALS IN WATER
BY INDUCTIVELY COUPLED ARGON PLASMA EMISSION SPECTROSCOPY (ICP)

Method 5515

I. SUMMARY

A. ANALYTES

This method is applicable to the analysis of the following elements:

ELEMENT	USATHAMA TEST NAME
Silver	Ag
Aluminum	Al
Arsenic	As
Barium	Ba
Beryllium	Be
Calcium	Ca
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Potassium	K
Magnesium	Mg
Manganese	Mn
Molybdenum	Mo
Sodium	Na
Nickel	Ni
Lead	Pb
Antimony	Sb
Selenium	Se
Thallium	Tl
Vanadium	V
Zinc	Zn

B. MATRIX

This method is applicable to the quantitative determination of the selected metals in environmental water samples.

C. GENERAL METHOD

This method employs sample digestion using nitric (HNO_3) and hydrochloric (HCL) acid followed by digestate analysis by ICP.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration ranges in standard water are given in Table 1.

B. SENSITIVITY

The instrument response for each element at the certfied reporting limit is given in Table 1.

C. REPORTING LIMIT

The certified reporting limit (CRL) and the upper certifed reporting limit (UCRL) determined for each element is given in Table 1.

D. INTERFERENCES

ICP interference can be any unwanted radiation that reaches the photomultiplier tubes. Interferences can arise from physical sources or as true spectral interferences. These are compensated for by measuring emission intensity on both sides of each analytical line. The average radiation detected "off-center" is subtracted from the intensity measurement taken at the analytical line. No major interferences were encountered during certification of this method.

TABLE 1. TESTED CONCENTRATION RANGE AND INSTRUMENT SENSITIVITY

Analyte	Tested Concentration Range (ug/L)	CRL (ug/L)	UCRL (ug/L)	Instrument Response at CRL	Wavelength(nm)
Ag	12.5 to 1,250	12.5	1250	330	328.068
Al	11.2 to 45,000	107	45000	290	396.152
As	50.0 to 10,000	62.9	10000	819	193.759
Ba	20.0 to 10,000	20.0	10000	260	233.527
Be	2.50 to 10,000	2.50	10000	70	234.861
Ca	500 to 50,000	500	50000	1600	422.673
Cd	5.00 to 5,000	5.00	5000	110	228.880
Co	25.0 to 50,000	25.0	50000	120	237.862
Cr	2.50 to 5,000	15.0	5000	180	267.716
Cu	20.0 to 10,000	20.0	10000	240	324.754
Fe	2.50 to 10,000	120	10000	440	259.940
K	1250 to 50,000	1250	50000	36	766.491
Mg	500 to 50,000	500	50000	310	279.079
Mn	0.500 to 2,000	5.11	2000	320	257.610
Mo	8.00 to 8,000	30.9	8000	16	202.030
Na	500 to 50,000	500	50000	600	589.592
Ni	7.50 to 15,000	63.1	15000	170	231.604
Pb	100 to 5,000	100	5000	200	220.353
Sb	30.0 to 60,000	37.9	60000	50	206.833
Se	75.0 to 75,000	75.0	75000	65	196.090
Tl	100 to 40,000	100	40000	92	190.864
V	20.0 to 20,000	20.0	20000	160	292.402
Zn	10.0 to 20,000	13.0	20000	560	213.856

E. ANALYSIS RATE

The maximum lot size shall be 40 samples. The rate limiting step ICP analysis, is based on approximately 5 samples being analyzed per hour over an eight hour period.

F. SAFETY INFORMATION

Precautions must be taken due to the corrosive nature of the acid solutions and the potential hazardous nature of environmental samples. Proper laboratory apparel will be worn by all analysts (with safety glasses and lab coats as the minimum). Digestions must be performed in a fume hood.

The laboratory maintains a current file of OSHA regulations regarding the safe handling of chemicals. Material Safety Data Sheets are available to laboratory personnel.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Beakers, (150 mL)
2. Hot Plate
3. Macropipetter with disposable tips
4. Disposable beakers (50 mL)
5. Class A volumetric flasks, as appropriate
6. Class A volumetric pipettes, as appropriate
7. 65 mm watch glass

B. INSTRUMENTATION

ARL 3410 ICP with minitorch (or equivalent). Operating conditions are in accordance with manufacturer's recommendations.

The instrument parameters are initially adjusted to the following settings. Some modifications may be made to optimize analysis conditions.

Incident RF power: 650 Watts

Reflected RF power: 0 Watts

Sample Argon flow rate: 0.8L/minute

Coolant Argon flow rate: 7.5L/minute

C. ANALYTES

The Chemical Abstract Service (CAS) registry numbers and basic physical properties for each element given in Table 2.

D. REAGENTS AND SARMS:

1. Nitric Acid (70.0-71.0%), Baker Instra-Analyzed, or equivalent.

2. Hydrochloric Acid (36.5-38.0%), Baker Instra-Analyzed, or equivalent.

3. ASTM Type I water.

4. The primary analytical standard solutions used for certification are given in Tables 3, 4, 5 and 7. All standard solutions used will be NIST traceable and certificates of lot analysis will be maintained in a file.

TABLE 2. CAS REGISTRY NUMBERS AND PHYSICAL PROPERTIES OF TARGET ANALYTES

Analyte	Atomic Weight	CAS Registry Number	M.P.°C
Ag	107.9	7440-22-4	926
Al	26.98	7429-90-5	660
As	74.92	7440-38-2	817
Ba	137.3	7440-39-3	725
Be	9.01	7440-41-77	1287
Ca	40.08	7440-70-2	845
Cd	112.4	7440-43-9	321
Co	58.93	7440-48-4	1493
Cr	52.0	7440-47-3	1900
Cu	63.54	7440-50-8	1083
Fe	55.8	7339-89-6	1535
K	39.1	7440-09-7	63.7
Mg	24.3	7439-95-4	648
Mn	54.9	7439-96-5	1244
Mo	95.94	7439-98-7	2622
Na	23.0	7440-23-5	97.8
Ni	58.7	7740-02-0	1555
Pb	207.19	7739-92-1	327.4
Sb	121.75	7740-36-0	630.7
Se	78.96	7782-49-2	217
Tl	204.4	7740-28-0	303.5
V	50.9	7740-62-2	1917
Zn	65.37	7740-66-6	419.5

IV. INSTRUMENT CALIBRATION

A. PREPARATION OF STANDARDS

1. The primary stock standards (PSS) are described in Table 3. Primary stock solutions are stored at room temperature in the original bottle and are useable for 1 year.

2. Two instrument calibration standards (ICS), are prepared by adding an appropriate aliquot of each primary stock to a 100-mL volumetric flask and diluting to volume with a 5% nitric acid solution. ICS solutions are stored at room temperature in polyethylene bottles. Instrument calibration standards will be prepared every 3 months, or sooner if warranted by analysis difficulties. The preparation of the ICS solutions is outlined in the table below and final concentrations are listed in Table 3. The elements Ba, Co, Cu, Fe, Mo, and V are not present in the commercially prepared primary standard mixes and are added individually to ICS1. ICS3 contains As only.

Standard Prepared	Volume PSS1 (mL)	Volume PSS2 (mL)	Volume PSS3 (mL)	Volume of Individual Element Stock (mL)						
				Ba	Co	Cu	Fe	Mo	V	As
Blank	-	-	-	-	-	-	-	-	-	-
ICS1	10	10	-	0.1	0.1	0.1	0.1	0.1	0.1	-
ICS2	-	-	10	-	-	-	-	-	-	-
ICS3	-	-	-	-	-	-	-	-	-	2.0

3. Multielement stock standards (MSS) are prepared by adding an appropriate volume of 1000-ug/mL individual analyte stock solutions to 1-L volumetric flask and diluting to volume with a 5% nitric acid solution. MSS solutions are stored at room temperature in polyethylene bottles. The preparation of the MSS solutions is outlined in Table 4.

Various aliquots of the MSS solutions are combined and diluted to create two sets of test calibration standards (TCS-A and TCS-B). Two sets are required due to the incompatibility of the elements.

MSS1 and MSS2 are used to prepare TCS-B and MSS3 and MSS4 are used in preparation of TCS-A. The TCS solution concentrations are identified as a factor of the certification target reporting limit, X. The dilution schemes for the preparation of the TCS solutions are given in Table 5 and resulting concentrations are given in Table 6.

4. Calibration check standards (CCS1 & CCS2) are prepared from primary stock solutions independent of the test calibration standards. The CCS solutions are prepared in a 5% nitric acid solution. CCS preparation is outlined in Table 7.

B. INITIAL/DAILY INSTRUMENT CALIBRATION

1. Initial calibration consists of a two-point calibration specified in the instrument operation manual. The instrument response produced by a standard and a blank is used to determine a linear calibration equation for each element. The standards analyzed are described in Section IV.A.2. Initial calibration is performed each day prior to sample analysis.

2. Initial calibration is followed by analysis of two calibration check standards, CCS1 and CCS2 (Table 7). Instrument calibration is considered acceptable if the result for at least 75% of the elements in each CCS are within 10% of the actual concentration. The blank and CCS1 will be analyzed after every 15 samples and at the end of the analysis day. CCS2 is analyzed at the beginning and end of each analysis day.

TABLE 3. INITIAL CALIBRATION STANDARD SOLUTIONS (ICS)

	Analyte	Atomic Source	Lot Number	Concentration (mg/L)	Concentration in ICS (mg/L)
ICS1	Al	b	-	200	20.0
	Ba	Spex	2-93-MD	1000	1.00
	Be	a	-	50	5.00
	Ca	b	-	1000	100
	Cd	a	-	150	15.0
	Co	Spex	1-86-MD	1000	1.00
	Cr	b	-	20	2.00
	Cu	Spex	2-122-MD	1000	1.00
	Fe	Spex	2-89-MD	1000	1.00
	K	b	-	400	40.0
	Mn	a	-	100	10.0
	Mo	Spex	2-136-MD	1000	1.00
	Na	b	-	200	20.0
	Ni	b	-	20	2.00
	Pb	a	-	500	50.0
	Se	a	-	200	20.0
	V	Spex	2-142-V	1000	1.0
	Zn	a	-	150	15.0
ICS2	Ag	c	-	50	5.00
	Mg	c	-	1000	100
	Sb	c	-	200	20.0
	Tl	c	-	200	20.0
ICS3	As	Plasma Pure	90-050	1000	20.0

a) Primary Stock Solution 1 (PSS1), Spex Industries, Inc., Lot No. 1-182-TH.
b) Primary Stock Solution 2 (PSS2), Spex Industries, Inc., Lot No. 2-68AS.
c) Primary Stock Solution 3 (PSS3), Spex Industries, Inc., Lot No. 2-155-TH.

TABLE 4. MULTIELEMENT TEST CALIBRATION STANDARD PREPARATION

MSS1

Element	Stock Stock Solution[a]	Volume of Stock Diluted to 1-L (mL)[b]
As	Inorganic Venture F-AS0114	5.00
Ba	Spex 2-93-MD	0.500
Ca	Spex 1-104-CA	50.0
Cd	Spex 1-126-MD	0.250
Cr	Plasma Pure 90-050	0.250
Cu	Spex 2-122-MD	0.500
Mg	Spex 1-105-MG	50.0
Na	Spex 3-42-NA	50.0
Pb	Plasma Pure 90-050	0.250
Zn	Spex 2-37-MD	1.00

MSS3

Element	Stock Solution	Volume of Stock Diluted to 1-L (mL)[b]
Ag	Spex 2-65-MD	50.0
Al	Spex 1-83-MD	45.0
Be	Spex 1-79-MD	10.0
Co	Spex 1-86-MD	50.0
Fe	Spex 1-89-MD	10.0
K	Spex 2-49-MD	50.0
Mn	Spex 2-73-MD	2.00
Mo	Spex 2-136-MD	8.00
Ni	Spex 2-69-MD	15.0
Sb	Spex 2-123-MD	60.0
Se	Spex 3-19-SE	75.0
Tl	Spex 3-21-TL	40.0
V	Spex 2-142-V	20.0

MSS2

Element	Stock Solution	Volume of Stock Diluted to 1-L (mL)[b]
Ba	Spex 2-93-MD	10.0
Cd	Spex 1-126-MD	5.00
Cr	Plasma Pure 90-050	5.00
Cu	Spex 2-122-MD	10.0
Pb	Plasma Pure 90-050	5.00
Zn	Spex 2-37-MD	20.0

MSS4

Stock Solution	Volume of Stock Diluted to 1-L (mL)
MSS3	10.0

a All stock solutions are 1000-ug/L

b Volume of stock in mL = final concentration in mg/L

TABLE 5. TEST CALIBRATION STANDARD DILUTIONS

Standard Prepared[a]	Volume of MSS1 (mL)	Volume of MSS2 (mL)	Volume of MSS3 (mL)	Volume of MSS4 (mL)
		TCS-A		
Blank	0.00	0.00	0.00	0.00
0.5X-A	-	-	-	2.50
1X-A	-	-	-	5.00
2X-A	-	-	-	10.0
5X-A	-	-	-	25.0
10X-A	-	-	-	50.0
20X-A	-	-	-	100
50X-A	-	-	2.50	-
100X-A	-	-	5.00	-
200X-A	-	-	10.0	-
500X-A	-	-	25.0	-
1000X-A	-	-	50.0	-
2000X-A	-	-	100	-
		TCS-B		
Blank	0.00	0.00	0.00	0.00
0.5X-B	1.00	-	-	-
1X-B	2.00	-	-	-
2X-B	4.00	-	-	-
5X-B	10.0	-	-	-
10X-B	20.0	-	-	-
20X-B	40.0	-	-	-
50X-B	-	5.00[b]		-
100X-B	-	10.0	-	-
200X-B	-	20.0	-	-
500X-B	-	50.0	-	-
1000X-B	-	100	-	-

a) All solutions are prepared in 100-mL volumetric flasks. Each solution was diluted to volume with ASTM Type I water.

b) 5.00-mLs of each 1000-ug/mL stock solution for Ca, Mg, and Na (Table 4) were also added to standard 50X-B.

TABLE 6. ELEMENT CONCENTRATIONS IN TEST CALIBRATION STANDARDS (ug/L)

Element Curve	Standard Identification from Table 5											
	0.5X	1X	2X	5X	10X	20X	50X	100X	200X	500X	1000X	2000X
TCS-B												
As-B	50	100	200	500	1000	2000	5000	10000	-	-	-	-
Ba-B	5	10	20	50	100	200	500	1000	2000	5000	10000	-
Ca-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Cd-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
Cr-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
Cu-B	5	10	20	50	100	200	500	1000	2000	5000	10000	-
Mg-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Na-B	500	1000	2000	5000	10000	20000	50000	-	-	-	-	-
Pb-B	2.5	5	10	25	50	100	250	500	1000	2500	5000	-
TCS-A												
Zn-A	10	20	40	100	200	400	1000	2000	4000	10000	20000	-
Al-A	1.25	22.5	45	112.5	225	450	1125	2250	4500	11250	22500	45000
Sb-A	15	30	60	150	300	600	1500	3000	6000	15000	30000	60000
Be-A	2.5	5	10	25	50	100	250	500	1000	2500	5000	10000
Co-A	12.5	25	50	125	250	500	1250	2500	5000	12500	25000	50000
Fe-A	2.5	5	10	25	50	100	250	500	1000	2500	5000	10000
Mn-A	1.5	1	2	5	10	20	50	100	200	500	1000	2000
Mo-A	2	4	8	20	40	80	200	400	800	2000	4000	8000
Ni-A	3.75	7.5	15	37.5	75	150	375	750	1500	3750	7500	15000
K-A	12.5	25	50	125	250	500	1250	2500	12500	25000	50000	-
Se-A	18.75	37.5	75	187.5	375	750	1875	3750	7500	18750	37500	75000
Ag-A	12.5	25	50	125	250	500	1250	-	-	-	-	-
Tl-A	10	20	40	100	200	400	1000	2000	4000	10000	20000	-
V-A	5	10	20	50	100	200	500	1000	2000	5000	10000	-

TABLE 7. CALIBRATION CHECK STANDARD PREPARATION

	CCS1			CCS2	
Analyte	Stock Concentration (mg/L)	Stock Volume diluted to 100-mL	Calibration Check Standard Conc. (mg/L)	Volume Stock [g] Solution diluted to 100-mL	Calibration Check Standard Conc. (mg/L)
Ag	100[a]	3.0	3.0	1.00	10.0
Al	100[a]	3.0	3.0	4.00	40.0
As	1000[b]	0.3	3.0	1.00	10.0
Ba	100[a]	3.0	3.0	1.00	10.0
Ca	100[a]	3.0	3.0	4.00	40.0
Cd	100[a]	3.0	3.0	-	-
Co	100[a]	3.0	3.0	4.00	40.0
Cr	100[a]	3.0	3.0	-	-
Cu	100[a]	3.0	3.0	1.00	10.0
Fe	100[a]	3.0	3.0	1.00	10.0
K	100[a]	3.0	3.0	4.00	40.0
[redacted]	100[a]	3.0	3.0	4.00	40.0
Mn	100[a]	3.0	3.0	-	-
Na	100[a]	3.0	3.0	4.00	40.0
Ni	100[a]	3.0	3.0	1.00	10.0
Pb	100[a]	3.0	3.0	-	-
V	100[a]	3.0	3.0	1.00	10.0
Zn	100[a]	3.0	3.0	1.00	10.0
Mo	1000[c]	0.3	3.0	1.00	10.0
Sb	1000[d]	0.3	3.0	4.00	40.0
Se	1000[e]	0.3	3.0	4.00	40.0
Tl	1000[f]	0.3	3.0	4.00	40.0
Be	100[a]	3.0	3.0	1.00	10.0

a) Inorganic Ventures, Lot. No. F07W6.
b) Plasma Pure 90-050
c) Spex, Lot No. 2-136-MD.
d) Spex, Lot No. 2-123-MD.
[redacted] Spex, Lot No. 3-19-SE.
f) Spex, Lot No. 3-21-TL.
g) All stock solutions are 1000-mg/L.

V. CERTIFICATION TESTING

A. CONTROL SPIKES

The recovery of each metal is tested through the complete analytical method including digestion. To facilitate this process, two mutlielement spiking solutions were prepared from a 1,000-ppm reference standard solution of each metal. The certification spike solutions are prepared from separate stock solutions but in the same manner as the TCS in Tables 4 and 5. Concentrations of each element in the certification spike solutions are found in Table 6.

The certification spike samples were digested and analyzed according to the procedures in Section VII.A.1-5.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURES

Field samples collected for analysis by this method require preservation with sufficient nitric acid to lower the pH to <2.

B. CONTAINERS

The field samples are to be collected in 1000-mL glass or polyethylene bottles for transport to the laboratory.

C. STORAGE CONDITIONS

Sample integrity is maintained during transport to the laboratory by properly preserving the sample with nitric acid and shipping them in coolers packed with blue ice.

D. HOLDING TIME LIMITS

The samples to be analyzed by this method have an analysis holding time of 6 months.

VII. PROCEDURE

A. SAMPLE PREPARATION

1. Transfer a 100-mL portion of the water sample to a 150-mL beaker.

   To prepare the method blank and control samples, transfer 100-mL of Type I water to each 150-mL beaker. There is no spike added to the method blank and appropriate volumes of standard are added to control samples as outlined in Table 8.

2. Add 2-mL of (1:1) nitric acid and 10-mL of (1:1) hydrochloric acid, cover the beaker with a watch glass and evaporate on a hot plate at 95°C to a volume of about 20-mL. Make certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry.

3. Wash down the sides of the beakers and the watch glass covers with ASTM Type I water.

4. Quantitatively transfer the solution to a 100-mL volumetric flask. If insoluble material is present, filter the sample through Whatman #41 filter paper (or equivalent).

5. Dilute each sample to a final volume of 100-mL with ASTM Type I water.

B. CHEMICAL REACTIONS

Non-specific oxidation of organic matter and some ionically bonded species such as carbonates and hydroxides occur.

C. INSTRUMENT ANALYSIS

Perform the procedures for calibration documented in Section IV.B. The daily analytical run will include analysis of the calibration blank and the CCS1 at a frequency of every 15 samples and at the end of the run. CCS2 will be analyzed after CCS1 at the beginning and end of the run.

VIII. CALCULATIONS

The computer software supplied with the ICP spectrometer provides direct readout of solution concentrations in mg/L. The software performs a calculation based on a linear regression line equation. The result is then converted to ug/L by multiplying the ICP readout by 1000.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

Daily quality control samples consist of a standard matrix method blank, a standard matrix spike at approximately two times the CRL and duplicate standard matrix spikes at approximately ten times the CRL. For extended range elements an additional order-of-magnitude control spike shall be prepared. These quality control samples are processed through the entire method with the environmental samples.

The control elements for this method will include Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Tl, and Zn. The control samples will be prepared according to Section VII.A. and percent recoveries used to maintain accuracy and precision control chart data. Control spike solution preparation and concentration along with the water matrix control spike concentrations are given in Table 8.

B. CONTROL CHARTS

Control charts will be maintained to monitor variations in precision and accuracy of routine analyses and to detect trends in these variations. The control charting procedure that will be followed is given in the USATHAMA QA Program, January 1990.

Single-Day X-Bar Control Chart
Single-Day R Control Chart
Three-Point Moving Average X-Bar Control Chart
Three-Point Moving Average R Control Chart
Extended Range Three-Point Moving Average X-Bar Control Chart
Extended Range Three-Point Moving Average R Control Chart

TABLE 8. QUALITY CONTROL SAMPLE PREPARATION

Control Element	Low Spike		High Spike		Extended Spike	
	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/L)	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/L)	Stock Volume[a] Diluted and Control Spike Concentration	Control[b] Sample Conc. (ug/L)
Ba	4.00	40.0	4.00	400	40.0	8000
Be	1.00	10.0	1.00	100	5.00	1000
Cd	2.00	20.0	2.00	200	20.0	4000
Co	10.0	100	10.0	1000	50.0	10000
Cr	4.00	40.0	4.00	400	20.0	4000
Cu	4.00	40.0	4.00	400	40.0	8000
Ni	15.0	150	15.0	1500	60.0	12000
Pb	20.0	200	10.0	1000	-	-
Sb	10.0	100	10.0	1000	50.0	10000
Se	15.0	150	15.0	1500	75.0	15000
Tl	20.0	200	10.0	1000	500	10000
Zn	6.5	65.0	17.0	1700	80.0	16000

a) All individual element stock solutions are 1000-mg/L. The volume given (mL) is diluted to 1-L with 5% nitric acid. This volume in mL is equal to the control spike solution concentration in mg/L.

b) Control samples are prepared by spiking the following volumes of control spike solution into 1-L of ASTM Type I water and following the procedure in Section VII.A.

Low Spike: 1-mL of the low control spike solution.
High Spike: 10-mL of the high control spike solution.
Extended Spike: 20-mL of the extended control spike solution.

X. REFERENCES

A. U.S. Army Toxic and Hazardous Materials Agency, January 1990, Quality Assurance Program. Revision No. 0.

B. United States Environmental Protection Agency. Method 200.7 Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes.

C. United States Environmental Protection Agency, SW-846 Third Edition, Method 6010, Inductively Coupled Plasma Atomic Emission Specroscopy.

XI. DATA

A. STANDARD CHARACTERIZATION

All standards were traceable to NBS/NIST.

B. INITIAL CALIBRATION

The instrument calibration followed Section IV.B.1.

C. STANDARD CERTIFICATION SAMPLE RESULTS

1. Tables and Graphs, LOF and ZI TESTS, Precision and Accuracy Data

2. Results of External Calibration Checks

3. Summary of Control Chart Data

SUMMARY OF CONTROL CHART DATA

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THREE DAY CONTROL CHART DATA FOR ICP METALS WATER CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AG	110.7	122.9	118.9	102.5	98.4	12.0	30.9	24.6
AS	102.5	107.9	106.1	99.0	97.2	5.2	13.4	10.7
AL	119.5	137.9	131.8	107.2	101.1	18.0	46.4	36.9
BA	101.3	111.6	108.2	94.5	91.1	10.0	25.8	20.5
BE	93.3	108.7	103.6	83.1	78.0	15.0	38.6	30.7
CA	109.3	111.9	111.0	107.5	106.7	2.5	6.6	5.2
CD	100.0	116.4	110.9	89.1	83.6	16.0	41.2	32.8
CO	105.2	113.8	110.9	99.5	96.6	8.4	21.6	17.2
CR	95.0	105.2	101.8	88.2	84.8	10.0	25.8	20.5
CU	92.7	94.7	94.0	91.3	90.6	2.0	5.2	4.1
FE	118.1	140.4	132.9	103.2	95.8	21.8	56.1	44.7
K	111.9	136.4	128.2	95.5	87.3	24.0	61.7	49.2
MG	102.2	105.9	104.7	99.7	98.4	3.7	9.4	7.5
MN	122.5	140.4	134.4	110.6	104.6	17.5	45.1	35.9
MO	97.1	116.3	109.9	84.3	77.9	18.8	48.3	38.4
NA	110.4	128.5	122.5	98.4	92.4	17.7	45.4	36.2
NI	90.4	110.6	103.9	77.0	70.3	19.7	50.6	40.3
PB	98.4	113.5	108.5	88.3	83.3	14.8	38.1	30.3
SB	119.4	174.9	156.4	82.5	64.0	54.2	139.5	111.0
SE	100.1	114.8	109.9	90.3	85.4	14.4	37.1	29.5
TL	91.8	104.5	100.3	83.2	79.0	12.5	32.2	25.6
V	107.3	118.1	114.5	100.2	96.6	10.5	27.0	21.5
ZN	107.5	116.2	113.3	101.7	98.8	8.5	21.9	17.4

SINGLE DAY CONTROL CHART DATA FOR ICP METALS WATER CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AG	102.2	112.0	108.7	95.7	92.4	5.2	17.0	13.1
AL	100.9	103.5	102.6	99.2	98.4	1.4	4.4	3.4
AS	105.0	111.5	109.3	100.7	98.5	3.5	11.3	8.7
BA	96.6	100.1	98.9	94.2	93.0	1.9	6.2	4.8
BE	96.8	101.5	99.9	93.6	92.1	2.5	8.2	6.3
CA	102.1	112.0	108.7	95.6	92.3	5.2	17.1	13.2
CD	98.0	109.3	105.5	90.5	86.7	6.0	19.6	15.1
CO	102.0	108.5	106.3	97.6	95.4	3.5	11.4	8.7
CR	98.0	103.0	101.3	94.6	92.9	2.7	8.8	6.8
CU	97.7	104.1	102.0	93.5	91.3	3.4	11.1	8.5
FE	103.8	105.8	105.1	102.4	101.7	1.1	3.5	2.7
K	98.6	101.6	100.6	96.5	95.5	1.6	5.3	4.1
MG	99.8	101.5	100.9	98.7	98.1	0.9	2.9	2.3
MN	101.8	107.4	105.5	98.0	96.1	3.0	9.8	7.5
MO	98.0	104.3	102.2	93.9	91.8	3.3	10.8	8.3
NA	99.0	111.2	107.1	90.9	86.8	6.5	21.2	16.3
NI	101.0	112.0	108.3	93.6	89.9	5.9	19.3	14.8
PB	98.5	105.6	103.2	93.8	91.5	3.8	12.3	9.4
SB	103.1	104.0	103.7	102.5	102.1	0.5	1.6	1.3
SE	102.0	103.5	103.0	101.0	100.4	0.8	2.7	2.1
TL	102.0	111.8	108.5	95.4	92.1	5.3	17.2	13.2
V	96.9	109.3	105.2	88.7	84.5	6.6	21.6	16.6
ZN	100.3	105.6	103.8	96.7	94.9	2.9	9.3	7.2

EXTENDED RANGE CONTROL CHART DATA FOR ICP METALS WATER CERTIFICATION

ANALYTE	XBARBAR	UCLx	UWLx	LWLx	LCLx	RBAR	UCLr	UWLr
AG	103.6	110.9	108.5	98.7	96.3	7.2	18.4	14.7
AL	99.1	101.0	100.4	97.9	97.2	1.9	4.8	3.8
AS	106.0	107.7	107.2	104.9	104.3	1.7	4.2	3.4
BA	98.9	102.9	101.6	96.1	94.8	4.0	10.3	8.2
BE	94.0	99.3	97.5	90.5	88.7	5.2	13.4	10.7
CA	103.2	111.8	108.9	97.4	94.5	8.4	21.7	17.3
CD	98.4	102.7	101.3	95.5	94.1	4.2	10.9	8.7
CO	100.8	104.7	103.4	98.2	96.9	3.8	9.9	7.9
CR	98.4	101.5	100.5	96.4	95.4	3.0	7.7	6.2
CU	99.6	101.4	100.8	98.5	97.9	1.7	4.5	3.5
FE	100.9	103.2	102.4	99.4	98.6	2.2	5.7	4.6
K	98.1	105.6	103.1	93.2	90.7	7.3	18.7	14.9
MG	99.0	103.9	102.3	95.7	94.1	4.8	12.4	9.9
MN	99.9	103.8	102.5	97.3	96.0	3.8	9.7	7.7
MO	95.7	99.2	98.0	93.3	92.2	3.4	8.9	7.0
NA	100.2	106.5	104.4	96.0	93.9	6.2	15.9	12.6
NI	97.8	102.6	101.0	94.5	92.9	4.8	12.2	9.8
SB	99.1	100.0	99.7	98.6	98.3	0.8	2.1	1.7
SE	99.6	101.7	101.0	98.2	97.5	2.0	5.3	4.2
TL	101.4	108.2	105.9	96.9	94.6	6.6	17.1	13.6
V	98.8	100.3	99.8	97.7	97.2	1.5	4.0	3.2
ZN	98.0	101.1	100.1	96.0	95.0	3.0	7.7	6.2

#2

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MERCURY IN WATER Method SB07

I. Summary

A. Analyte: Mercury, Hg

B. Matrix: Drinking, surface, and saline waters, domestic and industrial wastes.

C. General Method: Manual cold vapor technique. Mercury is reduced to the elemental state by addition of stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of the atomic absorption spectrophotometer. Peak height is measured as a function of mercury concentration and recorded. (EPA Method #245.1)

VI. Sample Handling/Storage

A. Sampling Procedure

1. All sample containers must be new or used containers should be prewashed with detergents, acids and Type II water. Plastic containers are suitable. See Chapter Three, Section 3.1.3, for further information.

2. Aqueous samples must be acidified to pH <2 with nitric acid

B. Containers

Plastic containers shall be used.

C. Mercury Storage Condition

Store aqueous samples when preserved at room temperature.

D. Holding Time Limits

28 days

E. Solution Verification

Solutions will be validated against working standards before their initial use and within seven days before subsequent usage. The recovery of the solution must be greater than the lower warning limit on the X control chart for mercury.

VII. Procedure

A. Separation or Digestions:

1. Use BOD bottles which have been rinsed with 1:1 Nitric acid for samples.

2. Shake samples to achieve homogeneity. Maximum sample volume is 100 ml I 1.0 ml. Use this or a smaller volume diluted to 100 mls. Place sample into BOD bottle and mark flask number next to sample number on digestion sheet.

3. To all samples and standards add 5 ml concentrated H_2SO_4 and 2.5 ml HNO_3.

4. Add 15 ml potassium permanganate to each bottle. If the purple color disappears, additional permanganate is added, with the increased volume noted. Allow to stand at least 15 minutes.

5. Add 10 ml potassium persulfate to each bottle.

6. Cover mouth of bottle with aluminum foil and place in hot water bath. Bring temperature to 95°C and maintain for 2 hours.

7. Cool to room temperature. The samples are now ready for analysis.

B. Chemical Reactions

Organic mercury compounds are decomposed by digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride and mercury vapor is produced.

C. Instrumental Analysis

1. Turn on instrument and set up for the following conditions:

   Install mercury hollow cathrode lamp

2. Allow 1/2 hour for instrument and lamp warm up.

3. Install mercury cold vapor cell in burner chamber and align with maximum energy through out.

4. Disconnect air line from nebulizer and connect to bubbler. Place bubbler in BOD bottle filled halfway with deionized water. Run hose from other end of bubbler to drying column (filled and packed with magnesium perchlorate) and then to left end of cell. Place vent hose from right end of cell in an appropriate hood.

5. Place 5.0 ml $(NaCl).(NH_2OH)_2.H_2SO_4$ into digested blank and mix. Allow 1 minute for the potassium permanganate to be dispersed.

6. With air running, add 5.0 m l of $SnCl_2$ to blank and quickly place bubbler into blank flask. Record peak height on strip chart recorder.

7. If blank is uncontaminated, run standards in the same manner. When the standards have been analyzed, their values and concentrations are entered into the linear regression program, which prints a curve on which to base all unknown samples.

8. Analyze EPA check to ensure that standards are correct.

9. Calibration of instrument is complete.

10. Analyze samples and checks and record on strip chart. Standards and EPA checks should be analyzed at least once every 15 samples to ensure proper analysis.

VIII. Calculations

Using target concentration versus peak height, a leust squares regression line is calculated as a calibration curve. Sample results are then calculated from this curve. If addtional potassium permanganate is required by any sample during digestion the result must be multiplied by the appropriate dilution factor.

IX. Daily Quality Control

A. Control Samples

1. Method Blank

2. For each lot of samples processed, method blanks (water and reagents) are carried throughout the entire sample preparation and analytical process. These blanks are useful in determining if samples are being contaminated.

3. Precision Analysis (Required by PACE QC Program)

Duplicate samples are processed on a routine basis. Duplicate samples are used to determine precision. The sample lot size will dictate the frequency but at least one of every ten samples for each matrix will be duplicated.

1. Matrix Duplicates

a. Two separate samples taken through entire sample preparation and analysis procedure

4. Accuracy Analysis

a. Spiked samples or standard reference materials are employed to determine accuracy. The following spiked samples will be included in each lot:

1. Certified Water Spikes

a. One low level spike 1.0 ug/l mercury

b. Two high level spikes 4.0 ug/l mercury

c. These are prepared per instructions in Section V. A.

2. Sample Matrix Spike (Required for PACE QC Program)

a. Prepared and spiked in the same manner as certified water high level spikes (4.0 ug/l mercury)

b. Spike one for every ten samples to be analyzed

B. Spiking Solution Control

Dilute working spike solutions will be validated against working standards before initial use and within seven days before subsequent usage.

C. Control Charts

As part of the QC program for this project single-day and three point moving average X-R control charts will be generated using either the software provided by USATHAMA or a manual method.

Initial Single-Day X-R Control Limits

Parameter	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Hg	99.3	98.9	97.4	97.1	2.0	1.5

Initial Three-Day X-R Control Limits

Parameter	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Hg	114.4	110.9	96.7	93.2	26.8	21.3

X. References

A. EPA Method 245.1 (manual cold vapor technique)

B. Perkin Elmer atomic absorption spectrophotometer operation and method manual

XI. Data

A. Off-The-Shelf Analytical Reference Materials Characterization

The standards for mercury were provided by Ricca Chemical Company and are traceable to either NBS or EPA standards.

B. Initial Calibration

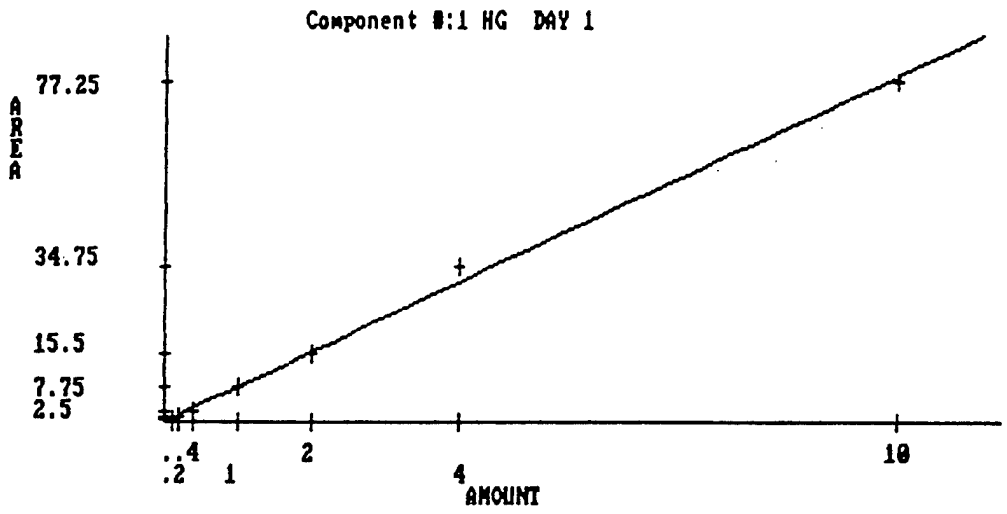
Response versus concentration data and graphs.

An initial calibration was performed on each day of analysis. The calibration levels are as follows:

0.0 (ug/L)
0.5 (ug/L)
1.0 (ug/L)
3.0 (ug/L)
5.0 (ug/L)
10.0 (ug/L)

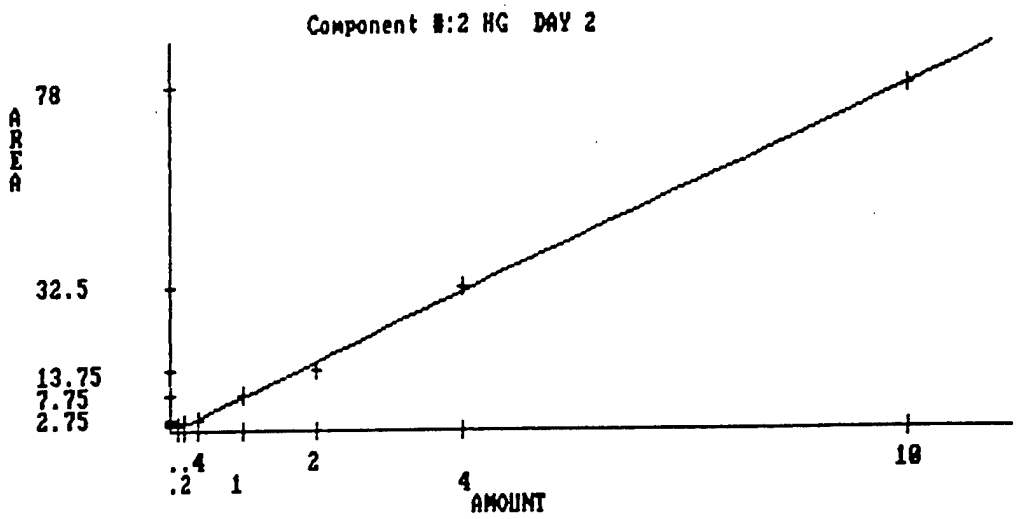
XII. Certification Data

A summary of the certification data is as follows:



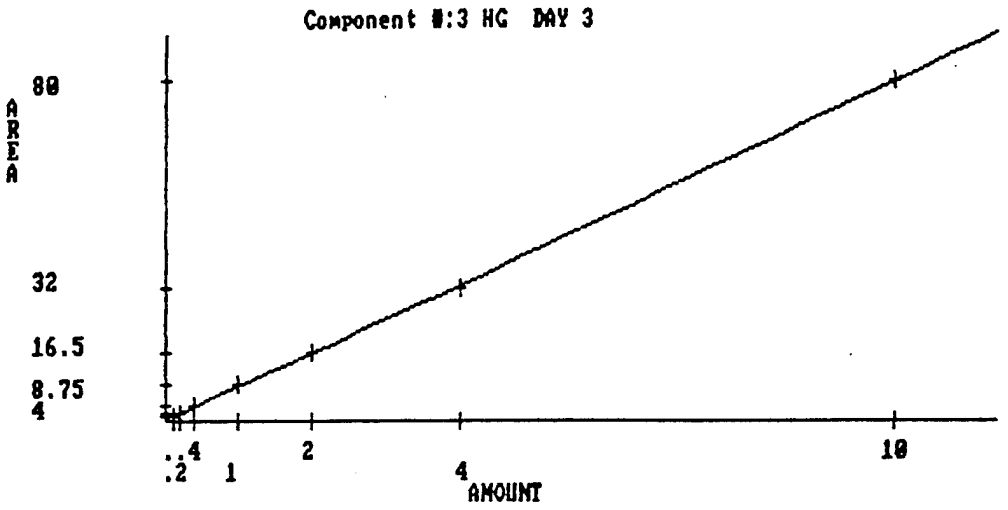
Concentration (ug/l)	Chart Units
0.10	0.75
0.20	1.00
0.40	2.50
1.00	7.75
2.00	15.50
4.00	34.75
10.0	77.25

The equation or the calibration curve for mercury is C = 0.1273971 * R + 0.08072641 where C = concentration in ug/l and R = response in chart units.



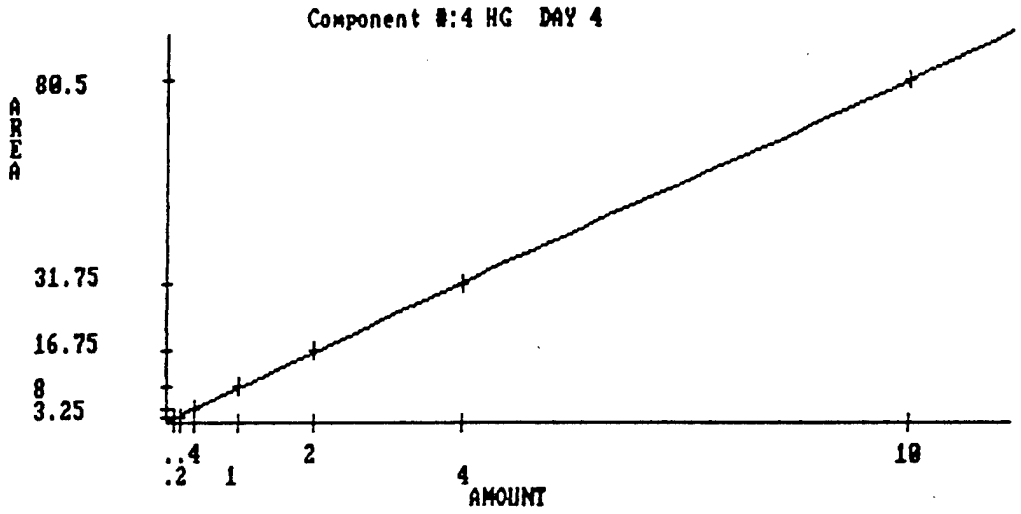
Concentration (ug/l)	Chart Units
0.10	1.25
0.20	1.75
0.40	2.75
1.00	7.75
2.00	13.75
4.00	32.50
10.0	78.00

The equation or the calibration curve for mercury is C = 0.1275922 * R + 0.0177404 where C = concentration in ug/l and R = response in chart units.



Concentration (ug/l)	Chart Units
0.10	1.00
0.20	2.00
0.40	4.00
1.00	8.75
2.00	16.50
4.00	32.00
10.0	80.00

The equation of the calibration curve for mercury is C = 0.1262307 * R - 0.01934577 where C = concentration in ug/l and R = response in chart units.



Concentration (ug/l)	Chart Units
0.10	1.00
0.20	1.25
0.40	3.25
1.00	8.00
2.00	16.75
4.00	31.75
10.0	80.50

The equation of the calibration curve for mercury is C = 0.1243307 * R + 0.1218848 where C = concentration in ug/l and R = response in chart units.

C. Daily Calibration

1. Response

A 10.0 ug/l calibration check and an EPA standard were run on each day of analysis.

Day 1: September 15, 1987

10 ug/l standard	10.0
EPA WP-386	4.95

Day 2: September 16, 1987

10 ug/l standard	9.87
EPA WP-386	5.12

Day 3: September 17, 1987

10 ug/l standard	9.98
EPA WP-386	5.09

Day 4: September 18, 1987

10 ug/l standard	9.76
EPA WP-386	5.10

2. Daily Calibration Limits

10 ug/l standard	(9.00 - 11.0)
EPA WP-386	(3.38 - 6.42)

D. Standard Certification Samples

1. Tabulation and graphs of found versus target concentrations.

CERTIFICATION ANALYSIS

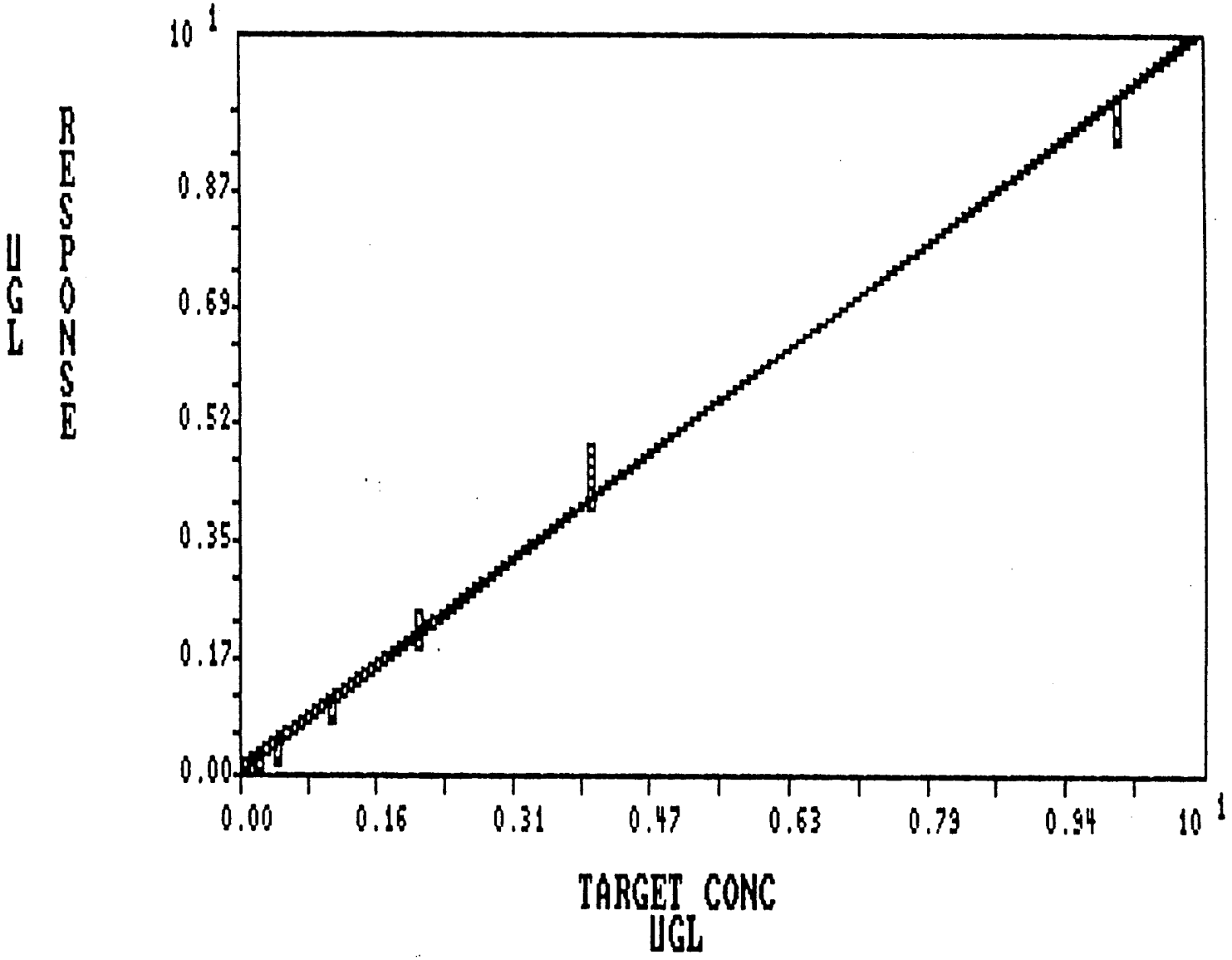
Report Date: 09/21/87

Method Name: METALS/WATER/COLD VAPOR
Compound: HG
Units of Measure: UGL

Laboratory: PC
Analysis Date: 09/18/87
Matrix: WA

TABLE OF DATA POINTS

Target Concentration	Found Concentration
0	0.0489000
	0.0815000
	0
	0.1200000
0.1000000	0.0807000
	0.0815000
	0.1400000
	0.1200000
0.2000000	0.2400000
	0.2090000
	0.1380000
	0.2460000
0.4000000	0.3670000
	0.3690000
	0.3280000
	0.4330000
1	1
	1.1000000
	1.0200000
	0.9920000
2	2.1200000
	2.0600000
	2.3200000
	2.1100000
4	4.1900000
	4.6100000
	4.7500000
	4.3500000
10	9.7000000
	9.6400000
	9.9400000
	10


HG
RESPONSE
UGL
10 1
0.87
0.69
0.52
0.35
0.17
0.00
0.00
0.16
0.31
0.47
0.63
0.79
0.94
10 1
TARGET CONC
UGL

2. LOF and ZI Test.

CERTIFICATION ANALYSIS

Report Date: 09/21/87

Method Name: METALS/WATER/COLD VAPOR
Compound: HG
Units of Measure: UGL

Laboratory: PC
Analysis Date: 09/18/87
Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

	--- Model with Intercept --- Y = (0.090934035) + (0.990226653)X			- Model through the Origin - Y = (1.003505530)X		
	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	1.326043830	26	0.051001686	1.472084680	27	0.054521655
Total Error:	0.354492450	21	0.016880593	0.354492450	21	0.016880593
Lack of Fit:	0.971551380	5	0.194310276	1.117592230	6	0.186265372
	LOF F-Ratio(F): 11.51086799			LOF F-Ratio(F): 11.03429087		
	Critical 95% F: 2.68			Critical 95% F: 2.57		
	Data Not Linear			Data Not Linear		

ZERO INTERCEPT HYPOTHESIS

** Models not linear. Do not test Zero Intercept hypothesis.

Diagnose and correct analytical system before continuing.

****

TABLE OF DATA POINTS

Targets: 7 Measures per Target: 4

	Target Value	Found Concentration			
1:	0.1000000	0.0807000	0.0815000	0.1400000	0.1200000
2:	0.2000000	0.2400000	0.2090000	0.1380000	0.2460000
3:	0.4000000	0.3670000	0.3690000	0.3280000	0.4330000
4:	1	1	1.1000000	1.0200000	0.9920000
5:	2	2.1200000	2.0600000	2.3200000	2.1100000
6:	4	4.1900000	4.6100000	4.7500000	4.3500000
7:	10	9.7000000	9.6400000	9.9400000	10

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***

3. Calculations

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CERTIFICATION ANALYSIS

Report Date: 09/21/87

Method Name: METALS/WATER/COLD VAPOR
Compound: HG
Units of Measure: UGL

Laboratory: PC
Analysis Date: 09/18/87
Matrix: WA

-- REGRESSION EQUATION --
Y = 0.9909907X + 0.0857018

-- UPPER REPORTING LIMIT --
10

-- SLOPE --
0.9909907

SUMMARY TRUNCATION TABLE

Target Concentrations Used	Slope	% Change from Total Data Set	% Change from Previous Data Se
Entire data set	0.9909907	0	0
minus 1 highest	1.1136688	12.379335	12.379335

Target Concentrations Used	Certified Reporting Limit	Upper Reporting Limit
Entire data set	0.7394689	10
Minus 1 highest	0.3578224	10

CERTIFICATION ANALYSIS

Report Date: 09/21/87

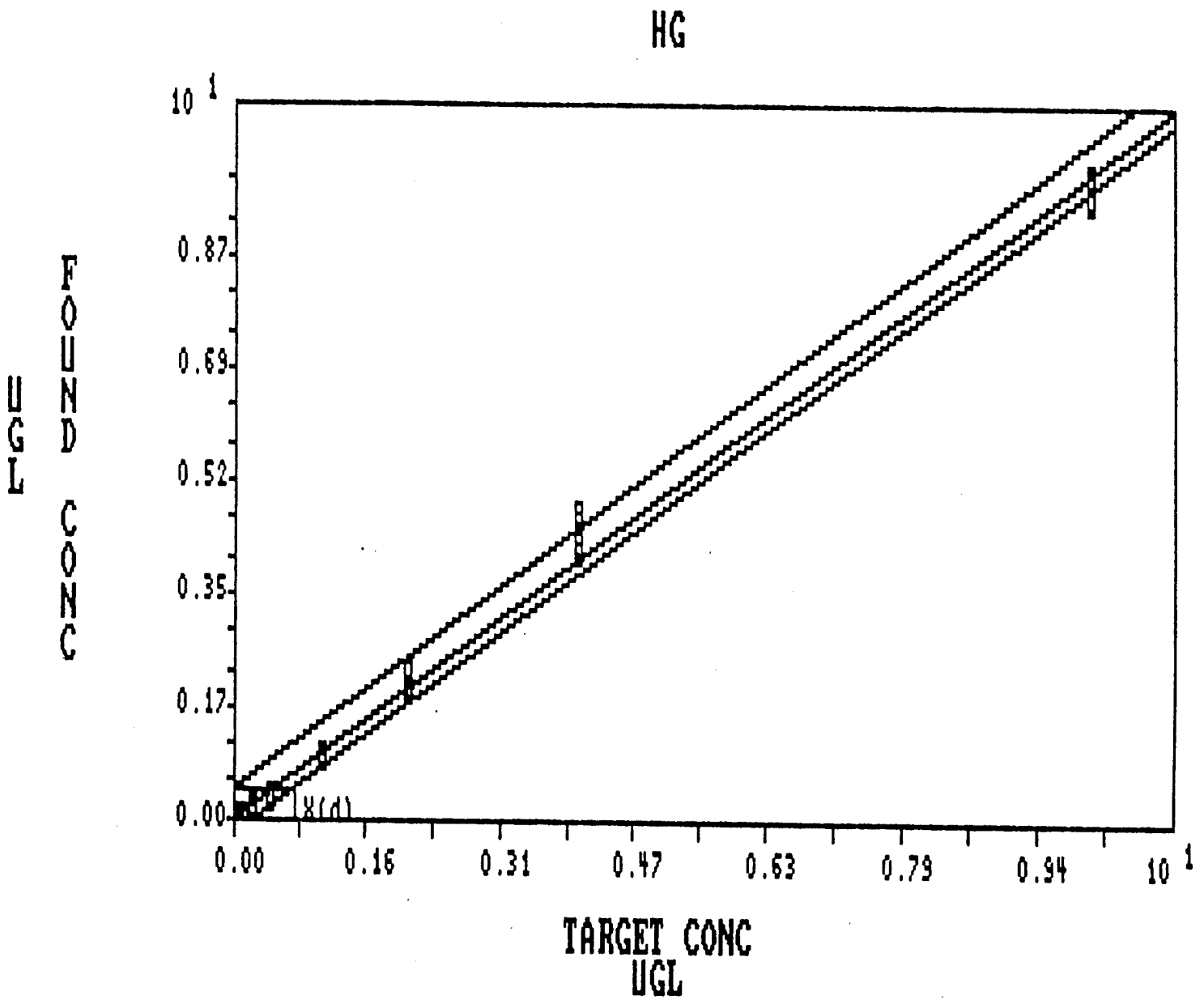
Method Name: METALS/WATER/COLD VAPOR
Compound: HG
Units of Measure: UGL

Laboratory: PC
Analysis Date: 09/18/87
Matrix: WA

TABLE OF RESULTS FOR TRUNCATED DATA SET

Target Concentration	Standard Deviation	Percent Inaccuracy	Percent Imprecision
0.1000000	0.0293912	5.5500000	27.845771
0.2000000	0.0495606	4.1250000	23.798593
0.4000000	0.0434770	-6.437500	11.617102
1	0.0494233	2.8000000	4.8077180
2	0.1147098	7.6250000	5.3291419
4	0.2521243	11.875000	5.6340627
10	0.1766352	-1.800000	1.7987293

4. Strip Charts


HG
10 1
0.87
0.69
0.52
0.35
0.17
0.00
FOUND CONC
UGL
0.00
0.16
0.31
0.47
0.63
0.79
0.94
10 1
TARGET CONC
UGL

#1

COPY

TOTAL CYANIDE IN WATER

Method TY03

I. Summary

A. Analyte: Total Cyanide

B. Matrix: Water and Wastewater

C. General Method: The cyanide as Hydrocyanic Acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing Sodium hydroxide solution. The cyanide is then determined colormetrically where it is converted to cyanogen chloride CNCL, by the reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on addition of pyridine-barbituric acid reagent. Absorbance is read at 578 nm and is proportional to cyanide concentration. (EPA # 335.2)

II. Application

A. Test Concentration Range: 2.50 to 250 ug/l

B. Sensitivity: 0.015 Absorbance units for 5 ug/l

C. Certified Reporting Limits: 8.17 ug/l

D. Interferences

1. Sulfides convert CN- to CNS-. Test for S^2 with lead acetate paper, precipitated with $Cd(NO_3)_2$ $4H_2O$ to form CdS and filter.

2. Oxidizing agents such as chlorine decompose cyanide. Test with KI starch paper, treat sample with ascorbic acid.

3. Thiocyanate, (CNS-) can mask cyanide determination; add Magnesium chloride soln. before distillation (20mls/500mls of sample).

4. Aldehydes, and ketones, convert cyanide to cyanohydrin, add 2 mls of Ethylene diamine solution per 100 mls of sample.

5. Nitrite, may react with organic contaminants to form HCN resulting in a positive interference, add 2 grams of Sulfamic acid per 500 mls of sample prior to the addition of H_2SO_4 in the distillation step.

6. Carbonate causes excessive gasing during distillation procedure, add hydrated lime for stabilization.

E. Analysis Rate. The maximum number of samples that can be analyzed by this method in an 8-hour shift after instrument calibration is 20 samples.

F. Safety Information. Care should be used while handling cyanide samples because of toxicity. Samples should be processed in a hood; avoiding contact, inhalation, or ingestion.

III. Apparatus and Chemicals

A. Glassware/Hardware

1. 500 ml flat bottomed boiling flask 24/40 Pyrex
2. Connecting Arm 3-way 24/40 Pyrex #9040
3. Thistle Tube Pyrex #__
4. Rubber Stopper 1 hole #4
5. Allihn Condensor 24/40 12"
6. Connecting tube
7. Gas Absorber 250 ml Pyrex
8. Gas dispersion tube with medium-porosity fritted outlet
9. Vacuum Flask Kimax no. 27060 1,000 ml
10. Vacuum Pump
11. Heating Mantel Glas-Col #0402
12. Cordtrol Power Control Glas-Col PL 112
13. Tygon tubing
14. Screw clamp
15. Neoprene tubing

16. Volumetric flasks and pipets, Class A Pyrex Various Sizes

17. Nessler Tubes 100 ml Exax no. 45315

18. Rubber Stopper #3 solid

19. Cuvette 1 cm pathlength Milton Roy Company #33-17-80

20. Boiling Chips

B. Instrumentation:

Spectrophotometer - Turner Model 350

a. Wavelength range 400-680 nm

b. Sensitivity 0.015 absorbance units for 5 ug/l

c. Wavelength 578 nm

C. Analytes: CN or HCN

1. Formula Weight: 27.06

2. Density: 0.901 g/l

3. Melting Point: 13.24°C

4. Boiling Point: 25.70°C

5. CAS#: 151-50-8

D. Reagents and Sarms

1. Chemical List

a.	Sodium Hydroxide pellets AR	98.3% pure	Mallinckrodt
b.	Sulfuric Acid Concentrated AR	96.4%	Mallinckrodt
c.	Sodium Phosphate Monobasic AR	100.97%	Mallinckrodt
d.	Potassium Cyanide AR	98.4%	Baker
e.	Potassium Hydroxide pellet AR	86%	Mallinckrodt
f.	Chloramine T		Kodak
g.	Barbituric Acid	98%	Mallinckrodt
h.	Pyrine AR	99%	Baker
i.	Hydrochloric acid - Concentrated AR		Mallinckrodt
j.	Magnesium Chloride, 6 Hydrate	99.54%	Mallinckrodt
k.	Cadmium carbonate		ICN Pharmacevticals
l.	Ascorbic acid AR		Kodak
m.	Ethylene diamine AR	98% min.	Kodak

2. Working Reagents

a. 0.25 N NaOH: dissolve 100 g NaOH in DI water and dilute to 10 liters.

b. 1.5N Sodium dihydrogen Phosphate: Dissolve 207 g $NaH_2PO_4.H_2O$ in DI water and dilute to one liter (keep refrigerated)

c. Stock Cyanide Solution (1 ml = 1 mg): Dissolve 2.51 g KCN and 2 g KOH in DI water and dilute to one liter. (keep refrigerated) This standard is verified by EPA standards.

d. Chloramine T solution: Dissolve 1.0 g of white, water soluble chloramine T in 100 ml of DI water (make fresh weekly, keep refrigerated).

e. Magnesium chloride solution: Dissolve 510 g of $MgCl_2.6H_2O$ in DI water and dilute to one liter.

f. Pyridine Barbituric Acid Reagent: Place 15 g barbituric acid in a 250-mL volumetric flask and add just enough water to wash side of flask and wet barbituric acid. Add 75 mL pyridine and mix. Add 15 mL conc hyrochloric acid (HCl), mix and cool to room temperature. Dilute to mark with water and mix. This reagent is stable for up to 1 month; discard if a precipitate develops.

IV. Calibration

A. Initial Calibration

1. Preparation of Standards

a. Prepare a working stock CN standard at 10 mg/L

Dilute 10 mls of stock CN standard (1000 mg/L) to 1,000 mls with deionized water.

b. Using the working stock CN standard (10 mg/L), prepare the following standards in the appropriate size volumetric flasks.

CYANIDE CONCENTRATION (ug/l)	mls OF WORKING STANDARD (10 mg/l)	FINAL VOLUME (ml)
0.00	0	250
2.25	0.225	1,000
5.00	1.000	2,000
10.00	1.000	1,000
25.00	5.000	2,000
50.00	5.000	1,000
100.00	5.000	500
275.00	55.000	2,000

c. The working stock standard and the working standards are prepared daily and stored at room temperature.

d. A 250 ml aliquot of each standard is used for analysis

2. Instrument Calibration

a. Turn on instrument and adjust wavelength to 578 nm.

b. Allow 20 minutes for instrument warmup.

c. Zero instrument with reagent blank consisting of 50 ml 0.25N NaOH, 15 ml NaH_2PO_4, 2 ml chloramine T, and 5 ml Pyridine-barbituric acid, diluted to 100 ml with deionized water.

d. Analyze standards and EPA checks to ensure proper instrument calibration.

3. Analysis of Calibration Data

Acceptability of calibration data occurs when the following are true:

a. Absorbance of the high standard is within 10% or 2 standard deviations (after seven calibrations) of the mean response determined from past data.

b. Linear regression data is similar to previous calibrations.

c. EPA check values are acceptable based on a 95% confidence level of the true value.

B. Daily Calibration

1. Preparation of Standards

same as initial calibration

prepare 250 ug/l standard only.

2. Instrument Calibration

same as initial calibration

analyze 250 ug/l standard only.

3. Analysis of Calibration Data

Absorbance for high standard must be within 10% or two standard deviations (after seven calibrations) of the mean response for the same concentration as determined from previous calibrations.

4. Calibration Checks

EPA check standards are employed as certified calibration check standards.

V. Certification Testing

Preparation of Certification Matrix for Water

1. Prepare a working stock CN standard at 10 mg/L

   a. Dilute 10 mls of stock CN standard (1,000 mg/L) to 1,000 mls with deionized water.

2. Using the working stock CN standard (10 mg/L), prepare the following standards in the appropriate size volumetric flasks.

UNIT (Flask #)	ANALYTE ADDITION (ml of working standard)	DILUTION VOLUME (ml)	CALIBRATION LEVEL ug/L	TRL MULTIPLIER
1	0	250	0	0x
2	0.5	2,000	2.5	0.5x
3	1.0	2,000	5.0	1x
4	1.0	1,000	10.0	2x
5	5.0	2,000	25.0	5x
6	5.0	1,000	50.0	10x
7	5.0	500	100.0	20x
8	25.0	1,000	250.0	50X

3. For each unit, a 250 ml aliquot is analyzed, corresponding to the 8 calibration levels.

VI. Sample Handling/Storage

A. Sampling Procedure

1. Samples are tested for the presence of oxidizing agents such as chlorine with potassium - iodine starch paper. A blue color indicates a need for treatment. Add ascorbic acid until no color is shown on indicator paper, then add an additional 0.6 g of ascorbic acid for each liter of sample collected.

2. Samples are tested for the presence of sulfides with lead acetate paper. A brown color indicates the presence of sulfides. If sulfides are present; add Cadmium nitrate until test shows negative, then filter sample.

3. Samples are to be preserved with sodium hydroxide to pH 12.

B. Containers

Samples are to be collected in one liter plastic or glass bottles.

C. Storage Condition

Samples should be stored at 4°C until time of analysis.

D. Holding Time Limits

Maximum holding time is 14 days

E. Solution Verification

Dilute working spike solutions will be validated against working standards before initial use and within seven days before subsequent usage.

VII. Procedure

A. Separation or Digestions:

1. Measure volumetrically 250 mls of sample and place in a 500 ml boiling flask along with 6-8 boiling chips.

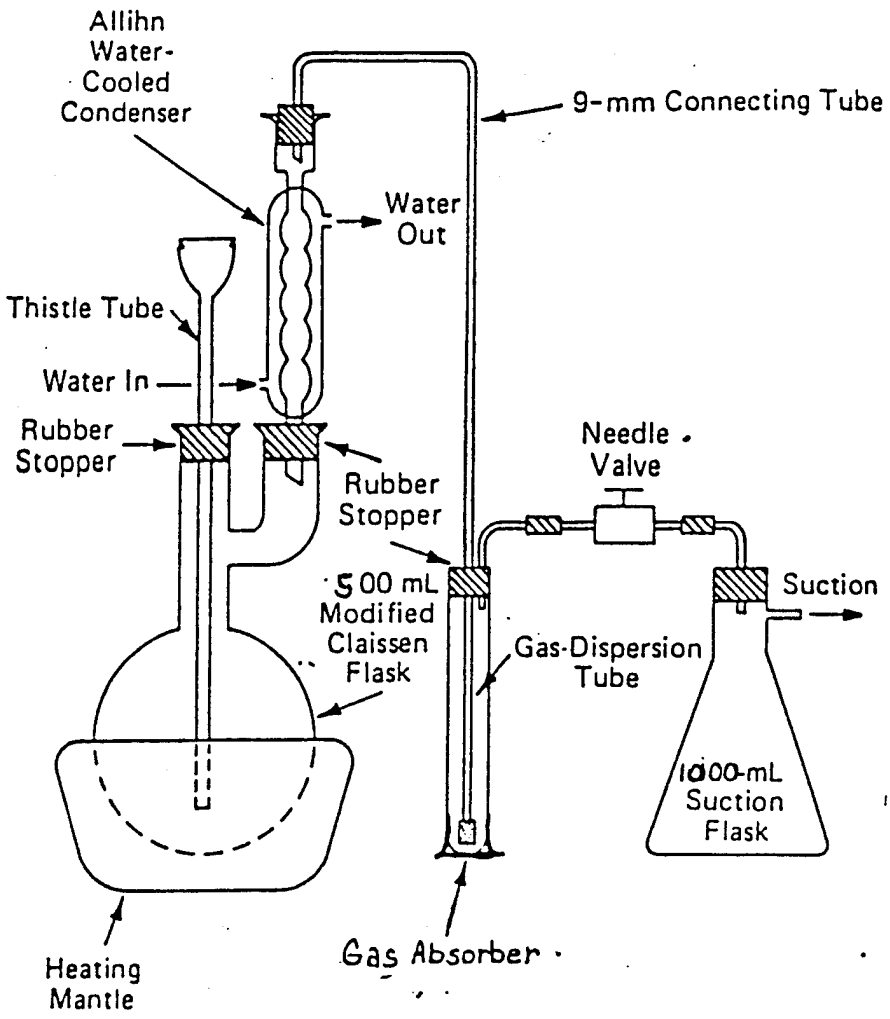
2. Pour 100 ml of 0.25 NaOH solution into a 250 ml gas absorber and inset a gas dispersion tube into the absorber, making sure that the fritted glass end of the dispersion tube is below the surface of the NaOH solution.

3. Assemble the distillation apparatus as illustrated below. (figure a)

   a. Place the connecting arm onto the boiling flask with one side connected to the condensor and the other side stopped with a thistle tube such that the end of the thistle tube projects below the surface of the sample.
   b. Place one end of the connecting tube at the top of the condensor and connect the other end to the gas dispersion tube.
   c. Attach the vacuum source to the gas absorber.

4. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.
   CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

fig. a


Allihn Water-Cooled Condenser
9-mm Connecting Tube
Water Out
Thistle Tube
Water In
Rubber Stopper
Rubber Stopper
Needle Valve
Suction
500 mL Modified Claissen Flask
Gas-Dispersion Tube
1000-mL Suction Flask
Heating Mantle
Gas Absorber

5. Slowly add 25 ml conc. Sulfuric acid through the thistle tube. Allow the airflow to mix the flask contents for 30 minutes, or until acid is mixed. Increase airflow to speed mixing. Pour 10 ml of Magnesium chloride into the air inlet and wash down with a stream of water.

6. Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Vapors should not rise more than halfway into condenser. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source. Distillation is now complete and the samples are now ready for instrumental analysis.

B. Chemical Reactions

1. The cyanide as hyrdocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2. In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent.

C. Instrumental Analysis

1. Withdraw 50 ml or less of the absorbing solution from the flask and transfer to a 100 ml nessler tube. If less than 50 ml is taken, dilute to 50 ml with 0.25 N Sodium hydroxide solution. Add 10.0 ml of Sodium phosphate solution and mix.

2. Pyridine - Barbituric acid method: Add 2 ml of chloramine T and mix. After 1 to 2 minutes, add 5 ml of pyridine - Barituric acid solution and mix. Dilute to 100 ml mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes. NOTE: Zero the spectrophotometer with a freshly prepared reagent blank.

VIII. Calculations

A. Absorbance is read on the instrument and the number of ug present is determined based on the linear regression formulated by the standards used during calibration.

B. Liquid Samples:

$$CN^-, (ug/L) = A \times 50/(B \times C)$$

A = ug CN from calibration curve

B = mls of original sample used

C = mls of distillate used for color development

IX. Daily Quality Control

A. Control Samples

1. Method Blank

a. For each lot of samples processed, method blanks (deionized water and reagents) should be carried throughout the entire sample preparation, distillation, and analytical process. These blanks are useful in determining if samples are being contaminated.

2. Precision Analysis (Required by PACE QC Program)

Duplicate samples are processed on a routine basis. Duplicate samples are used to determine precision. The sample load will dictate the frequency, but at least one of every ten samples for each matrix will be duplicated. Duplicates should be carried throughout the entire sample preparation, distillation, and analytical process.

3. Accuracy Analysis

a. Spiked samples or standard reference materials are employed to determine accuracy. The following spiked samples will be included in each lot:

1. Certified Water Spikes

a. One low level spike 20 ug/L cyanide

b. Two high level spikes, 50 ug/L cyanide

c. These are prepared per instructions in Section V. A.

2. Sample Matrix Spike (Required by PACE QC Program)

a. Prepared and spiked in the same manner as certified water high level spikes (100 ug/L cyanide)

b. Spike one for every ten samples to be analyzed

B. Control Charts

As part of the QC program for this project, single day and three-point moving average X - R control charts will be generated using either the software provided by USATHAMA or a manual method.

Initial Single-Day X-R Control Limits

	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Cyn	140.7	129.9	86.9	76.1	56.2	43.2

Initial Three-Day X-R Control Limits

	UCL-X	UWL-X	LWL-X	LCL-X	UCL-R	UWL-R
Cyn	104.7	93.1	46.7	35.1	87.5	69.7

X. References

A. American Public Health Association and Others, 1976, Standard Methods for the Examination of Water and Waste Waters (15th edition): New York, American Public Health Association, Incorporated, p. 312.

B. American Society for Testing and Materials, 1984, Annual Book of ASTM Standards, Section 11, Water: Philadelphia, American Society for Testing Materials Method D 2036-82, p. 110.

C. United States Environmental Protection Agency, 1979, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020

Environmental Monitoring and Support Laboratory, Cincinnati, Method 335.2

#2

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Section No.
Revision No. 1
Date 7/02/91
Page 1 of 29
Doc. No. WPPSOP95

ANALYSIS OF ORGANOCHLORINE PESTICIDES (OCP) AND POLYCHLORINATED BIPHENYLS (PCB) IN ENVIRONMENTAL WATER SAMPLES BY GAS CHROMATOGRAPHY (GC)

METHOD UH21

I. SUMMARY

A. ANALYTES

The following analytes can be determined by this method:

USATHAMA DESIGNATION	COMPOUND
CL4XYL	Tetrachloro-m-xylene (surrogate)
CL10BP	Decachlorobiphenyl (surrogate)
ABHC	alpha-BHC
BBHC	beta-BHC
DBHC	delta-BHC
LIN	gamma-BHC
HPCL	Heptachlor
ALDRN	Aldrin
HPCLE	Heptachlor epoxide
AENSLF	alpha-Endosulfan
DLDRN	Dieldrin
PPDDE	4,4'-DDE
ENDRN	Endrin
BENSLF	beta-Endosulfan
PPDDD	4,4'-DDD
ESFSO4	Endosulfan sulfate
PPDDT	4,4'-DDT
MEXCLR	Methoxychlor
ENDRNK	Endrin ketone
ENDRNA	Endrin aldehyde
ACLDAN	alpha-Chlordane
GCLDAN	gamma-Chlordane
TXPHEN	Toxaphene
PCB016	Aroclor 1016
PCB221	Aroclor 1221
PCB232	Aroclor 1232
PCB242	Aroclor 1242
PCB248	Aroclor 1248
PCB254	Aroclor 1254
PCB260	Aroclor 1260

B. MATRIX

This method is applicable to the quantitative determination of the selected OCP/PCB compounds in environmental water samples.

C. GENERAL METHOD

A measured volume of water, nominally 1 liter, is serially extracted with dichloromethane (DCM) using liquid-liquid extraction technique. The DCM extract is dried through sodium sulfate, concentrated and solvent exchanged to hexane, then passed through a florisil column to remove potential interferences. The extract is then analyzed by capillary GC using an electron capture detector (ECD). Dual column analysis allows for simultaneous identification, quantitation, and confirmation of target compounds. Sample results are calculated by an external standard method.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

The tested concentration range for each target analyte in standard water samples is given in Table 1.

B. SENSITIVITY

The instrument response for each analyte at the certified reporting limit is given in Table 1.

C. REPORTING LIMITS

The certified reporting limit (CRL) and upper certified reporting limit (UCRL) calculated for each analyte according to the USATHAMA reporting limit software is given in Table 1.

TABLE 1. TESTED MATRIX CONCENTRATION, CERTIFIED REPORTING LIMIT, AND INSTRUMENT SENSITIVITY.

ANALYTE	TEST CONCENTRATION RANGE (UG/L)	CRL (UG/L)	UCRL (UG/L)	AREA COUNTS AT CRL
CL4XYL	0.006 to 0.300	0.0767	0.300	83,600
CL10BP	0.006 to 0.300	0.0143	0.300	29,900
ABHC	0.006 to 0.300	0.0434	0.300	40,300
BBHC	0.006 to 0.300	0.0109	0.300	7,340
DBHC	0.006 to 0.300	0.0488	0.300	48,900
LIN	0.006 to 0.300	0.0429	0.300	44,100
HPCL	0.006 to 0.300	0.0631	0.300	96,900
ALDRN	0.006 to 0.300	0.0638	0.300	81,300
HPCLE	0.006 to 0.300	0.00600	0.300	8,590
AENSLF	0.006 to 0.300	0.00856	0.300	8,860
DLDRN	0.012 to 0.600	0.0321	0.600	20,100
PPDDE	0.012 to 0.600	0.0946	0.600	121,000
ENDRN	0.012 to 0.600	0.0372	0.600	23,100
BENSLF	0.012 to 0.600	0.0120	0.600	2,810
PPDDD	0.012 to 0.600	0.0848	0.600	78,200
ESFSO4	0.012 to 0.600	0.0200	0.600	15,200
PPDDT	0.012 to 0.600	0.0316	0.600	17,800
MEXCLR	0.060 to 3.00	0.267	1.50	208,000
ENDRNK	0.012 to 0.600	0.0283	0.600	24,900
ENDRNA	0.012 to 0.600	0.0697	0.600	73,200
ACLDAN	0.006 to 0.300	0.0202	0.300	27,800
GCLDAN	0.006 to 0.300	0.0450	0.300	76,900
TXPHEN	0.600 to 30.0	0.600	30.0	12,100
PCB016	0.120 to 6.00	0.859	6.00	61,400
PCB260	0.120 to 6.00	0.137	6.00	11,200

D. INTERFERENCES

Method interferences may be caused by solvents, reagents, glassware, and other sample processing equipment. These interferences may yield artifacts and/or elevated baselines in chromatograms. All sample processing materials will be routinely monitored for potential interferences by analyzing reagent and laboratory blanks. Extra caution must be taken to avoid phthalate contamination which severely interfere with chlorinated pesticide analysis by GC/ECD. Laboratory personnel must eliminate any contact between sample extracts and latex gloves, tubing, polyethylene bottles, etc.

E. ANALYSIS RATE

The lot size shall not exceed 14 samples plus control samples per 24 hr. period.

F. SAFETY

The compounds of interest are toxic and potentially carcinogenic. All chemicals and samples should be handled as potential health hazards. Only personnel trained in the safe handling of such materials will be allowed to work on this procedure. At a minimum laboratory personnel will wear lab coats, safety glasses, and latex gloves when handling samples or standards. Cartridge respirators and other special protective equipment is available if needed.

The laboratory maintains a current file of OSHA regulations regarding the safe handling of chemicals. Material Safety Data Sheets are also available to laboratory personnel.

III. APPARATUS AND CHEMICALS

A. HARDWARE/GLASSWARE

1. Separatory funnels, 2000-mL with Teflon® stopcock
2. Amber screw-cap vials with Teflon®-lined septa, as appropriate
3. Chromatographic columns [30 cm x 11 mm inside diameter (ID) and 250 ml reservoir]
4. Disposable volumetric pipettes, 1-mL
5. Class A volumetric flasks, as appropriate
6. Class A volumetric pipettes, as appropriate
7. Pasteur pipettes (disposable)
8. Graduated cylinders, as appropriate
9. Crimp-top 2-mL amber autosampler vials, Hewlett-Packard or equivalent
10. Gas-tight microliter syringes, as appropriate
11. Analytical balances (0.0001-g and 0.01-g sensitivity), American Scientific Products or equivalent
12. Florisil cartridges, 1-g with teflon frit, Analytichem or equivalent
13. Solid Phase Extraction (SPE) Manifold (Analytichem International, Vac-Elut, or equivalent)

14. Kuderna-Danish Apparatus; including 10-mL graduated concentrator tubes, 500-mL evaporative flask, 3-ball macro Snyder column, and 3-ball micro Snyder column

15. Heated water bath with temperature control

16. Organomation Associates N-Evap nitrogen blowdown apparatus, or equivalent

17. Wide range pH paper

18. Grab sample bottle, 1000-mL narrow mouth amber glass, fitted with a screw cap lined with Teflon®

19. Glass culture tubes, 16 X 100 mm, Baxter Healthcare Corporation or equivalent

B. INSTRUMENTATION

A Hewlett-Packard 5890 gas chromatograph (or equivalent) equipped with dual electron capture detectors and an autosampler. Integration is performed using VG Minichrome or Nelson Analytical 2600 chromatography data system (or equivalent, capable of integrating peak heights and areas and recording retention times).

1. ANALYTICAL CONDITIONS - PRIMARY COLUMN

Column: DB-608 (J & W Scientific or equivalent) fused silica capillary (fscc), 30-m length, 0.53-mm ID with a 0.83-um film
Temperature Program: 150°C-170°C for 3-5-min, then 5°C/min to 270°C with a 15-25 min final hold
Injector Temperature: 210-230°C
Detector Temperature: 300°C
Carrier Gas: Helium at 3.5-4 mLs/min
Make-up Gas: 5% Methane/Argon at 60 mLs/min
Injection Volume: 5-ul

2. ANALYTICAL CONDITIONS - SECOND COLUMN

Column: DB-1701 (J&W Scientific or equivalent) fscc, 30-m length, 0.53mm ID with a 1-um film
Other conditions: same as primary column

3. RETENTION TIMES

Absolute analyte retention times are given in Section XI. Retention time windows (RTW) are set at ± 0.04 minutes. Daily retention time adjustments are based on the retention time from the daily standard +/- the RTW obtained during certification.

C. ANALYTES

The target analyte CAS numbers and physical properties are given in Table 2.

D. REAGENTS AND STANDARD MATERIALS

Standard materials and reagents are identified in Table 2 along with source, purity, concentration, and preparation information.

TABLE 2. STANDARD MATERIALS AND REAGENTS IDENTIFICATION

COMPOUND	CAS NUMBER	MW	SOURCE/PURITY
CL4XYL	877-09-8	244	Supelco/LA25453
CL10BP	1336-36-3	498.5	Supelco/LA25453
ABHC	319-84-6	290.8	a
BBHC	319-85-7	290.8	b
DBHC	319-86-8	290.8	b
LIN	58-89-9	290.8	a
HPCL	76-44-8	373	a
ALDRN	309-00-2	365	b
HPCLE	1024-57-3	389	b
AENSLF	959-98-8	407	a
DLDRN	60-57-1	381	a
PPDDE	72-55-9	318	b
ENDRN	72-20-8	381	a
BENSLF	33213-65-9	407	b
PPDDD	72-54-8	320	a
ESFSO4	1031-07-8	423	b
PPDDT	50-29-3	354.5	a
MEXCLR	72-43-5	345.7	a
ENDRNK	53494-70-5	381	b
ENDRNA	7421-36-3	382	b
ACLDAN	5103-71-9	410	Velsicol Chemical/82075
GCLDAN	5103-74-2	410	Velsicol Chemical/51983
TXPHEN	9001-35-2	413.8	Restek/A000038
PCB016	12674-11-2	NA	Restek/A000041
PCB221	11104-28-2	NA	Restek/A000043
PCB232	11141-16-5	NA	Restek/A000044
PCB242	53469-21-9	NA	Restek/A000046
PCB248	12672-29-6	NA	Restek/A000048
PCB254	11097-69-1	NA	Restek/A000051
PCB260	11096-82-5	NA	Restek/A000032
Dichloromethane	75-09-2	84	Burdick & Jackson [c]
Hexane	100-54-3	86	Burdick & Jackson [c]
Acetone	67-64-1	58	Burdick & Jackson [c]
Methanol	67-56-1	32	Burdick & Jackson [c]
Toluene	108-88-3	92	Burdick & Jackson [c]
Trimethylpentane	540-84-1	114	Burdick & Jackson [c]
NaOH	1310-73-2	40	Mallinckrodt [d]
H_2SO_4	7664-93-9	98	Mallinckrodt [d]
Florisil Cartridges	-	-	Analytichem International
Sodium Sulfate	-	-	J. T. Baker

a) Supelco Standard Pesticide Mix, LA 24691.
b) Supelco Standard Pesticide Mix, LA 24711.
c) Pesticide grade, distilled in glass solvents or equivalent.
d) Analytical grade.

IV. CALIBRATION

A. STANDARD PREPARATION

1. Individual stock standard solutions are useable for 12 months and mixed working standards are useable for 6 months unless analysis difficulties warrant sooner replacement. All pesticide standard dilutions are in hexane. All standards will be stored at 4°C in amber glass vials with teflon lined caps.

2. Mixed analyte stock solutions obtained commercially are used to prepare the calibration standards. The commercially obtained standard mixes are characterized by direct comparison with USATHAMA SARMs or EPA repository standards. Concentration agreement within +/-30% is considered acceptable. The surrogate compounds are tetrachloro-m-xylene and decachlorobiphenyl. The surrogate stock standard solution is at a concentration of 200-ug/mL. Target analyte concentrations in the pesticide mix used to prepare calibration standards are as follows:

PESTICIDE STOCK STANDARD SOLUTION (PSSS)

COMPOUND	CONCENTRATION (ug/ml)	COMPOUND	CONCENTRATION (ug/ml)
ABHC	15.0	ENDRN	30.0
BBHC	15.0	BENSLF	30.0
DBHC	15.0	PPDDD	30.0
LIN	15.0	ESFS04	30.0
HPCL	15.0	PPDDT	30.0
ALDRN	15.0	MEXCLR	15.0
HPCLE	15.0	ENDRNK	30.0
AENSLF	15.0	ENDRNA	30.0
DLDRN	30.0	ACLDAN	15.0
PPDDE	30.0	GCLDAN	15.0

3. An intermediate pesticide calibration standard is prepared from the PSSS (Section IV.A.2) as follows:

Compound	CMC. Stock Conc.	Aliquot	Dilution	Final Conc.
ABHC	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
LIN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
HPCL	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
AENSLF	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
DLDRN	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRN	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDD	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDT	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
MEXCLR	150 ug/mL	1.25 mL	50 mL	3.75 ug/mL
BENSLF	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
DBHC	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
ALDRN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
GCLDAN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
ACLDAN	15 ug/mL	1.25 mL	50 mL	0.375 ug/mL
BENSLF	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRNA	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ESFSO4	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
ENDRNK	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
PPDDE	30 ug/mL	1.25 mL	50 mL	0.750 ug/mL
CL4XYL	200 ug/mL	0.100 mL	50 mL	0.400 ug/mL
CL10BP	200 ug/mL	0.100 mL	50 mL	0.400 ug/mL

Calibration standards are diluted down from this intermediate in the following way:

Volume Diluted	Final Volume	Standard #
0.10 mL	7.5 mL	WCSP5
1.0 mL	10 mL	WCSP4
2.0 mL	10 mL	WCSP3
4.0 mL	10 mL	WCSP2
8.8 mL	12 mL	WCSP1
0.0 mL	10 mL	Blank

4. The concentrations of the pesticides are found in Table 3.

TABLE 3. PESTICIDE CONCENTRATIONS IN THE WORKING CALIBRATION STANDARDS (UG/ML)

TEST NAME	BLANK	WCSP5	WCSP4	WCSP3	WCSP2	WCSP1
ABHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
BBHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
DBHC	0.00	0.00500	0.0375	0.0750	0.150	0.275
LIN	0.00	0.00500	0.0375	0.0750	0.150	0.275
HPCL	0.00	0.00500	0.0375	0.0750	0.150	0.275
ALDRN	0.00	0.00500	0.0375	0.0750	0.150	0.275
HPCLE	0.00	0.00500	0.0375	0.0750	0.150	0.275
AENSLF	0.00	0.00500	0.0375	0.0750	0.150	0.275
DLDRN	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDE	0.00	0.0100	0.0750	0.150	0.300	0.550
ENDRIN	0.00	0.0100	0.0750	0.150	0.300	0.550
BENSLF	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDD	0.00	0.0100	0.0750	0.150	0.300	0.550
ESFSO4	0.00	0.0100	0.0750	0.150	0.300	0.550
PPDDT	0.00	0.0100	0.0750	0.150	0.300	0.550
MEXCLR	0.00	0.0500	0.375	0.750	1.50	2.75
ENDRNK	0.00	0.01	0.0750	0.150	0.300	0.550
ENDRNA	0.00	0.01	0.0750	0.150	0.300	0.550
ACLDAN	0.00	0.005	0.0375	0.0750	0.150	0.275
GCLDAN	0.00	0.005	0.0375	0.0750	0.150	0.275
CL4XYL	0.00	0.00530	0.0400	0.0800	0.160	0.293
CL10BP	0.00	0.00530	0.0400	0.0800	0.160	0.293

5. A 1-level calibration is analyzed for Aroclor 1016, Aroclor 1260, and toxaphene prior to sample analysis. If positive results for PCB's or toxaphene are detected in a sample; the sample will be reanalyzed and quantitated against a 1-level calibration of the detected aroclor.

6. An external calibration check standard (CCS) is analyzed to verify each initial calibration. The CCS is prepared from separate stock solutions than the calibration standards and contains as many target analytes as possible at a concentration near the middle of the calibration curve. A CCS prepared from SARM or EPA traceable materials will serve as a concentration verification for commercially availab3e premixed standard solutions. Comparison results within 30% of the expected value indicate acceptable results and the commercial mix is then useable. The external check standard concentrations are as follows:

COMPOUND	CONCENTRATION (ug/mL)	COMPOUND	CONCENTRATION (ug/mL)
ABHC	0.125	ENDRIN	0.250
BBHC	0.125	BENSLF	0.125
DBHC	0.125	PPDDD	0.250
LIN	0.150	ESFS04	0.300
HPCL	0.250	PPDDT	0.301
ALDRN	0.250	MEXCLR	0.250
HPCLE	0.125	ENDRNK	0.308
AENSLF	0.125	ACLDAN	0.177
DLDRN	0.300	GCLDAN	0.163
PPDDE	0.250		

Note: As new stocks are made, concentrations will vary slightly.

7. The low level control spike solution is prepared by combining and diluting individual stock solutions for each control analyte in a 25-mL volumetric flask and diluting to volume with acetone. Preparation and final analyte concentrations in the mixed analyte control spike solution are as follows:

Control Analyte	Stock Solution Concentration (ug/mL)	Volume of Stock Diluted to 25-mL (uL)	Control Spike Solution Concentration (ug/mL)
ALDRN	10.0	250	0.100
DLDRN	10.0	250	0.100
ENDRN	10.0	250	0.100
PPDDT	10.0	250	0.100
HPCL	10.0	250	0.100
LIN	10.0	250	0.100
GCLDAN	10.0	250	0.100
AENSLF	5.00	125	0.025
BENSLF	5.00	125	0.025
MEXCLR	10.0	1250	0.500

8. The high level control spike solution is prepared by combining and diluting 1.25-mLs of 5.00-ug/mL individual stock solutions for a-endosulfan, g-BHC, aldrin, g-chlordane and heptachlor, 1.25-mLs of 10.0 ug/mL individual stock solutions for b-endosulfan, dieldrin, endrin and p,p-DDT, and

3.00-mLs of individual stock solutions for each control analyte in a 25-mL volumetric flask and diluting to volume with acetone. Preparation and final analyte concentrations in the mixed analyte control spike solution are as follows:

Control Analyte	Stock Solution Concentration (ug/mL)	Volume of Stock Diluted to 25-mL (uL)	Control Spike Solution Concentration (ug/mL)
AENSLF	5.00	1250	0.250
ALDRN	10.0	2500	0.250
GCLDAN	10.0	2500	0.250
HPCL	10.0	2500	0.250
LIN	10.0	2500	0.250
BENSLF	5.00	2500	0.500
DLDRN	10.0	1250	0.500
ENDRN	10.0	1250	0.500
PPDDT	10.0	1250	0.500
MEXCLR	10.0	3000	1.20

Control spike solutions must be prepared from separate stock solutions as those used for calibration standards. Control spike solutions require concentration verification before use and weekly during continued usage.

B. INSTRUMENT CALIBRATION

1. INITIAL INSTRUMENT CALIBRATION

a. Initial calibration for target pesticide compounds requires the analysis of a solvent blank and five calibration standards bracketing the certified reporting range. The nominal pesticide standard concentrations analyzed during initial calibration are at 0, 5.00, 37.5, 75.0, 150, and 275-ng/mL.

b. The responses for the five standard levels are plotted versus concentration of each compound and the linear regression equation is calculated. This linear regression equation creates an external standard method for quantitation of the target analytes in environmental samples.

c. Following each initial calibration, a calibration check standard (CCS) must be analyzed. The CCS results calculated from the linear regression equation generated from the initial calibration curve must be within +/-30% of the true value.

d. If samples are analyzed on the same day as an initial calibration is performed, the highest standard concentration is analyzed again after sample analyses are completed. The response for each compound must agree within 25% of the response for the same standard concentration in the initial calibration curve.

2. DAILY INSTRUMENT CALIBRATION

a. Calibration standards are analyzed each day to verify that instrument response has not changed from previous calibration.

b. Before sample analysis each day, the highest concentration standard is analyzed. The response must fall within 25% of the response for the same standard concentration in the current acceptable initial calibration curve. After seven daily calibrations, analyte responses for the daily standard must agree within two standard deviations of the mean response

determined from the current initial calibration and seven current initial calibration and seven daily calibrations. If the response fails this check, the daily standard is reanalyzed. If the response from the reanalysis does not meet the acceptable criteria, then initial calibration is repeated before samples are analyzed.

c. After sample analyses are completed each day, the highest concentration standard is reanalyzed. If the response is not within the acceptable range, the daily standard is reanalyzed. If the response from the second analysis is not acceptable, the system is considered to have failed calibration. In this case, initial calibration is performed and all samples analyzed since the last acceptable calibration are reanalyzed.

C. ANALYSIS OF CALIBRATION DATA

Initial calibration acceptability is based on:

1) the baseline instrumental detector signal (blank)
2) the linearity of each analyte over the calibration range
3) accurate quantitation of an external standard (CCS).

Once analysis of a solvent blank exhibits acceptable instrument signal to noise ratio (baseline), the five point initial calibration curve is analyzed. The response vs. concentration data for each analyte is plotted and the resulting linear regression data is evaluated. If the linear regression fit coefficient for at least 67% of the target analytes is 0.995 or greater, the initial calibration shows acceptable linearity.

Once linearity is acceptable, the CCS standard is quantitated using the external standard linear regression equations. If the calculated CCS values are within ±30% of the actual concentration, the initial calibration is considered acceptable and sample analysis may proceed.

V. CERTIFICATION TESTING

Certification samples are spiked then prepared and analyzed through this entire procedure to determine reporting limits for each target analyte. For pesticides in water samples, the nominal target reporting limit (TRL) is 0.006 ug/L. Spikes are prepared at 0, 0.5, 1, 2, 5 10, and 20 times the TRL. Certification spikes are prepared according to Table 4.

One-liter aliquots of standard water are spiked as outlined in Tables 4 and 5 and then extracted and analyzed according to this method. Target versus found concentration data are entered into the IRDMS IRPQAP program for certified reporting limit calculation.

TABLE 4. PESTICIDE CERTIFICATION SPIKE PREPARATION AND NOMINAL CONCENTRATIONS

Composite Spike Solution	Spike Solution Concentration (ug/mL)	Volume Spiked (mL)	Certification Concentration (ug/L)
CSS1	1.25	0.240	0.300
CSS2	0.100	1.00	0.100
CSS2	0.100	0.500	0.0500
CSS2	0.100	0.250	0.0250
CSS3	0.0100	1.00	0.0100
CSS3	0.0100	0.600	0.00600
Blank	0.00	0.500	0.00

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE. Sampling procedures will be performed according to the Sampling Design Plan, Site Specific Quality Assurance Plans, and the USATHAMA QA Program, January 1990.

B. SAMPLE HANDLING. Samples must be received in the laboratory as soon as possible after field sampling. Samples received at the laboratory are checked in by the designated sample custodian.

C. SAMPLE HOLDING TIMES. The holding time is 7 days from the date sampled until the sample is solvent-extracted. After extraction, sample extracts must be analyzed within 40 days.

D. SPIKE SOLUTION VERIFICATION. The control and surrogate spike solutions are verified by GC/ECD every 7 days during use. Verification acceptability is determined according to the USATHAMA QA Program, January 1990.

VII. PROCEDURE

A. GLASSWARE CLEANING

1. Wash glassware with an appropriate brush in hot, soapy water. Use a micro-cleaning solution such as Alconox, or an equivalent detergent.

2. Rinse the washed glassware three times with hot water followed by three rinses with deionized water.

3. Rinse the glassware well with reagent grade acetone; cover the open ends with aluminum foil and store as appropriate. (If glassware is to be used immediately after washing, use high-purity acetone rather than reagent grade.) Immediately prior to use all glassware is triple rinsed with high-purity methylene chloride.

4. Prior to using stored glassware, remove the aluminum foil from the glassware, and rinse all surfaces three times with high-purity acetone followed by rinsing three times with high-purity methylene chloride.

B. SEPARATIONS

The initial separation involves a solvent partition of the target analytes from the water into the methylene chloride extraction solvent. Chromatographic separation is utilized in the florisil cleanup. The florisil adsorbent retains more polar compounds which may interfere with analyte detection and quantitation by GC/ECD. Selective compound affinity is the basis for analyte separation in the fused-silica capillary column (fscc). The stationary phase in the fscc provides analyte resolution and unique retention times for compound identification and confirmation.

C. CHEMICAL REACTIONS

There are no chemical reactions occurring in the performance of this method.

D. SAMPLE EXTRACTION, CONCENTRATION, AND CLEANUP

1. Measure each 1-L sample aliquot into separate graduated cylinders. Transfer the sample into a 2-L separatory funnel. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required.

2. Additionally, set up 4 separatory funnels for control samples with each sample lot. Add 1 L of ASTM Type II water to each. One of the QC samples serves as the method blank. The other three QC samples are spiked with the control analytes for accuracy and precision monitoring. Section IX describes control sample requirements.

3. Using a syringe or a volumetric pipet, add 1.0 mL of the 0.200 ug/mL surrogate solution to the method blank, control samples, and all environmental water samples. Allow spiked samples to equilibrate for 1 hr.

4. Add 60 mL of methylene chloride to each separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation. The

optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation or other physical means. Drain the methylene chloride into a 250-mL Erlenmeyer flask.

5. Add a second 60-mL volume of methylene chloride to each separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

6. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Pour the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the column with two additional 20- to 30-mL portions of methylene chloride to complete the quantitative transfer.

7. Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60° - 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the concentration in 15 to 30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

8. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip; and reattach the Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

9. Remove the Snyder column; using 1 to 2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Place the concentrator tube in a heated bath (30 to 35°C) and evaporate the solvent to near 2-mL by blowing a gentle stream of clean, dry nitrogen onto the solvent. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

10. Attach a vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 1 and 5 pounds of vacuum. Place one Florisil cartridge into the vacuum manifold for each sample extract.

11. Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge in the vacuum manifold, pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

12. After the cartridges in the manifold are washed, the vacuum is released, and a rack containing labeled culture tubes is placed inside the manifold. Vacuum to the manifold is restored, and the extract from each sample, blank, or control spike is transferred to the top frit of the appropriate Florisil cartridge.

13. The pesticides/Aroclors in the extract concentrates are then eluted through the column with 9 mL of hexane/acetone (90:10) and are collected into the culture tubes held in the rack inside the vacuum manifold.

14. Concentrate the extract to 1.0-mL using nitrogen blowdown. The final volume is measured with a syringe, volumetric pipet, or calibrated concentrator tube.

E. INSTRUMENTAL ANALYSIS

Instrumental analysis is performed by injecting 5 uL of the blank, standards, controls, and samples into the GC. The instrument parameters, analytical conditions, and standard preparation and sample preparation described within this method allow for separation, identification, and quantitation of each target compound.

Run sequence has been defined as the following:

1. Non-target list pesticide as the following:
2. Toxaphene and aroclor 1016/1260 standard
3. Hexane blank
4. Calibration standards 1-5
5. External Check
6. 8 samples, blanks, qc
7. Calibration std. #5
8. 10 samples, blanks qc
9. Calibration std #5

Calibration criteria applies only to the quantitation column, DB608. This criteria will only apply to the confirmation channel when values are taken from the confirmation channel.

F. CONFIRMATION ANALYSIS

The gas chromatograph is equipped with a dual-column system. A single injection volume is split immediately after the injection port into two fscc allowing for simultaneous analyte identification, quantitation, and confirmation. Evaluation of the calibration acceptability will be performed on both columns and analyte quantitation may be performed from either column.

VIII. CALCULATIONS

A. INITIAL CALIBRATION

The initial calibration linear regression equation determined for each analyte is used to calculate sample concentrations. The instrument response is plotted on the ordinate and the concentration on the abscissa. The regression equation for each analyte is then calculated as:

$y = mx + b$ where: y = response (area)
m = slope of the line
x = concentration (ug/mL)
b = intercept

B. SAMPLE QUANTITATION

Analyte concentration is determined by translating the above regression equation to:

$A = (y - b)/m$ where: A = calculated amount of material in the sample extract, within the calibration range (ug/mL)

then $\frac{(A)\ (\text{extract final volume (1 mL)})}{\text{sample volume (L)}}$ = Sample Concentration (ug/L)

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

Daily control requirements include extraction and analysis of a method blank and three standard matrix spikes. Each analytical lot contains the method blank to check for background contamination and three matrix spikes to monitor method accuracy and precision through percent recoveries.

The method blank contains the surrogate compound at 0.200 ug/L. The method blank should not contain any confirmed analyte of interest above the CRL.

The control spike solutions are prepared in Sections IV.A.7 and IV.A.8. One-liter aliquots of standard water are spiked according to Table 6. Percent recovery results for each analyte are determined by quantitation of the found amount of each analyte from the current acceptable initial calibration. Control results

are to be calculated and plotted on control charts to monitor method accuracy and precision. Control charting is conducted according to the USATHAMA QA plan using computer software provided by USATHAMA.

The control spiking solution concentration must be verified before use and weekly during use against working calibration standards. Dilute the spiking solution in hexane and analyze using a GC/ECD. The found amount of each control analyte is calculated using the current acceptable initial calibration curve. Recovery must be above the lower warning limit on the single-day XBAR control chart for each analyte.

TABLE 6. PREPARATION OF SAMPLE LOT CONTROL SPIKES

Daily Control Spike Sample	Volume of Control Spiking Solution Added (mL)	Volume of 0.200 ug/mL Surrogate Added (mL)
Blank	0.00	1.00
Low Spike	1.00 (from IV.A.7)	1.00
High Spike	1.00 (from IV.A.8)	1.00
High Spike Dup	1.00 (from IV.A.8)	1.00

CONCENTRATION OF CONTROL ANALYTES

Compound	Concentration of Blank (ug/L)	Low Spike Concentration (ug/L)	High Spike Concentration (ug/L)
CL4XYL	0.000	0.200	0.200
CL10BP	0.000	0.200	0.200
AENSLF	0.000	0.025	0.250
ALDRN	0.000	0.100	0.250
BENSLF	0.000	0.025	0.500
DLDRN	0.000	0.100	0.500
ENDRN	0.000	0.100	0.500
GCLDAN	0.000	0.100	0.250
HPCL	0.000	0.100	0.250
LIN	0.000	0.100	0.250
MEXCLR	0.000	0.500	1.20
PPDDT	0.000	0.100	0.500

B. CONTROL CHARTS

Control charts will be maintained to monitor variations for each control analyte in precision and accuracy during routine analyses and to detect trends in these variations. The control charting procedure that will be followed is given in Section 7.0 of the USATHAMA QA Program, January 1990. The reports will include:

Single-Day XBAR Control Data and Chart

Single-Day RBAR Control Data and Chart

Three-Day Average XBAR Control Data and Chart

Three-Day Average RBAR Control Data and Chart

X. REFERENCES

1. U.S. Environmental Protection Agency (EPA). 1982. Method 608 -- Test Method for Organochlorine Pesticides and PCBs. In: Compendium of Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA-600/4-82-057.

2. U.S. Environmental Protection Agency (EPA). May, 1990. Statement of Work for Organic Analysis. USEPA Contract Laboratory Program.

3. USATHAMA Quality Assurance Program, January, 1990, USATHAMA PAM 11-41.

XI. DATA

A. ANALYTICAL STANDARD CHARACTERIZATION

B. INITIAL CALIBRATION

C. DAILY CALIBRATION

D. STANDARD CERTIFICATION DATA

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METHOD:

The Determination of Volatile Organic Compounds in Water
by GC/MS

METHOD umØS

Written By:

Steven P. Sanders

Approved By:

Lisa Shanahan

Last Review: 7-2-91

Next Scheduled Review: _____

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The Determination of Volatile Organic Compounds in Water by GC/MS

I. Summary

A. Analytes

This method is applicable for the determination of volatile organics. The following parameters were certified by this method:

1,2-Dichloroethane-D4 (12DCD4)
Toluene-D8 (MEC6D8)
4-Bromofluorobenzene (4BFB)

B. Matrix

This is a purge & trap gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of the compounds identified above in environmental water samples.

C. General Method

An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is complete, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

II. Application

A. Tested Concentration Range

12DCD4	2-55 ug/L
MEC6D8	2-55 ug/L
4BFB	2-55 ug/L

B. Sensitivity

The instrumental response for an absolute quantity of analyte varies with the compound. In a water matrix a concentration of 10 ug/L (50 ng) produces a typical response of 15000, 54000, and 13000 area counts for 12DCD4, MEC6D8, and 4BFB respectively.

C. Reporting Limit

12DCD4	5.0 ug/L
MEC6D8	3.9 ug/L
4BFB	1.9 ug/L

D. Interferences

1. Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

2. Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3. Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105^{o} C oven between analyses. The trap and other parts of the system are also subject to contamination. Therefore, frequent bakeout and purging of the entire system may be required.

E. Analysis Rate

The amount of time for one analysis is approximately 50 minutes for megabore or capillary columns. A typical 24 hour analytical run would be as follows: tuning standard (BFB), daily calibration check standard, method blank/control, and samples for the remainder of the 12-hour time period; the second 12-hour analytical run would be the same as the first 12-hour period where the 24-hour period would end with a successful analysis of a 55 x TRL standard. Occasionally the second 12-hour tuning

standard, daily calibration check standard, and method blank/control are run in duplicate because the instrument will be unattended during that period. The first of the two runs will always be reported unless a laboratory accident (sparge vessel leak, wrong amount of standard spiked, software glitch, etc.) effects the analytical integrity of the first run. This would allow up to 18 samples to be run in a 24-hour day. If an initial calibration needed to be performed, then, 4 additional standards would be analyzed with a corresponding decrease in the number of samples analyzed. The frequency of the MS and MSD is one in 20 samples and therefore not all 24-hour time periods will include these runs.

F. Safety Information

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

III. Apparatus and Chemicals

A. Glassware/Hardware

1. Vial--40-mL capacity, equipped with a screw cap with a hole in the center. Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

2. Septum--Teflon-faced silicone. Detergent wash, rinse with tap and distilled water, and dry at 105°C for 1 hr. before use.

3. Syringes--5-mL, glass hypodermic with Luerlok end.

4. Micro syringes--10-uL, 25-uL, 50-uL, 100-uL, 250-uL, and 1.0-mL 0.006 in. ID needle.

5. Vial--15-mL, crimp-cap, with Teflon cap liner.

6. Balance--Analytical, capable of accurately weighing 0.0001g.

7. 5-mL, 10-mL, 25-mL, 50-mL and 100-mL volumetric flasks - class A, with ground-glass stoppers.

8. Spatula--stainless steel

B. Instrumentation

1. A purge and trap autosampler (Model LSC 2000 and ALS 2016) manufactured by Tekmar Corporation is used to purge the samples. The autosampler has 16 sparge vessels that accept 5-mL samples for purging. The trapping system consists of a 25 cm long 1/8" O.D. stainless tube packed with activated charcoal, silica gel and TENAX. This trap can be rapidly heated to 180°C and desorbed via a six port valve onto the GC analytical column for analysis.

2. A gas chromatograph (Model 3400) manufactured by Varian Instruments is utilized. This gas chromatograph is temperature programmable and can utilize megabore or capillary columns.

3. A DB-624 megabore column (0.53 mm ID, 30 m, 3.0 um film thickness) or a DB-624 capillary column (0.32 mm ID, 30 m, 1.8 um film thickness) may be used (J & W Scientific or equivalent).

4. A glass jet separator is utilized for interfacing into the mass spectrometer when the megabore column is used. If the capillary column is used, a direct connection into the ion source is made.

5. Extrel Model 400 Mass spectrometer--Capable of scanning from 35 to 260 amu every 0.5 seconds or less, utilizing 70 eV (nominal) in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 4 when 50 ng of 4-bromofluorobenzene (BFB) is purged from a 5-mL aliquot of water.

6. Data system--A Digital Equipment PDP11 computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching any GC/MS data file for specific m/z (mass/charge ratio) and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software also allows integrating the abundance in any EICP between specified time or scan number limits.

C. Analytes

	CAS number
12DCD4	17060-07-0
MEC6D8	2037-26-5
4BFB	460-00-4

See Table in Section XI.A. for a complete listing of the compounds which can be determined by this method.

D. Reagents and SARM's

1. PACE utilizes deionized water (DI) which is treated with ultraviolet light using an Organic pure system manufactured by Barnstead, Inc.

2. Trap materials: PACE purchases #3 traps from Tekmar Corporation. These are packed with Tenax, silica gel, and charcoal.

3. Methanol--Purge and Trap grade. Burdick & Jackson.

4. Reagents and SARM's

Standards	Source
1,2-dichloroethane-D4	Supelco, Inc. or
Toluene-D8	equivalent
4-Bromofluorobenzene	

Internal Standards	Source
Bromochloromethane	Supelco, Inc. or
1,4-Difluorobenzene	equivalent
Chlorobenzene-D5	

IV. Calibration

A. Initial Calibration

1. Preparation of Standards

a. Vendor-certified stock standard solutions of internal standards, surrogates, and target compounds are purchased and are diluted to an appropriate level for daily use.

b. Store stock standards at -10°C or colder in septum capped bottles. All stock standards must be replaced each month.

c. All standards prepared for use throughout the laboratory are assigned a code number. The standard code number is entered in the standard notebook with all information regarding the preparation of that standard, i.e., date, analyst, name of each compound and amount used, final volume, and solvent used. All standard containers are labeled with the standard's code, date and analyst's initials.

d. The instrument response obtained for each compound in a newly prepared standard is compared to the response obtained from the previously prepared standard.

e. Surrogate standard spiking solution--Working standard solutions of 12DCD4, MEC6D8, and 4BFB are prepared by diluting the stocks in a. above. A surrogate standard spiking solution is prepared from the stock standard at a concentration of 25-ug/mL in methanol. Store the solution at 4°C in Teflon-sealed glass container with a minimum of headspace. The addition of 8-uL of the 25-ug/mL solution to 5-mL of sample or standard is equivalent to a concentration of 50-ug/L of each surrogate standard. Typically spiking solutions are made up fresh each week or as needed as determined by comparison to the initial calibration data.

F. A working intermediate spiking solution of bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-D5 is prepared by diluting the stock in Section IV.A.1.a. to a final concentration of 25-ug/mL in methanol. Store the solution at -10°C or colder in Teflon-sealed glass containers with a minimum of headspace. The addition of 10-uL of the 25-ug/mL solution to 5-mL of sample or standard is equivalent to a concentration of 50-ug/L of each internal standard. Spiking solutions are made up fresh each week or as needed.

2. Instrument Calibration

a. Using the 25-ug/mL stock standard for surrogates and a 100-ug/mL standard for non-certified targets, prepare

calibration standards. The following table lists the initial calibration levels of certified (surrogates) and non-certified targets:

Surrogates (ug/L)	2	10	20	40	55
Non-certified targets (ug/L)	10	20	50	100	200

b. 10-uL of internal standard (25-ug/mL) is added to each 5-mL calibration standard. Tabulate the area response of the characteristic ion against concentration for each compound and internal standard and calculate response factors (RF) for each compound using the equation provided in Section VIII, Calculations.

A certified calibration check standard, obtained from USEPA or other commercial source, should be analyzed following the initial calibration standards.

The calculated concentration for each analyte must agree within ± 25% of the true concentration. If this external calibration check fails, sample analysis shall be halted and not resumed until the initial calibration is successfully completed.

After the successful analysis of the calibration check standard, the calibration is validated and will be used until a daily calibration fails.

3. Analysis of Calibration Data

a. Calculate response factors (RF) for each standard compound using Equation 1.

Equation 1:

$$RF = \frac{(A_X)(C_{is})}{(A_{is})(C_X)} \quad \text{and} \quad \overline{RF} = \left(\sum_{i=1}^{N} RF \right) / N$$

where:

A_X = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard (ug/L).

C_X = Concentration of the compound to be measured (ug/L)

$\overline{RF}$ = Average response factor

N = Number of calibration levels

This value is used in sample concentration calculations in Section VIII.

B. Daily Calibration

1. Standard Preparation and Analysis

A continuing calibration check standard is analyzed at the beginning of each 12-hour period. This standard contains surrogates at 55-ug/L and non-certified targets at 50-ug/L.

2. Analysis of Calibration Data

Daily calibration is acceptable if 67% of daily the response factors fall within ± 25% of the the average response factors from the initial calibration. If this criteria is not met, a new initial calibration curve must be constructed.

V. Certification Testing

A. For certification sample analyses, a series of water matrix samples were prepared and analyzed. All samples have 10-uL of 25-ug/mL internal standard added.

B. A four point calibration curve was analyzed at the following levels:

	12DCD4	MEC6D8	4BFB
I	0.45 ug/L	0.45 ug/L	0.45 ug/L
II	2.0 ug/L	2.9 ug/L	2.0 ug/L
III	10 ug/L	10 ug/L	10 ug/L
IV	55 ug/L	55 ug/L	55 ug/L

See Table II Section XI for standard preparation description. The standards were analyzed in duplicate and the results was for generating precertification data.

C. The water certification testing was done as follows:

At the start of the certification testing, a 55-ug/L check standard was analyzed by adding 11-uL of 25-ug/mL surrogate stock to 5-mL of reagent water. The response for the compounds must fall within 25 percent of the true value, (68.8 - 41.2 for a 55-ug/L true value). Water certification samples were then prepared as follows:

Sample Concentration	Stock Solution Concentration	Amount of Stock Solution added to 5-mL water
0	NA	0
0.5 ug/L	2.5 ug/mL	1.0 uL
2.0 ug/L	2.5 ug/mL	4.0 uL
10 ug/L	25 ug/mL	20 uL
50 ug/L	25 ug/mL	10 uL

These samples were prepared and analyzed in duplicate. After completion of the certification samples, a 55-ug/L check standard was again analyzed. The concentration of this check standard must also fall within ± 25 percent of the true value. For stock solution preparation see Table I.

VI. Sample Handling Storage

A. Sampling Procedure

1. All water samples must be iced or refrigerated from the time of collection until analysis. If the sample contains residual chlorine, add sodium thiosulfate preservative (10mg/40mL is sufficient for up to 5 ppm Cl_2). EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine. Field test kits can be used for this purpose.

2. Grab samples must be collected in glass containers having a total volume of at least 25-mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

3. Experimental evidence indicates that some aromatic compounds, notable benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions (particularly samples with high bacteria populations). Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500-mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1+1 HCl while stirring vigorously. Check pH with narrow range (1.4 to 2.8) pH paper.

B. Containers

Samples are collected in amber glass bottles with Teflon-lined lids. Sample containers must be cleaned following the procedure presented below:

Amber-Glass 40-mL Vials

1. Wash bottles in phosphate-free soap.
2. Rinse 3 times with tap water.
3. 3 times with organic-free DI.
4. Bake at 105°C for 4 hours.
5. Allow to cool.
6. Cap with clean caps with Teflon liners.

Bottle Caps

1. Wash with phosphate-free detergent.
2. Rinse with tap water.
3. Rinse with DI water.
4. Dry at 105°C

Teflon Liners (avoid contact with fingers)

1. Wash with phosphate-free detergent
2. Rinse 3 times with tap water.
3. Rinse 3 times with DI.
4. Heat to 105°C for 2 hours.

5. Allow to cool.
6. Use to cap cleaned bottles.

C. Storage Conditions

Store samples at 4°C until analysis

D. Holding time limits

All samples must be analyzed within 14 days of collection

E. Solution verification

Solutions will be validated against working standards before their initial use and within seven days before subsequent usage. The recovery of the solution must be greater than the lower warning limit on the X control chart for each control analyte.

VII. Procedures

A. Separations

Not applicable to this procedure

B. Chemical reactions

Not applicable to this procedure.

C. Instrumental analysis

1. Daily GC/MS Performance Tests

a. At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for 4-bromofluorobenzene. The performance test must be passed before any samples, blanks, or standards are analyzed.

b. These performance tests require the following instrumental parameters:

Electron Energy: 70 eV (nominal)
Mass Range: 35 to 260 amu
Scan Time: To give at least 5 scans per peak.

c. At the beginning of each day, add 2-uL of a 25-ug/mL BFB solution to 5.0-mL of reagent water and analyze. Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 4 are achieved. If all the criteria are not achieved, the analyst must re-tune the mass spectrometer and repeat the test until all criteria are achieved.

2. Sample Purging and Gas Chromatography

a. Table 3 summarizes the recommended operating conditions for the gas chromatograph.

b. After achieving the key m/z abundance criteria in Table 4, calibrate the system daily as described in Section IV.

c. Adjust the purge gas (helium) flow rate to 35-40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge. Open the syringe valve located on the purging device sample introduction needle.

d. Allow the sample to come to ambient temperature prior to introducing it into the syringe. Remove the plunger from a 5-mL syringe. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. If a lesser volume is being analyzed an appropriate dilution can be in the syringe by injecting into 5-mL of reagent water.

Replace the syringe plunger and compress the sample. Vent any residual air while adjusting the sample volume to 5.0-mL. Add 10-uL of a 25-ug/mL internal standard spiking solution and 8-uL of a 25-ug/mL surrogate spiking solution through the valve bore.

e. Attach the syringe assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

f. The following are typical Tekmar purge and trap conditions:

Stand by: 35°C
Purge: 11.0 minutes
Desorb Preheat: 175°C
Desorb 1.5-3.0 minutes at 180°C
Bake 12-18 minutes at 225°C
Moisture Control Module: Heat to 90°C
Moisture Control Module: Cooldown to 5-10°C
Capillary Interface: ⁻150° to ⁻180°C
Tekmar lines: 100-140°C
Tekmar Valve: 100-140°C

3. Qualitative Identification

a. Obtain EICPs for the primary m/z and at least two secondary masses for each parameter of interest. The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

b. Structural isomers that have very similar mass spectra and less than 30 seconds difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights.

Otherwise, structural isomers are identified as isomeric pairs.

VIII. Calculations

A. Calculate the concentration in the sample using the following equations:

Equation 1:

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)} \quad \text{and} \quad \overline{RF} = \left(\sum_{i=1}^{N} RF \right) /N$$

Equation 2:

$$\text{Concentration ug/L} = \frac{(A_x)(C_{is})}{(A_{is})(RF)}$$

where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard (ug/L).

C_x = Concentration of the compound to be measured (ug/L).

RF = Response factor as determined from the initial calibration.

$\overline{RF}$ = Average response factor

N = Number of calibration levels

IX. Daily Quality Control

A. Control Samples

1. Each day the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

   a. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control.

   b. The laboratory spikes all samples with surrogate standards to monitor continuing laboratory performance.

   c. The laboratory maintains performance records to document the quality of data that is generated.

2. When more than 10% of the parameters tested fall outside of the +/-25% acceptance range, or any of the daily calibration standard parameters fail to meet the +/-25% of the average response factor determined from initial calibration or less than 2 standard deviations criteria, the analyst must proceed according to subsection a. or b.

   a. Locate and correct the source of the problem and repeat the test for all parameters of interest.

   b. Repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

3. The laboratory must, on an ongoing basis, surrogate spike 100% of the samples from each sample site monitored to assess accuracy. The spike level should be performed at approximately 10 CRL.

   a. Each lot of samples will have 1 standard matrix blank.

   b. Calculate the percent recovery (P) of surrogates in all samples using the equation $P = (A/T) \times 100\%$ where A is the measured concentration in the spiked sample and T is the true value of the spike.

B. Control Charts

As part of the QC program for this project three-point moving average control charts will be generated using the software provided by USATHAMA.

X. References

1. United States Environmental Protection Agency
Contract Laboratory Program Statement of Work, 1986 EMSL

2. "Methods for Organic Chemical analysis of Municipal Industrial Wastewater" - Method 624 - Purgeables by GC/MS
USEPA 40 CFR Part 136 Fed. Reg. Oct. 26, 1984

3. "Methods for the Determination of Organic Compounds in Water by Purge and Trap GC/MS"
USEPA Sep. 1986 Cincinnati, Ohio

XI. Data

A. Compounds which can be determined by this method:

	Name	CAS Number
1.	Chloromethane	74-87-3
2.	Bromomethane	74-83-9
3.	Vinyl Chloride	75-01-4
4.	Chloroethane	75-00-3
5.	Methylene Chloride	75-09-2
6.	1,1-Dichloroethene	75-35-4
7.	1,1-Dichloroethane	75-34-3
8.	Chloroform	67-66-3
9.	1,2-Dichloroethane	107-06-2
10.	1,1,1-Trichloroethane	71-55-6
11.	Carbon Tetrachloride	56-23-5
12.	Bromodichloromethane	75-27-4
13.	1,2-Dichloropropane	78-87-5
14.	cis-1,3-Dichloropropene	10061-01-5
15.	Trichloroethene	79-01-6
16.	Dibromochloromethane	124-48-1
17.	1,1,2-Trichloroethane	79-00-5
18.	Benzene	71-43-2
19.	trans-1,3-Dichloropropene	10061-02-6
20.	Bromoform	75-25-2

21.	Tetrachloroethene	127-18-4
22.	1,1,2,2-Tetrachloroethane	79-34-5
23.	Toluene	108-88-3
24.	Chlorobenzene	108-90-7
25.	Ethyl Benzene	100-41-4
26.	trans-1,2-Dichloroethene	544-59-0
37.	Acetone	67-64-1
28.	Carbon Disulfide	75-15-0
29.	2-Butanone	78-93-3
30.	2-Hexanone	591-78-6
31.	4-Methyl-2-pentanone	108-10-1
32.	Styrene	100-42-5
33.	Xylenes (total)	1330-20-7

Compounds on this list are identified by retention times (relative to appropriate internal standards) and comparison to fragmentation patterns specific to PACE Laboratories, Inc. instrumentation. Quatitation is accomplished by developing mean response factors relative to appropriate internal standards. Unknown peaks are tentatively identified by comparing the fragmentation pattern of the unknown to 44,000 compounds in the NIST/EPA library. Quantitation is estimated by assuming the response factor for the unknown compound is the same as the response factor of the nearest internal standard. This data will be reported into the data base.

B. Off the shelf Analytical Reference Materials Characterization

Toluene-D8, 4-Bromofluorobenzene, and 1,2-Dichloroethane-D4 were provided by Supelco, Inc.

C. Initial Calibration

. Response versus concentration data

1,2-Dichloroethane-D4

Concentration	Response	
0	0	0
0.45	0.2	0.1
2	1.7	1.8
10	9.6	9.6
55	87.5	58.8

Toluene-D8

Concentration	Response	
0	0	0
0.45	0.4	0
2	1.1	0.9
10	21.1	13.2
55	67.3	53.0

4-bromofluorobenzene

Concentration	Response	
0	0	0
0.45	0.7	0.5
2	1.2	1.2
10	17.1	10.3
55	49.0	53.8

2. Response versus concentration graphs

The graphs of response vs. concentration for each analyte are provided on the following pages.

D. Daily Calibration

1. Response

June 25, 1987 08:32:51

55 ug/l standard

1,2-Dichloroethane-D4	52.1*
Toluene-D8	66.1
4-bromofluorobenzene	50.0

June 25, 1987 03:12:07

55 ug/l standard

1,2-Dichloroethane-D4	62.0
Toluene-D8	55.6
4-bromofluorobenzene	63.4

2. Daily Calibration limits

To be considered in control the analysis of the daily calibration standard should be within the limits below.

1,2-Dichloroethane-D4	(54.9-91.4)
Toluene-D8	(45.1-75.2)
4-bromofluorobenzene	(38.6-64.3)

* - The criteria used to review this data was 25 percent from the true value not 25 percent from the mean value.

E. Standard Certification Samples

1. Tabulation and graph of found versus target concentration.

2. LOF and ZI tests.

3. Calculations

4. Chromatograms

TABLE 1

	12DCD4	MEC6D8	4BFB
Primary Stock Solution Concentrations	0.2573 g/10 ml	0.2592 g/10 ml	0.3243 g/10 ml
Combined Working Spike Solution Preparation from Primary Stocks	10 ul/10 ml MeOH	10 ul/10 ml MeOH	8 ul/10 ml MeOH
Final Concentrations of Working Spike Solution	25 ug/ml	25 ug/ml	25 ug/ml
1:10 Dilution of working Spike Solution (1 ml/10 ml MeOH)	2.5 ug/ml	2.5 ug/ml	2.5 ug/ml

TABLE 2

	12DCD4	MEC6D8	4BFB
Primary Stock Solution Concentrations	0.2573 g/10 ml	0.2592 g/10 ml	0.3243 g/10 ml
Combined Working Spike Solution Preparation from Primary Stocks	10 ul/10 ml MeOH	10 ul/10 ml MeOH	8 ul/10 ml MeOH
Final Concentrations of Working Spike Solution	25 ug/ml	25 ug/ml	25 ug/ml
Level IV Standard Preparation from Working Standard (11 ul/5 ml H_2O)	55 ug/L	55 ug/L	55 ug/L
1:10 Dilution of working Spike Solution (1 ml/10 ml MeOH)	2.5 ug/ml	2.5 ug/ml	2.5 ug/ml
Level I Standard Preparation from 1:10 Dilution of Working Standard (0.9 ul/5 ml H_2O)	0.45 ug/L	0.45 ug/L	0.45 ug/L
Level II Standard Preparation from 1:10 Dilution of Working Standard (4.0 ul/5 ml H_2O)	2.0 ug/L	2.0 ug/L	2.0 ug/L
Level III Standard Preparation from 1:10 Dilution of Working Standard (20 ul/5 ml H_2O)	10 ug/L	10 ug/L	10 ug/L

Table 3
Column Conditions

DB-624, 30 meter 0.32 mm I.D. capillary column or equivalent

Helium gas at 3 mL/min

Temperature program: -10°C for 1 min, 10°C/min to 100°C

6°C/min to 140°C, 20°C/min to 170-190°C, hold for 4-10 min.

TABLE 4.--BFB KEY M/Z ABUNDANCE CRITERIA

Mass	a/z Abundance Criteria
50	8.0 - 40.0% of mass 95.
75	30.0 - 66.0% of mass 95.
95	Base Peak, 100% Relative Abundance.
96	5.0 - 9.0% of mass 95.
173	< 2% of mass 174.
174	50.0 - 120.0% of mass 95.
175	4.0 - 9.0% of mass 174.
176	93.0 - 101.0% of mass 174.
177	5.0 - 9.0% of mass 176.

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Table 5.-- SURROGATE AND INTERNAL STANDARDS

Compound	Primary m/z	Secondary masses
Bromochloromethane	128	49, 130
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-D5	117	82, 119
1,2-Dichloroethane-D4	65	51, 67
Toluene-D8	98	100, 42
4-bromofluorobenzene	95	174, 176

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STANDARD OPERATING PROCEDURE

The Determination of Extractable Base/Neutral and Acid Compounds in Water by Gas Chromatography/Mass Spectrometry (UM06)

SOP NUMBER

AUTHOR Gabriel J. LeBrun

EFFECTIVE DATE June 27, 1991

SUPERSEDES

APPROVAL

Gabriel J. LeBrun 7-8-91
Section Supervisor Date

Lissa Shanahan 7-8-91
Organic Laboratory Manager Date

William H. Scott 7-8-91
Quality Assurance Officer Date

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I. SUMMARY

A. ANALYTES

1. This method is applicable for the determination of extractable organics. The parameters certified by this method are given in Table I.

B. MATRIX

1. This method involves the determination of target analyte list compounds in environmental water samples. The target analyte list is found in Table II.

C. GENERAL METHOD

1. A measured volume of sample, nominally one liter, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2, using a separatory funnel. A portion of this extract is concentrated five fold and is screened by GC/FID or GC/MS. If peaks are present the extract is diluted to reduce the major peaks to the mid portion of the calibration range. If no peaks are present, the extracts are concentrated separately to a volume of 1 ml, combined, and analyzed by capillary column gas chromatography/mass spectrometry.

II. APPLICATION

A. TESTED CONCENTRATION RANGE

1. The tested concentration range for certified analytes is given in Table III. The instrument calibration range is from 5.0-ug/mL to 160-ug/mL.

B. SENSITIVITY

1. The instrumental response for an absolute quantity of analyte varies with the compound. The response calculated at the certified reporting limit for each compound can be found in Table III.

C. CERTIFIED REPORTING LIMIT

The certified reporting limit (CRL) and upper certified reporting limit (UCRL) as determined by method certification are given in Table III.

D. INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles.

All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

E. ANALYSIS RATE

The analysis rate shall not exceed 16 samples (including lot control samples) per 24 hour period.

F. SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

III. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Separatory funnels - 2000-mL, with teflon stopcock.

2. Drying columns - 19-mm chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts).

3. Concentrator tubes - Kuderna-Danish, 10-mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

4. Evaporation flasks - Kuderna-Danish, 500-mL. Attach to concentrator tube with springs.

5. Snyder columns - Kuderna-Danish, Three-ball macro and Three-ball micro.

6. Vials - Disposable glass, 2-mL capacity with Teflon-lined screw cap, or crimp-top caps.

7. Water bath - Heated with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

8. Balance - Analytical, capable of accurately weighing 0.0001-g.

9. Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C.

B. INSTRUMENTATION

1. Hewlett Packard Model 5995 Gas Chromatograph - Mass Spectrometer and a Hewlett Packard Auto Sampler Model 7673. Computer 7936 Hewlett Packard with 7958 HP additional memory, 7974 Magnetic Type Storage device and a Rugged Writer printer (or equivalent).

2. Column - 30-m x (0.25-0.32)mm ID with film thickness of 0.25 - micron bonded-phase silicone-coated fused-silica capillary column (fscc). (J & W Scientific DB-5 or equivalent).

3. Operating parameters:

Initial column temperature: 40-45°C for 0-4 minutes
Temperature range rate: 7-10°C/min
Final column temperature: 290-320°C
Injector temperature: 240-290°C

Transfer line temperature: 240-320°C
Source temperature: 200-250°C
Injector: Grob-type, splitless
Sample injection volume: 1-uL
Carrier gas: Helium at 2 mL/min

a. The following initial parameters are required for all performance tests and for all sample analyses:

Electron Energy:	70 volts (nominal)
Mass Range:	35 to 500 amu
Scan Time:	$\leq$ 1 second/scan

4. Retention Time and Retention Time Windows

a. The internal standards are added to all calibration standards and sample extracts just prior to analysis by GC/MS. The selected internal standards permit most of the semivolatile target compounds to have a relative retention time from 0.8 to 1.20 minutes to its associated internal standard. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within $\pm$ 0.06 units of the RRT of the standard component. If coelution of interferring components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

5. GC/FID screening instrument complete with a temperature programmable gas chromatograph and splitless injection port for capillary column and a flame ionization detector.

C. ANALYTES

1. Chemical Abstract Service Registry numbers and basic physical properties for the target analytes are given in Table IV.

D. REAGENTS AND SARMS

1. Reagents and standard materials for the target analytes identified in Table IV were commercially obtained. Concentration and preparation information differ depending on the compound. This information is given in Section IV.A.1.

2. Sodium hydroxide solution (10 N) - Dissolve 40 g NaOH in reagent water and dilute to 100 ml. J.T. Baker or equivalent.

3. Sulfuric acid solution (1+1) - Slowly add 50 ml of H_2SO_4 (sp gr. 1.84) to 50 ml of reagent water. Mallinckrodt or equivalent.

4. Acetone, methanol, methylene chloride - Pesticide quality. Burdick & Jackson or equivalent.

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Standard Solution Preparation

Prepare primary mix stock solution of the standard compounds in methylene chloride at a concentration of 160-ug/mL as given in Table V. Prepare in methylene chloride standards at 5, 20, 50, 80, 120 and 160-ug/mL. The working standards are serially diluted from the 160-ug/mL stock standard according to the scheme in Table VI, and placed in limited volume vials.

a. Store all stock solutions at 4°C (±2°C) in Teflon-Sealed Containers. The working calibration solutions must be replaced after 6 months, or sooner, if comparison with quality control check samples indicate a problem.

b. All standards prepared for use throughout the laboratory are assigned a code number. The standard code number is entered in the standard notebook with all information regarding the preparation of that standard, i.e., date, analyst, name of each compound, amount used, and final volume. All standard containers are labeled with the standard's code, date and analyst's initials.

c. The instrument response obtained for each compound in a newly prepared standard is compared to the response obtained from the previously prepared standard. Corrective actions such as checking calculations, remaking the standard, and instrument maintenance will be employed if response is not comparable.

2. Instrument Calibration

a. The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as FC-43 or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution decafluorotriphenylphosphine (DFTPP).

b. Prior to the analysis of any samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria in Table VII for DFTPP.

c. The analysis of the DFTPP solution is performed by injecting 1-uL of a 50-ug/mL solution of DFTPP and/or by adding 50-ug/mL of DFTPP to the mid-level calibration standard.

d. The selected internal standards permit most components of interest in a chromatogram to have relative retention times of 0.80 to 1.20. The width of the retention time window used to make identifications is the mean relative retention time window from certification ± three standard deviations. Daily adjustments to the retention time window will be made based on the relative retention time of the daily calibration standard ± three standard deviations as determined during certification. The base peak ion from the specific internal standard is used as the primary ion for quantification. If interferences are noted, a secondary ion is used according to Table VIII.

e. Analyze 1-uL of each standard and blank by direct injection into the fused silica capillary column. GC/MS operating conditions to be used are given in Section B.

f. Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be inspected for malfunctions and corrections made as required. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to +100%), from the latest daily (12 hour) calibration standard, the mass spectrometric system must be inspected for malfunction, corrections made as appropriate, and explanation given for affected samples.

g. The mean response factor (RRF) is calculated for each analyte of interest from the initial calibration standards at 20, 50, 80, 120 and 160-ug/mL. The relative standard deviation for at least 67% of the target compounds must be <35%.

h. A certified calibration check standard, obtained from USEPA or other commercial source, should be analyzed after the initial calibration. The check standard should be near the high end of the calibration and contain as many of the target analytes as possible. Calculated values within 25% of the true value are considered acceptable.

3. ANALYSIS OF CALIBRATION DATA

1. Initial Calibrations are verified by utilizing USEPA traceable check standards, SARMS, or second-vendor sources. An initial calibration is acceptable if the relative response factor (RRF) for at least 67% of the analytes is less than 35% relative standard deviation (RSD) over the 5-point calibration curve.

B. DAILY CALIBRATION

1. Preparation of Standards

See Section IV.A.1.

2. Insturment Calibration

a. The GC/MS system must be hardware tuned by injection of DFTPP to meet the criterion listed in Table VII.

b. The initial calibration curve as established in Section IV.A.2., is utilized to determine continuing calibration acceptability. The initial calibration curve RRF for each target analyte must be verified on each working day by the measurement of a continuing calibration standard at 50-ug/mL for each target analyte.

C. ANALYSIS OF CALIBRATION DATA

1. The daily calibration is considered acceptable if the RRF for at least 67% of the analytes is within 25% of the average RRF from the current acceptable initial calibration curve. If the daily standard fails, it is reanalyzed. If daily calibration fails twice, initial calibration must be performed prior to continuing sample analysis. At the end of each day of sample analysis the daily standard must be analyzed and meet the RRF criteria. If the standard fails it is reanalyzed. If the end of day standard fails twice, initial calibration must be performed and all samples analyzed since the last acceptable calibration must be reanalyzed.

2. A continuing calibration standard will be run each 12 hours (after the DFTPP tune). In the event the continuing calibration standard run in the middle of a 24-hour run fails, yet the end of the day standard meets the acceptance criteria, the samples will be reviewed for problems and either reanalyzed or submitted with technical justification.

V. CERTIFICATION TESTING

A. PREPARATION OF STANDARD MATRIX CERTIFICATION SAMPLES

1. Preparation of Sample Spike Solution

   a. Prepare primary stock solutions of the sample spike compounds in methanol. Prepare a combined working spike solution in methanol from the primary stock solutions at concentrations of 100 ug/mL for base/neutral compounds and 250 ug/mL for acid compounds. Prepare a 1:25 dilution of this solution in methanol with a final concentration of 4 ug/mL for base/neutral compounds and 10 ug/mL for acid compound. (See Table V.A.1) Store all spike solutions at 4°C (+/-2°C) in Teflon-sealed containers. The solutions must be replaced after 6 months, or sooner if comparison with quality control check samples indicate a problem.

2. Prepareation of Certification Samples

   a. A specified volume of spike solution is added to 1L ASTM Type II water to yield the sample concentrations. (See Table V.A. 2)

   b. Certification samples are prepared in duplicate along with blanks.

TABLE V.A.1

	NBD5	PHEND6	TRPD	2FBP	2FP	146TBP
Primary stock solution conc.	0.2668 g/10 mL	0.2145 g/10 mL	0.0687 g/10 mL	0.2040 g/10 mL	0.3280 g/10 mL	0.3179 g/10 mL
Combined working spike solution preparation from primary stocks	0.093 mL/25mL	0.291 mL/25mL	0.364 mL/25mL	0.122 mL/25mL	0.191 mL/25mL	0.196 mL/25mL
Final conc. of combined working spike	100ug/mL	250ug/mL	100ug/mL	100ug/mL	250ug/mL	250ug/mL
Conc. of a 1:25 dilution of working spike	4ug/mL	10ug/mL	4ug/mL	4ug/mL	10ug/mL	10ug/mL

TABLE V.A.2

	NBD5	PHEND6	TRPD	2FBP	2FP	146TBP
Level I- 250 ug (1:25) spike dilution	1.0ug/L	2.5ug/L	1.0ug/L	1.0ug/L	2.5ug/L	2.5ug/L
Level II- 1mL (1:25) spike dilution	4ug/L	10ug/L	4ug/L	4ug/L	10ug/L	10ug/L
Level III- 200uL (1:25) spike dilution	20ug/L	50ug/L	20ug/L	20ug/L	50ug/L	50ug/L
Level IV- 1mL (1:25) spike dilution	100ug/L	250ug/L	100ug/L	100ug/L	250ug/L	250ug/L

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE

Environmental water samples are collected according to the Sampling Design Plan, Site Specific Quality Assurance Plan, and the USATHAMA QA Program, January 1990.

B. CONTAINERS

Samples are collected in amber glass bottles prepared according to the USATHAMA QA program, January 1990, Appendix F.

C. STORAGE CONDITIONS

All samples and extracts are stored in locked refrigerators at 4°C.

D. HOLDING TIME LIMITS

Holding times are seven days from date of collection for sample extraction, and 40 days from extraction for sample analysis.

E. SOLUTION VERIFICATION

All calibration standard solutions are double-checked to the previous preparation of that solution. There should be no more than 25% difference between each preparation as determined from GC/MS analysis.

VII. PROCEDURE

A. SEPARATIONS

1. Water samples are pH adjusted and extracted 3 times with methylene chloride using a separatory funnel technique. Extracts are concentrated to a volume of 1-mL. This process is performed once at a base pH and once at an acid pH.

2. Using a 1-liter graduated cylinder, measure out a 1-liter aliquot of water sample and place it into a 2-liter separatory funnel. Pipet appropriate amount of spike solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to pH 11 with 10 N sodium hydroxide.

3. Add 60-mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

4. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure , combining the extracts in an Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

5. Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1+1). Serially extract three times with 60-ml aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extract as the acid fraction.

6. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

7. Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10-cm of anhydrous sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30-mL of methylene chloride to complete the quantitative transfer.

8. Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1-mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80^{o} to 90^{o}) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the verical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1-mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-mL of methylene chloride.

9. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride. Further concentration is performed using nitrogen blowdown.
10. When the liquid reaches an apparent volume of less than 1.0-mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 min. Adjust the final volume to 1.0-mL.

11. Internal Standards - 1,4-dichlorobenzene-D4, napthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12. A 20-uL portion of this solution should be added to each 1-mL aliquot of sample extract prior to analysis. This will give a concentration of 40-ug/mL of each constituent.

12. Transfer the concentrated extract to a clean screw-cap or crimp-top vial. Seal the vial with a Teflon-lined lid. Label with the sample number and store in the dark at less than 0°C.

B. CHEMICAL REACTIONS

Not applicable to this procedure.

C. INSTRUMENTAL ANALYSIS

1. Analyze 1-uL of each sample extract by direct injection onto the GC/MS system.

VIII. CALCULATIONS

A. Calculate response factors (RF) for each standard compound using Equation 1.

$$\text{Equation 1: } RF = \frac{(A_x) \times (C_{is})}{(A_{is}) \times (C_x)} \quad \text{and} \quad \overline{RF} = \left(\sum_{i=1}^{N} (RF)\right)/N$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the internal standard (ug/mL).

C_x = Concentration of the compound to be measured (ug/mL).

$\overline{RF}$ = Average response factor

N = Number of calibration levels

A. Calculate the concentration in the sample using the following equation:

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_o)(V_i)}$$

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected in nanograms (ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected (uL)

V_t = Volume of total extract (uL)

$\overline{RF}$ = Response factor as determined in the initial calibration.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES

1. Each day, the analyst must analyze an instrument blank to demonstrate that interferences from the analytical system are under control.

   a. The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control samples and calibration standards that the operation of the measurement system is in control.

   b. The laboratory spikes all samples with surrogate compounds to monitor continuing laboratory performance.

   c. The laboratory maintains performance records to document the quality of data that is generated.

2. Daily control requirements include the extraction and analysis of a method blank spiked with the six surrogate compounds. Each analytical lot contains the method blank to check for background contamination and to monitor method efficiency through percent recoveries of the surrogate compounds.

3. The method blank contains no known addition of target compounds.

4. The control spike levels are given below:

Compound	Control Spike Level (ug/L)
2FP	200
PHEND6	200
NBD5	100
2FBP	100
246TBP	200
TRPD14	100

5. The control samples consist of a 1-liter aliquot of ASTM Type II water. After spiking, the method blank is processed as a sample with the environmental samples.

6. The control spiking solutions require concentration verification weekly against working calibration standards using the current acceptable calibration regression equation. Recoveries must be above the lower warning limit on the X-bar control charts.

B. CONTROL CHARTS

1. Control charts will be maintained to monitor variation in precision and accuracy for each control analyte during routine sample analysis. The control charting procedure that will be followed is given in Section 11.0 of the USATHAMA QA Program, January 1990. The reports will include:

   a. Three-Day Moving Average X-Bar Control Chart

   b. Three-Day Moving Average R-Bar Control Chart

2. Control limits initiated from certification data are given in Section XI.A.

X. DATA

A. SEE ORIGINAL CERTIFICATION SUBMITTAL

XI. REFERENCES

A. 40 CRF Part 136, Appendix B., Friday, October 26, 1984.

B. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, D.C. 20460.

C. "Interlaboratory Method Study for EPA Method 625 - Base/Neutrals, Acids, and Pesticides," Final report for EPA Contract 68-03-3102 (In preparation).

D. EPA Test Methods for Evaluating Solid Waste. Physical/Chemical Methods SW-846, Method 3550, Method 3640, Method 8270, Sept. 1986.

E. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, October, 1986.

F. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, May, 1990.

TABLE I

IRDMS	TARGET ANALYTE
246TBP	2,4,6-Tribromophenol
2FBP	2-Fluorobiphenyl
2FP	2-Fluorophenol
NBD5	Nitrobenzene-D5
PHEND6	Phenol-D6
TRPD14	Terphenyl-D14

TABLE II

TARGET COMPOUND LIST AND DETECTION LIMITS FOR NON-CERTIFIED COMPOUNDS

Compounds	Detection Limit ug/L
Phenol	10
bis(2-Chloroethyl)ether	10
2-Chlorophenol	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
Benzyl Alcohol	10
1,2-Dichlorobenzene	10
2-Methylphenol	10
bis(2-Chloroisopropyl)ether	10
4-Methylphenol	10
N-Nitroso-di-n-propylamine	10
Hexachloroethane	10
Nitrobenzene	10
Isophorone	10
2-Nitrophenol	10
2,4-Dimethylphenol	10
Benzoic acid	50
bis(2-Chloroethoxy)methane	10
2,4-Dichlorophenol	10
1,2,4-Trichlorobenzene	10
Naphthalene	10
4-Chloroaniline	10
Hexachlorobutadiene	10
4-Chloro-3-methylphenol (para-chloro-meta-cresol	10

TABLE II (continued)

TARGET COMPOUND LIST AND DETECTION LIMITS FOR NON-CERTIFIED COMPOUNDS

Compounds	Detection Limit ug/L
2-Methylnaphthalene	10
Hexachlorocyclopentadiene	10
2,4,6-Trichlorophenol	10
2,4,5-Trichlorophenol	50
2-Chloronaphthalene	10
2-Nitroaniline	50
Dimethylphthalate	10
Acenaphthylene	10
2,6-Dinitrotoluene	10
3-Nitroaniline	50
Acenaphthene	10
2,4-Dinitrophenol	50
4-Nitrophenol	50
Dibenzofuran	10
2,4-Dinitrotoluene	10
Diethylphthalate	10
4-Chlorophenyl-phenylether	10
Fluorene	10
4-Nitroaniline	50
4,6-Dinitro-2-methylphenol	50
N-nitrosodiphenylamine	10
4-Bromophenyl-phenylether	10
Hexachlorobenzene	10
Pentachlorophenol	50
Phenanthrene	10
Anthracene	10

TABLE II (continued)

TARGET COMPOUND LIST AND DETECTION LIMITS FOR NON-CERTIFIED COMPOUNDS

Compounds	Detection Limit ug/L
Di-n-butylphthalate	10
Fluoranthene	10
Pyrene	10
Butylbenzylphthalate	10
3,3'-Dichlorobenzidine	20
Benzo(a)anthracene	10
Chrysene	10
bis(2-Ethylhexyl)phthalate	10
Di-n-octylphthalate	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Indeno(1,2,3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(g,h,i)perylene	10
alpha-BHC	3
beta-BHC	3
delta-BHC	3
gamma-BHC (Lindane)	3
Heptachlor	3
Aldrin	3
Heptachlor epoxide	3
Endosulfan I	3
Dieldrin	6
4,4'DDE	6
Endrin	6
Endosulfan II	6

TABLE II (continued)

TARGET COMPOUND LIST AND DETECTION LIMITS FOR NON-CERTIFIED COMPOUNDS

Compounds	Detection Limit ug/L
4,4'DDD	6
Endosulfan sulfate	6
4,4'DDT	6
Methoxychlor	30
Endrin ketone	6
alpha-Chlordane	30
gamma-Chlordane	30
Toxphene	60
PCB-1016	30
PCB-1221	30
PCB-1232	30
PCB-1242	30
PCB-1248	30
PCB-1254	60
PCB-1260	60

TABLE III

IRDMS Designation	TESTED CONCENTRATION RANGE (ug/L)	CRL (ug/L)	UCRL (ug/L)	INSTRUMENT RESPONSE AT BASE/NEUTRAL 4.0-ug/L 10-ug/L acid
2FP	2.5-250	19	250	10,853
PHEND6	2.5-250	46	250	9,544
NBD5	1.0-100	21	100	2,521
2FBP	1.0-100	7.0	100	8,965
246TBP	2.5-250	59	250	104
TRPD14	1.0-100	20	100	2,224

TABLE IV

STANDARD MATERIALS AND REAGENTS IDENTIFICATION

USATHAMA DESIGNATION	CAS NUMBER	MW	MOLECULAR FORMULA
246TBP	118-77-6	330	C6H3BR30
2FBP	321-60-8	172	C12H9F
2FP	367-12-4	112	C6H5FO
NBD5	4165-60-0	128	C6D5NO2
PHEND6	4165-62-2	99	C6HD5O
TRPD14	1718-51-0	244	C18D14

TABLE V

PREPARATION OF INITIAL CALIBRATION STANDARD

Compound	Parent Sol.* Number	Conc. of Parent Sol. ug/mL	Allq. Vol. mL	Mixture** Number	Final Con./Sol. ug/mL
Acid Surr.	LA24266	2000	0.120	8	160
Base Surr.	LA22975	1000	0.240	9	160
IS	LA23103	2000	0.030	10	40
CH_2CL_2	NA	--	0.102	--	--
DFTPP	902	5000	0.048	--	160

* Refers to Lot# of Solution

** Refers to the contents of the mixture (see below)

Mixture 8: Acids Surrogate Standard Mix

This mixture contains 2000 ug/mL of each of the following components in methanol:

2-Fluorophenol
Phenol-D_6
2,4,6-Tribromophenol

Mixture 9: Base-Neutrals Surrogate Standard Mix

This mixture contains 1000 ug/mL of each of the following components in methylene chloride:

Nitrobenzene-D_5
2-Fluorobiphenyl
4-Terphenyl-D_{14}

TABLE V (Continued)

PREPARATION OF INITIAL CALIBRATION STANDARD

Mixture 10: Internal Standards Mix

This mixture contains 2000 ug/mL of each of the following components in methylene chloride:

Acenaphthene-d_{10}	Chrysene-d_{12}
1,4-Dichlorobenzene-d_4	Naphthalene-d_8
Perylene-d_{12}	Phenanthrene-d_{10}

TABLE VI

Primary Stock Concentration	Volume of Primary Stock	Volume of Methylene Chloride Fortified with 40 ug/mL of IS	Final Conc. ug/mL
160-ug/mL	80-uL	0-uL	160
160-ug/mL	60-uL	20-uL	120
160-ug/mL	40-uL	40-uL	80
160-ug/mL	25-uL	55-uL	50
160-ug/mL	10-uL	70-uL	20
160-ug/mL	2.5-uL	77.5-uL	5.0
Blank	0.0-uL	80-uL	0.0

TABLE VII

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z may be up to 110 percent that of m/z 198.

TABLE VIII

CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS

Parameter	Primary Ion	Secondary Ion(s)
SURROGATES		
Phenol-D_6	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-D_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl-D_{14}	244	122, 212
1,2-Dichlorobenzene-D_4	152	115, 150
Naphthalene-D_8	136	68
Acenapthene-D_{10}	164	162, 160
Phenanthrene-D_{10}	188	94, 80
Chrysene-D_{12}	240	120, 236
Perylene-D_{12}	264	260, 265

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COPY #3

STANDARD OPERATING PROCEDURE

Method for Antimony by A.A.
Graphite Furnace

SOP NUMBER	MN-I-308-A
AUTHOR	Starla Enger
EFFECTIVE DATE	April 25, 1991
SUPERSEDES	WPPMTHUI52

APPROVAL

Starla Enger — 4/25/91
Inorganic Laboratory Manager — Date

[signature] — 25 Apr 91
Regional Director — Date

Susan Lantz — 4/25/91
Quality Assurance Officer — Date

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I. PURPOSE

A. The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the determination of Antimony by Atomic Absorption Graphite Furnace.

II. APPLICATION

A. The procedure in this SOP will be carried out by a person designated as a metals analyst.

III. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

1. Overall responsibility for ensuring that the SOP is implemented and followed.

B. INORGANIC LABORATORY MANAGER

1. Responsible for ensuring that analysts perform analysis according to the method described by this SOP.

2. Notify the QAO regarding changes in the method to ensure that SOP's are updated.

C. ANALYST

1. Responsible for performing the analysis by the method described in this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

VI. GENERAL POLICIES AND PROCEDURES

A. SUMMARY

1. Analyte: Antimony, Sb

2. Matrix: Ground water, surface water, drinking water, generally water with little or no suspended solids.

3. General Method: Antimony Graphite Furnace EPA #204.2

a. A predetermined volume of sample is injected into a pyrolytically coated graphite tube inside the furnace unit then dried, ashed and atomized, through a temperature scheme entered into the furnace programmer. At the instant of atomization the resulting absorption of Hollow Cathode Radiation will be directly proportional to antimony Concentration.

B. APPLICATION

1. Test Concentration Range: 3 to 50 ug/L

2. Sensitivity: 0.02 ABS. for a 3 ug/L standard

3. Reporting Limits

a. The certified method detection limit for antimony is 3 ug/L.

b. The EPA Contract Laboratory Program certified detection limit for antimony is 60.0 ug/L.

4. Interferences

1. High lead concentrations may cause a measurable spectrial interference. If this interference is expected an alternate line of resonance (wavelength) should be used.

5. Analysis Rate:

a. Approximately 40 samples per 8 hour period

6. Safety Information

a. Standard laboratory safety practices must be followed.

C. APPARATUS AND CHEMICALS

1. Glassware/Hardware

a. Eppendorf Mechanical Pipets: various sizes

b. Sterile Polystyrene Culture Tubes: 17x100mm, Baker, T1340-23

c. Pyrolytically Coated Graphite Furnace Tubes: partitioned

d. Dispo Sample Cups: 2.0 mL Conical, Baker, B2713-2

2. Instrumentation

a. Varian Model 1475 Dual Beam Atomic Absorbtion Spectrophotometer with Varian Model GTA95 Graphite Tube Atomizer: DS15 Data Base and Citizen MSP10 Printer

b. Perkin Elmer 603 Atomic Absorbtion Spectrophotometer with HGA-400 Graphite Furnace and Hitachi Chart Recorder.

c. Sb Hollow Cathode Lamp

d. Instrument Operating Parameters for antimony

1. A.A. Operating Parameters

a. Lamp Current: 10 MA

b. Wavelength: 217.6 NM

c. Slit Width: 0.2 NM

d. Background: On

e. Mode: Absorbance - Peak Height

2. Furnace Operating Parameters

STEP NO.	TEMPERATURE C	TIME SEC.	GAS FLOW(1)	GAS TYPE(2)	READ COMMAND(3)
1	40	3.0	3.0	Normal	
2	90	70	3.0	Normal	
3	150	5.0	3.0	Alt	
4	150	5.0	3.0	Alt	
5	250	5.0	3.0	Alt	
6	250	5.0	3.0	Alt	
7	900	10	3.0	Alt	
8	900	10	3.0	Alt	
9	900	2.0	3.0	Normal	
10	900	2.0	.0	Normal	
11	2100	.9	.0	Normal	*
12	2100	2.0	3.0	Normal	*
13	2700	.2	3.0	Normal	
14	2700	.5	3.0	Normal	

Sampler Parameters — Normal Calibration

SAMPLES AND STANDARDS TYPE	LOCATION	VOLUME	BLANK VOLUME	MODIFIER VOLUME (4)
Blank	---	---	22	4
Std 1	51	5	17	4
Std 2	51	10	12	4
Std 3	51	20	2	4
Std 4				
Std 5				
Samples	---	20	2	4

(1) L/min.
(2) Normal Gas - Argon
Alternate Gas - 98% Argon, 2% hydrogen
(3) Instrument reads at point of atomization
(4) 100 PPM palladium

3. Analytes: Antimony

a. CAS Registry #7440-28-0

b. Melting Point: 303.5°C

c. Boiling Point: 1457± 10C

4. Reagents and Sarms

a. ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

b. Concentrated nitric acid, Baker Instra-analyzed or equivalent.

c. Argon, should be of high purity.

d. Argon with 2% hydrogen, should be at high purity

e. Palladium solution, 1000 ppm: Dissolve 0.25 g of palladium nitrate dihydrate ($Pd(NO_3)2-H_2O$) in a small amount of nitric acid (Ultrex) and dilute to 100 mls with deionized water.

f. Stock Antimony Solution: Carefully weigh 2,7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1

liter with deionized distilled water 1 ml = 1 mg Sb (1000 mg/L) alternatively, procure a certified standard which is NIST traceable.

g. Antimony Working Standards: Prepare dilutions of stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration range as the samples to be analyzed. Refer to Section VI.D.1.

D. CALIBRATION

1. Initial Calibration

a. Preparation of Standards

1. Prepare a working stock antimony standard at 100 ug/L.

a. Dilute 10 mLs of stock antimony standard 1000 mg/L to 1000 mLs with deionized water(1) (equals 10,000 ug/L).

b. Dilute 1.0 mLs of 10,000 ug/L antimony standard to 100 mLs with deionized H_2O (equals 100 ug/L). This is the working standard.

2. Using the working stock antimony standard (100 ug/L), prepare the following standards using the appropriate volumes below:

CONCENTRATION OF STANDARD IN ug/L	MLS OF WORKING STANDARD	FINAL VOLUME (mL)
4.0	1.0	4.8
50.0	2.0	2.5

(1) Deionized water with 0.1% HNO_3

b. Instrument Calibration

1. Turn on instrument and set up for the following conditions:

   a. Install Sb Hollow Cathode Lamp (HCL)

   b. Set HCL Current to 10 MA (milliamperes)

   c. Wavelength: 217.6 nm

   d. Slit width: 0.2 nm

   e. Background: on

   f. Mode: Absorbance - peak height

2. Allow system to warm up, approximately 1/2 hour.

3. Adjust and fine tune A.A. and GTA95 furnace by:

   a. Adjust HCL lamp for maximum energy.

   b. Adjust wavelength for maximum energy.

   c. Align graphite furnace head.

   d. Let system warm up for an additional 15 minutes, then recheck system.

4. Turn on Argon Purge Gas to furnace unit.

5. Turn on Argon/hydrogen purge gas to furnace unit.

6. Turn on cooling water to Furnace unit.

7. Turn on power to GTA95 Furnace and Programmer and enter proper program for antimony. Refer to furnace operating parameters Section VI.C.2.

8. Select proper standard injection sizes and input on GTA95 Programmer Refer to furnace operating parameter Section VI.C.2.

   * These temperatures and times are subject to modification due to graphite tube conditions and sample matrix.

9. Condition graphite tube by applying a heating sequence from ambient temperature to 3000°C.

10. Run top standard through program to check absorbance, peak uniformity and tube condition.

11. Obtain typical response (in absorbance) for antimony approximately 0.49 ABS. units for a 50 ug/L standard.

12. Turn on DS15 Data Station

    a. Select: Sb Method

    b. Select: Run Sb Method

13. Explanation of DS15 & GTA95 Automated Run Calibration

    a. In order to accomplish automated run capabilities, the GTA95 furnace and DS15 calibrates itself to 3 standards which are made by the Autosampler System automatically, from the top standard (50 ug/L). Once the instrument has calibrated itself, the auto-run begins.

14. Analyze calibration verification standard (EPA) and MDL standard (4 ug/L) to ensure proper optimization and calibration.

15. Calibration of instrument is complete.

c. Analysis of Calibration Data

1. EPA or external check is run to verify calibration curve and must meet 95% confidence levels to meet acceptability.

2. For Contract Laboratory Program projects the calibration verification must be ± 10% of the true value.

2. Daily Calibration

a. Preparation of Standards

1. Follow "Preparations of Standards" outlined in Section VI.D.1.

b. Instrument Calibration

1. Found in "Instrument Calibration" procedure outlined in Section VI.D.1.

c. Analysis of Calibration Data

1. See "initial calibration", Section VI.D.1.

d. Calibration verification solutions

1. Presently being used are EPA Trace Metal Checks for water pollution.

e. For Contract Laboratory Program projects, a standard must be analyzed at the CRDL (60.0 ug/L for antimony). No acceptance limits are set a this time.

E. SAMPLE HANDLING/STORAGE

1. Sampling Procedure

a. All sample containers must be new, and subject to rigorous cleaning procedures to insure minimum contamination of metals.

b. Cleaning Procedure is as follows:

1. Rinse bottles and lids with 5% sodium hydroxide.

2. Rinse with deionized water.

3. Rinse with 5% nitric acid in deionized water.

4. Rinse with deionized water.

5. Drain and air dry

c. Aqueous samples must be acidified to pH 2 with nitric acid preferably at a concentration of 0.1% - 0.5% in solution.

2. Containers

a. Plastic or glass containers may be used, however plastic containers are prefered.

3. Storage Condition

a. Store aqueous samples (preserved when with HNO_3) at room temperature.

4. Holding Time Limits

a. Samples must be analyzed within a 6 month period.

F. PROCEDURE

1. Separations Digestions: Samples require preparation before analysis. Refer to the appropriate method (numbers P301.0 - water, P305.0 - solids, P704.8 - filters.)

2. Chemical Reactions

a. The graphite tube located within the furnace chamber is electrically heated, thus drying a given amount of aqueous sample and, with a programmed sequence of electrical power, is heated rapidly producing a dense population of ground state atoms which can be identified by atomic absorbtion.

3. Instrumental Analysis

a. Follow "initial calibration" procedures outlined in Section IV.D.1.

G. CALCULATIONS

1. Instrument will display values for samples in concentration (mg/l) based on a curve formed by the instrument (concentration vs. absorbence) during calibration.

2. Water Samples

[(A)(D)-B][C/E] = result in mg/l
Refer to Chart A

1. The Method detection limit (MDL) changes according to the digestion ratio. ie: MDL (C/E).

2. Samples with values below the MDL are reported as ND.

3. Significant Figures: Sample concentrations below 10 ug/L report 1 significant figure (ie: 6.7 mg/L is reported as 7 ug/L); between 10 ug/L and 10,000 ug/L report 2 significant figures (ie: 1879 ug/L is reported as 1900 ug/L); above 10,000 ug/L report 3 significant figures (ie: 131,972 ug/L is reported as 132,000 ug/L).

2. Solid Samples

[(A)(D)-B][C/F] = result in mg/kg
Refer to Chart A

a. The MDL changes according to the digestion ratio. ie: MDL (C/F).

b. Samples with values below the MDL are reported as ND.

c. Significant Figures: Sample concentrations between the MDL and 10,000 mg/kg are reported with 2 significant figures (ie: 4.89 mg/kg is reported as 4.9 mg/kg); above 10,000 mg/kg report 3 significant figures (ie: 19,769 mg/kg is reported as 19800 mg/kg).

3. Filter Samples

a. Filter samples without known air volumes listed on greenbar. [Sample concentration (ug/mL-(Blank)][Final Vol.(mL)] = result in ug.

1. Samples with values below the MDL are reported as <values, not ND.

2. Dash out MDL on computer with 1 dash.

3. Report up to 3 significant figures, but not going past the ones column:
ie (1) - 24.3 ug would be reported as 24 ug
ie (2) - 1139 ug would be reported as 1140ug

4. When sample is <2.5 ug, round up and report <3 ug.

b. Filter Samples with known air volumes listed on greenbar.

$$\frac{[\text{Sample Value (mg/l)} - \text{Blank}][\text{Final Volume (ml)}]}{[1000][\text{Air Volume (ml)}]} = \text{result in mg/m}^3$$

1. Samples with values below the MDL are reported as <n, not ND.

2. Do NOT dash out the MDL on the computer screen - this valve is actually the TLV for the requested parameter and not the MDL.

3. Report up to 3 significant figures, but not past the thousanths column:
ie (1) - 0.0089 mg/m^3 would be reported as 0.009 mg/m^3
ie (2) - 1.139 mg/m^3 would be reported as 1.14 mg/m^3

CHART A

A = Sample value within standard range (mg/L)

B = Matrix or preparation blank value (mg/L)

C = Final volume of digestate (50 mls)

D = Any dilution factor used during analysis to adjust the sample concentration to within the standard range

E = Volume of sample used during preparation or digestion (ml)

F = Weight of sample used during preparation or digestion (grams)

H. DAILY QUALITY CONTROL

1. Control Samples

a. Analytical Quality Control

1. Analyze one preparation blank and laboratory control sample with each batch digested.

b. Matrix Quality Control

1. For precision and accuracy determinations, samples are spiked in duplicate prior to digestion in the following manner:

a. Analyze one prepared matrix spike for every 20 samples in duplicate so that the sample contains 1.0 ug/L Antimony.

2. The technique of "Method of Standard Additions" may need to be used on difficult matrices.

3. Quality Control Acceptance Criteria

1. Laboratory control sample - recovery 80-120%

2. Calibration verification standard - recovery 90-110%.

2. Documentation

a. Instrumentation Log Books

1. Record the applicable information in the instrument log book of the instrument being used for the analysis. Information must include program deviations, run sequence, maintenance, etc.

b. Standard Preparation Log Book

1. Record the necessary information in the prep log book. Information must include volumes, standard source, date, etc.

c. Shewhart Charts

1. After analysis plot the following % recoveries on Shewhart charts:

a. Analytical spikes

b. Matrix spikes

c. Matrix duplicates

D. Data Validation

1. After analysis, someone other than the analyst needs to recheck all data for calculation and data entry errors. After this has been completed, the reviewer shall initial validation sheet and raw data sheet.

I. REFERENCES

A. Methods for Chemical Analysis of Water and Wastes, EPA-600 / 4-82-055, December 1982, Method 213.2.

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COPY #15

STANDARD OPERATING PROCEDURE

THALLIUM BY GFAA (SW-846)

SOP NUMBER	MN-I-377-B
AUTHOR	Angela Benson
EFFECTIVE DATE	September 22, 1993
SUPERSEDES	First Issue

APPROVAL

Metals Supervisor — Date: 1-28-94

Inorganic Laboratory Manager — Date: 1/28/94

Quality Assurance Officer — Date: 02/03/94

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XIV. REFERENCES 11

I. PURPOSE

A. The purpose of this Standard Operating Procedure (SOP) is to establish a procedure for the determination of Thallium by Atomic Absorption Graphite Furnace (GFAA).

II. APPLICATION

A. This procedure is applicable to ground water, surface water, drinking water, sediments, soils, and sludges.

B. SAFETY INFORMATION

1. Standard laboratory safety practices must be followed.

C. ANALYTE INFORMATION

1. Chemical Abstract Services registry (CAS) number: 7440-38-2

III. SUMMARY

A. A predetermined volume of sample is injected into a pyrolytically coated graphite tube inside the furnace unit, then dried, ashed and atomized through a temperature scheme entered by the furnace programmer. At the instant of atomization, the resulting absorption of discharge radiation will be directly proportional to Thallium concentration.

IV. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER

1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

2. The Quality Assurance Officer will conduct semi-annual audits of the facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

B. INORGANIC LABORATORY MANAGER/METALS SUPERVISOR

1. The manager/supervisor has responsibility to ensure adherence to this SOP.

2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3. The manager/supervisor will ensure that the Quality Assurance Office is notified when revisions to the SOP are required.

C. ANALYST

1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

V. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated and the superseded document replaced.

VI. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Office.

B. Distribution records will be maintained by the Quality Assurance Office.

VII. GENERAL INFORMATION

A. Reporting Limit: 5 to 50 μg/L

B. Sensitivity: 0.015 ABS for a 5 μg/L standard.

VIII. SAMPLE HANDLING AND STORAGE

A. CONTAINERS

1. Plastic or glass containers may be used; however, plastic is preferable.

2. Precleaned containers are purchased from a supplier.

B. STORAGE CONDITIONS

1. Store aqueous samples (when preserved with HNO_3 to pH <2) at room temperature.

2. Solid samples should be refrigerated at 4° C $\pm$ 2° C.

C. HOLDING TIME LIMITS

1. Samples must be analyzed within a 6 month period.

IX. APPARATUS AND CHEMICALS

A. GLASSWARE/HARDWARE

1. Eppendorf Mechanical Pipets: various sizes
2. Sterile Polystyrene Culture Tubes: 17x100 mm, Baker T1340-23 or equivalent
3. Pyrolytically Coated Graphite Furnace Tubes: unpartitioned
4. Dispo Sample Cups: 2 mL Conical, Baker B2713-2 or equivalent
5. Beakers, 150 mL with watch glasses
6. Filter paper, Whatman 41 or equivalent
7. Balance, with the ability to weigh to the nearest 0.01 gm.

B. REAGENTS AND SARMS

1. ASTM Type II water

2. Concentrated nitric acid, Baker Instra-analyzed grade or equivalent

3. Hydrogen Peroxide, 30%

4. Stock Thallium Solution - NIST traceable (1000 mg/L TL)

5. Preparation of Thallium Solutions

   a. Calibration standards

      (1) Dilute 0.1 mL of stock Thallium standard, 1000 mg/L, to 100 mL with DI water (0.5% HNO_3). Concentration equals 1000 μg/L.

      (2) Dilute 0.5 mL of the 1000 μg/L Thallium standard to 10 mL with DI water (0.5% HNO_3). The concentration of this working standards is 50 μg/L. This is the calibration standard and should be prepared at the time of the analysis. The instrument is programmed such that the autosampler prepares the 5, 10, and 25 μg/L standards used in the calibration curve generation.

   b. LCS and Matrix Spike solution

      (1) Dilute 0.1 mL of 1000 mg/L stock Thallium solution to 100 mL using DI water (5% HNO_3 concentration). Concentration equals 1 mg/L TL.

6. Modifier Solutions

   a. Stock Palladium: - 5,000 mg/L, available from Inorganic Ventures.

   b. Dilute stock Pd 1:10 with 5% HNO_3 - Resulting conc = 500 ppm Pd.

X. PROCEDURE

A. Regionally specific instrumentation specifications and operating parameters are addressed in Attachments and Appendices following.

B. SEPARATIONS/DIGESTIONS

1. Water Sample Preparation

   a. Transfer a 100 mL aliquot of well-mixed sample to a Griffin

beaker and add 3.0 mLs of concentrated nitric acid. Place beaker on a hot plate and cautiously evaporate to a low volume, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3 mL portion conc HNO_3. Return beaker to hot plate and increase temperature of the hot plate so that a gentle reflux action occurs.

b. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated by light yellow appearance of the digestate). When the digestion is complete, evaporate to a low volume (approximately 3 mLs). Remove the beaker and add approximately 10 mLs of Type II water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

c. Remove the beaker from the hot plate and wash down the beaker walls with Type II water. When necessary, filter the sample to remove any silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. Adjust the final volume to 100 mLs with Type II water. The sample is now ready for analysis.

2. Soil/Sediment Preparation

a. Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a beaker. For the matrix spike sample, add 1.0 mL of the solution specified in Section IX.B.5.b.

b. Add 10 mL of 1:1 nitric acid, mix the slurry, and cover with a watch glass. Heat the sample to 95° C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated nitric acid, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

c. After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide. Return the beaker to the hot plate for warming to start

the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

d. Continue to add 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total of 10 mL peroxide.

e. Continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL, add 10 mL Type II water, and warm the mixture. After cooling, filter through Whatman No. 41 filter paper (or equivalent) and dilute the sample to 100 mL with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 5% (v/v) nitric acid.

C. INSTRUMENT CALIBRATION

1. Turn on the instrument and allow the system to warm up, approximately 0.5 hours.

2. Adjust and fine tune the instrument and furnace by:

   a. Adjusting the lamp for maximum energy
   b. Adjusting the wavelength for maximum energy
   c. Aligning the graphite furnace head.
   d. Letting the system warm up for an additional 15 minutes, then rechecking the system.

3. Turn on the Argon Purge Gas to the furnace unit.

4. Turn on the cooling water to the furnace unit.

5. Turn on the power to the furnace and Programmer and enter the proper program for lead. Refer to furnace operating parameters given in Attachment 1, Appendix A - MN.

6. Refer to the manufacturer's instrument manual for detailed operation instructions.

D. SAMPLE ANALYSIS/RUN SEQUENCE

1. All furnace analyses must fall within the calibration range and require duplicate injections except during Method of Standard Additions (MSA). For concentrations greater than the reporting limit (5.0 μg/L) if the duplicate injection readings are not within 20% RSD, rerun the sample once (i.e. two additional injections).

2. See Appendix B for the required run sequence. See Section XII for Quality Control requirements and data acceptance criteria.

XI. CALCULATIONS

A. Instrument will display values for samples in concentration (μg/L) based on a curve generated by the instrument (concentration vs. absorbance) during calibration.

B. A separate determination of percent solids must be performed.

C. The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample:

$$\text{Concentration (dry wt.), mg/kg} = \frac{(C)(V)}{(W)(S)} \qquad \text{Equation 1}$$

Where: C = Concentration, μg/L
V = Final volume in L after sample prep
W = Weight in g of wet sample
S = % solids/100

XII. DAILY QUALITY CONTROL

A. INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

1. Immediately after the instrument has been calibrated, the accuracy of the calibration shall be verified. A standard will be analyzed that is from a source other than the calibration standards. The concentration should be at or near the midpoint of the calibration curve. When the deviation of the ICV exceeds 10% of the true value, the analysis must be terminated, the

problem corrected, the instrument recalibrated and the calibration reverified.

2. The CCV is the same solution as the ICV and is analyzed every 10 analytical samples, i.e. 20 injections. This solution ensures calibration accuracy during the run. If the deviation of the CCV is greater than 20% of the true value, the analysis must be stopped, the problem corrected and all samples analyzed since the last compliant CCV must be reanalyzed.

B. INITIAL CALIBRATION BLANK (ICB) AND CONTINUING CALIBRATION BLANK (CCB)

1. A blank must be run after every ICV and CCV. If the absolute value of the blank exceeds the reporting limit (5.0 μg/L) terminate the analysis, correct the problem, recalibrate, verify calibration and reanalyze all samples since the last compliant blank.

C. PREPARATION BLANK (PB)

1. A blank consisting of deionized water processed through the sample preparation procedure will be prepared and analyzed with each batch of samples digested or for every 20 samples, whichever is more frequent.

D. SPIKE SAMPLE ANALYSIS (Sample MS)

1. A sample must be spiked for each SDG or per 20 samples digested, whichever is more frequent. The spike must be added before the digestion begins. The sample should be spiked so that the final concentration of TL in solution is 10 μg/L or 2 mg/kg. Recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} (100) \qquad \text{Equation 2}$$

Where SSR = Spiked sample result, μg/L or mg/kg dry
SR = Sample result, μg/L or mg/kg dry
SA = Spike added, μg/L or mg/kg dry

E. SPIKE DUPLICATE SAMPLE ANALYSIS (Sample MSD)

1. One sample must be prepared and analyzed in spike duplicate for each SDG or for each 20 samples, whichever is more frequent. Calculate the Relative Percent Difference (RPD) as follows:

$$RPD = \frac{(2)(|S - D|)}{(S + D)}(100) \qquad \text{Equation 3}$$

Where: S=Spike sample result, μg/L or mg/kg dry
D=Duplicate sample result, μg/L or mg/kg dry

2. The MS/MSD recoveries must also be within 75% to 125%. If these fail and the SD (see section XII.G.1.) spike worked, every sample must then be run at a 1:4 dilution and spiked analytically. (Don't include the PBW, LCSW, and sample that the SD was done on.)

Acceptable analytical spike recoveries are 75%-125%. If the analytical spike date is unacceptable the Method of Standard Additions (MSA) should be used to determine the concentration of that analyte. The correlation coefficient of the MSA analysis must be ≥0.9950. If the correlation coefficient is less than 0.9950 the MSA will be performed one additional time. The reported result will be from the MSA analysis with the better correlation coefficient.

MSA's are run using single injections. The PE 5100's can be programmed to auto dilute and add the appropriate amount of standard to each sample.

The Perkin Elmer instruments are programmed to run MSA's using the sample and 3 standard additions of 10, 20, and 30 μg/L to calculate the concentration of arsenic in the original sample.

The instrument autozeros using a blank of 5% HNO_3.

Then 20 μL of sample is injected in the furnace and analyzed. For the 10 μg/L standard addition, 4 μL of 50 μg/L standard (IX.B.5.a.2) is added

to 20 μL of sample and analyzed. This continues for the 20 standard addition where 8 μL of the 50 μg/L standard is added to 20 μL of sample and for the 30 standard addition, 12 μL of the 50 μg/L standard is added to the 20 μL of sample and for the 30 standard addition, 12 μL of the 50 μg/L standard is added to 20 μL of the sample.

After all four analyses are complete, the instrument will calculate the thallium concentration in the original sample using linear regression and plotting the standard addition results on a curve with the absorption on the y-axis and concentration on the x-axis. The x-intercept is the concentration of arsenic in the sample.

F. LABORATORY CONTROL SAMPLE (LCS)

1. An LCS will be analyzed for each SDG or for every 20 samples prepared. The LCS is prepared and analyzed using each procedure applied to the samples. The result of the aqueous LCS must be within 20% of its true value. If the LCS is not within acceptance criteria, the analyses must be terminated, the problem corrected and the samples associated with the LCS redigested and reanalyzed.

G. SERIAL DILUTIONS

1. One sample per batch or every 20 samples, whichever is more frequent, is chosen for the serial dilution. Dilute the sample 1:4 with 5% HNO_3. For the serial dilution spike, add 1 part calibration standard (50 μg/L) to the serial dilution solution. The true value of the spike will be 12.5 μg/L. Field blanks, trip blanks and equipment rinses cannot be used for the serial dilution.

   Example: Serial Dilution: 0.5 mls of sample + 1.5 mls 5% HNO_3
   SD Spike: 0.5 mls sample + 0.5 mls calib. std. + 1.0 mls 5% HNO_3.

   The SD Spike recovery must be within 75% to 125%. If this fails the first time, rerun once.

H. DETECTION LIMIT

1. The method detection limit (MDL) will be determined annually.

I. DOCUMENTATION

1. Instrument Log Books

   a. Record the applicable information in the instrument log book of the instrument being used for the analysis. Information must include program deviations, run sequence, maintenance, etc.

2. Standard Prep Log Book

   a. Record the necessary information in the prep log book, including source, lot numbers, and volumes utilized.

3. Shewhart Charts

   a. After analysis, plot the following % recoveries on Shewhart charts:

      (1) Laboratory control samples

4. Data Validation

   a. After analysis, a peer or supervisor review of data will be performed. After this validation, the reviewer shall initial the raw data sheet.

XIII. REFERENCES

A. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

B. Analytical methods for Graphite Tube Atomizers, Varian and Associates Co., No. 85-100447-00.

C. Test Methods for Evaluating Water and Solid Waste, SW-846, 1986, Method 3050 and 7421.

APPENDIX A - MN

INSTRUMENT OPERATION PARAMETERS

TABLE I - VARIAN SPECTRA 300/400

TABLE II - PE 5100

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ATTACHMENT 1

I. INSTRUMENTATION

A. Make/Model

1. Varian Spectra 300/400 with Zeeman GTA

2. Perkin-Elmer 5100 with Zeeman HGA 600

B. 1. Thallium Hollow Cathode Lamp

2. Thallium Electrodeless Discharge Lamp

C. Operating Parameters

1.	Wavelength:	276.8 nm
2.	Slit Width:	0.7 nm on PE 5100, 0.5 nm on Varian
3.	Background:	On - Zeeman
4.	Mode :	Absorbance - Peak Area

D. Furnace Operating Parameters - See Appendix A - MN

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APPENDIX B

RUN SEQUENCE

Calibration	
1	ICV
2	ICB
3	PBW
4	LCSW
5	Sample 1
6	Sample 2
7	Sample 3
8	Sample 4
9	Sample 5
10	Sample 6
11	Sample 7
12	CCV1
13	CCB1
14	Sample 8
15	Sample 9
16	Sample 10
17	Sample 11
18	Sample 12
19	Sample 13
20	Sample 14
21	Sample 15
22	Sample 16
23	CCV2
24	CCB2

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TABLE I
VARIAN SPECTRA 300/400

Step No.	Temperature C°	Time, S	Gas Flow, L/min	Gas Type, Argon	Read Command (1)	
1	70	5.0	3.0	Normal		
2	95	70	3.0	Normal		
3	150	5.0	3.0	Normal		
4	150	5.0	3.0	Normal		
5	850	5.0	3.0	Normal		
6	850	5.0	3.0	Normal		
7	850	2.0	0.0	Normal		
8	2000	0.9	0.0	Normal		*
9	2000	2.0	0.0	Normal		*
10	2700	0.5	3.0	Normal		
11	2700	0.5	3.0	Normal		

Sampler Parameters Normal Calibration

SAMPLES AND STANDARDS TYPE	LOCATION	VOLUME	BLANK VOLUME	MODIFIER VOLUME (2)
Blank	---	---	30	5
Std 1	51	3	27	5
Std 2	51	6	24	5
Std 3	51	15	15	5
Std 4	51	30	0	5
Std 5				
Samples	---	30	0	5

(1) Instrument reads at point of atomization
(2) 500 ppm Pd

Last sample no.	= 45	Multiple injections	= 1
No. of replicates	= 2	Last dry phase step	= 2
Injection temp.	=AMB	First sample no.	= 1

TABLE II
PERKIN ELMER 5100

Step No.	Temperature C°	Ramp	Hold	Gas Flow, L/min	Gas Type, Argon	Read Command (1)
1	120	1	30	300	Normal	
2	180	1	30	300	Normal	
3	1000	1	30	300	Normal	
4	20	1	10	300	Normal	
5	1600	0	5	0	Normal	On
6	2600	1	5	300	Normal	

Sampler Parameters Normal Calibration

SAMPLES AND STANDARDS TYPE	LOCATION	VOLUME	BLANK VOLUME	MODIFIER VOLUME (2)
Blank	---	---	20	5
Std 1	39	2	18	5
Std 2	39	4	16	5
Std 3	39	10	10	5
Std 4	39	20	0	5
Std 5				
Samples	---	20	0	5

(1) Instrument reads at point of atomization
(2) 500 ppm Pd

Last sample no.	= 36	Multiple injections	= 1
No. of replicates	= 2	Last dry phase step	= 2
Injection temp.	= 80°C	First sample no.	= 1

Note: Changes in matrices may require an analyst to modify the furnace programs.

COPY #5

STANDARD OPERATING PROCEDURE

Waste Classification
Qualitative

SOP NUMBER	MN-I-462
AUTHOR	David W. Mack
EFFECTIVE DATE	March 18, 1994
SUPERSEDES	First Issue

APPROVAL

Jane Costello — 3-18-94

General Chemistry Supervisor — Date

[signature] — 3-18-94

Inorganic Laboratory Manager — Date

ACCEPTANCE

[signature] — 03/19/94

Quality Assurance Officer — Date

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I. PURPOSE

A. To qualitatively evaluate samples for waste characteristics to aid in identifying and evaluating waste streams.

II. SCOPE/APPLICATION

A. SUMMARY OF METHOD

1. Samples will be qualitatively evaluated for the following parameters: % solids, % liquids, Color, Viscosity, Phase layering, Pumpability, Ph, Reactive Cyanide, Reactive Sulfide, Oxidizer, Flash Point, Specific gravity, and % water. These parameters will be reported by visual techniques, such as Ph strips.

B. ANALYTE INFORMATION

1. The procedure section of this document will identify the acceptable results for each of the above mentioned parameters.

D. HAZARDS AND PRECAUTIONS

1. Standard laboratory precautions should always be followed. Chemical exposure must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, eye protection, fume hoods). Reference files of OSHA regulations and Material Safety Data Sheets (MSDS) are available to all personnel.

III. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER (QAO)

1. The QAO has overall responsibility for ensuring that the SOP is implemented and followed.

2. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audits will be reported to Regional Management and Corporate Quality Control.

3. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

4. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

B. DEPARTMENT SUPERVISOR/MANAGER

1. The department managers/supervisors are responsible for ensuring that this SOP is understood, implemented, and adhered to by all designated personnel.

C. ANALYST

1. The analysts are responsible for adherence to the policies and procedures set forth in the document.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. Required revisions will be incorporated at the time of the review.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

VI. SAMPLE HANDLING AND STORAGE

A. Samples should be collected, with minimum aeration, in clear glass or bottles

and stored in refrigerated storage.

VII. APPARATUS AND CHEMICALS

A. GLASSWARE/EQUIPMENT

1. pH strip paper
2. Chloramine-T, Barbituric acid reagents
3. Lead acetate paper
4. Potassium Iodide paper
5. Flash Point apparatus Closed cup
6. Analytical balance
7. Various sizes of pipettes
8. Miscellaneous laboratory glassware/equipment.

B. REAGENTS

1. Chloramine-T - Dissolve 1.0 g of white, water soluble chloramine-T in DI water and dilute to 100 ml (make fresh weekly, store at 4 degrees Celsius +/- 2 degree Celsius).
2. Pyridine Barbituric Acid Reagent - Place 15 g barbituric acid in a 250 ml volumetric flask and add just enough water to wash sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. add 15 ml concentrated hydrochloric acid, mix and cool to room temperature. Dilute to volume with DI water and mix. This reagent is stable for up to one month. Discard if a precipitate develops.

VIII PROCEDURE

A. 1. % Solids - Visually inspect the sample without opening the sample container. Record the approximate % solids in whole numbers (e.g. 23%).

2. % Liquid - Visually inspect the sample without opening the sample container. Record the approximate % liquid in whole numbers (e.g. 95%).

3. Apparent Color - Visually identify the color of the sample, record on the raw data sheet.

4. Viscosity - Visually identify the viscosity of the sample, record one of the following four descriptions on the data sheet, Liquid, syrup, gel, or solid.

5. Phase Layering - Identify the amount of layers in the sample, and recorded on the data sheet.

6. Pumpability - Identify if the sample would be pumpable, record yes or no on the data sheet.

7. pH - Using a pH strip identify the approximate pH of the sample.

8. Reactive Cyanide - Place 2 drops of sample in a test tube or beaker, add 1 drop chloramine-T and 1 drop pyridine barbituric acid reagent. A purple color indicate a positive result, not purple indicates a negative result. Identify and record the result as ether "positive" or "negative".

9. Reactive Sulfide - Remove approximately 5 mls of sample and acidify with 1-3 drops of phosphoric acid to acidify. Place the lead acetate paper in the fumes or directly above the acidified sample. If the paper turns black the test result is positive, if the paper does not react the result is negative. Note submerge the paper for at least 5 seconds for best results.

10. Oxidizer - Place the potassium iodide paper in the sample, if the paper turns black the test results are positive if the paper does not turn a color the results are negative.

11. Flash Point - Analyze samples according to Flash Point standard operating procedures.

12. Specific gravity - Pipette 5 mls of sample into a tared weighing tray. Record the weight of the sample. Divide the weight of the sample by the volume of the sample and record this number as the specific gravity on the data sheet.

13. % water - Use Carl Fisher method to determine % water.

B. DOCUMENTATION

1. Highlight all acceptable data on data sheet with a yellow highlighter. Draw a single line through any unacceptable data and provide a written explanation for its unacceptability.

2. Data is validated by laboratory personnel. Validation sheets are attached to raw data sheets and filed.

3. Make all necessary entries in the Standard Preparation Logbook including date of preparation, analyst's initials, and notation of any unusual occurrences or observations.

XI. REFERENCES

A. Standard Methods for the Examination of Water and Wastewater, 17th Edition (1989). Method 4500.

QUALFORM.XLS

Waste classification Qualitative

Date: _____
Time: _____
Analyst: _____
Reviewed: _____

Sample Number	% Solids	% Liquid	Color	Viscosity	Phase Layering	Pumpability	PH	Reactive Cyanide	Reactive Sulfide	Oxidizer	Flash Point	Specific Gravity	% Water

pace
INCORPORATED
THE ASSURANCE OF QUALITY

COPY #8

STANDARD OPERATING PROCEDURE

The Determination of Specific Aromatic Compounds and Gasoline Range Organics in Water

SOP NUMBER	MN-O-427-B
AUTHOR	Dennis Seeger
EFFECTIVE DATE	August 10, 1994
SUPERSEDES	MN-O-427-A

APPROVAL

Dennis R Seeger 8/17/94
Section Supervisor Date

Melvin D Rozeboom 8/18/94
Department Manager Date

08/18/94
Quality Assurance Officer Date

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MN-O-427-B

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Tables I-VI

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I. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to define a purge and trap gas chromatographic method for analysis of 10 individual compounds and total hydrocarbons/gasoline range organics (THC/GRO) in drinking water, ground water, and wastewater.

II. SCOPE/APPLICATION

A. CONCENTRATION RANGES

1. All of the ranges of the compounds start at their particular MDL (as determined by 40 CFR136, Appendix B, July 1, 1987) and a majority end at 500 ppb for individual compounds and 7800 ppb for THC/GRO. The concentration ranges are listed in Table III.

B. METHOD DETECTION LIMITS

1. The method detection limit (MDL) is the minimum concentration of a compound that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects; therefore, quantitation limits have been set. The quantitation limits are higher than MDL and have been chosen to account for contamination from the sample preparation area and for some inherent instrument and matrix effects.

C. INTERFERENCES

1. Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap may cause contamination problems. The analytical system must be demonstrated to be free from contamination by running method blanks under the condition of analysis.

2. Samples can be contaminated by diffusion of volatile organic compounds (i.e., freons and methylene chloride) through the sample vial septum or between the vial and septum interface. A sample blank prepared with organic-free water and carried to the site with the sample vials is used to check for this contamination.

3. Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Rinsing the sample loop or the sample loading syringe twice with organic-free water between samples prevents cross-contamination during sample loading. Analyses of organic free water

are used to verify sparge cleanliness following highly contaminated samples.

D. HAZARDS AND PRECAUTIONS

1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available (i.e., gloves, lab coats, goggles, and masks). Reference files of OSHA regulations and MSDS's are available to all personnel involved in the analysis. Additional references to laboratory safety have been identified and are available for inspection by the analyst.

2. Benzene has been tentatively classified as known or suspected human or mammalian carcinogen. Primary standards of this toxic compound should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when an analyst handles high concentrations of this toxic compound.

III. RESPONSIBILITY

A. PERSONNEL

1. All personnel are responsible for adherence to the SOP.

2. All personnel are responsible for notifying the section supervisor/manager of any required revisions to the SOP.

B. DEPARTMENT SUPERVISOR/MANAGER

1. Supervisors/Managers are responsible for ensuring adherence to this SOP.

2. Supervisors/Managers are responsible for performing an annual review of the SOP.

C. QUALITY ASSURANCE OFFICER (QAO)

1. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.

2. The QAO is responsible for ensuring that all revisions to the SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control for this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revision will be incorporated.

C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

This SOP will be issued to the Organic Chemistry Manager, the Section Supervisor, Corporate QAO, Regional QAO, and any other areas deemed appropriate by Regional QAO.

VI. SUMMARY OF METHOD

A. ANALYTES

1. The 12 volatile organic compounds are listed in Table I.

2. Gasoline Range Organics (GRO) or total hydrocarbon (CA LUFT Method.)

B. MATRIX

1. This method is appropriate for analyzing drinking water, ground water, and wastewater.

C. DESCRIPTION

1. Volatile organic compounds are volatilized by bubbling an inert gas through a 5 ml water sample. The vapor is then swept through a sorbent tube where the volatiles are trapped. When the purging is complete, the trap is heated and backflushed with inert gas to desorb the volatiles onto a chromatographic column. A temperature program is used in the gas

chromatographic system to separate the volatiles before detection with a photoionization detector and then a flame ionization detector connected in series.

VII. APPARATUS AND MATERIALS

A. GLASSWARE AND EQUIPMENT

1. Sampling Equipment: 40-ml vial, Teflon-faced silicone septum, screw cap with hole in center. Detergent wash vial and septum, then rinse with tap and organic-free water, and dry at 105° before use.

2. Syringes: 5-mL glass hypodermic with Luerlock tip.

3. Microsyringes: 10-uL, 25-uL, 100-uL and 250-uL.

4. Bottle: 15-mL, crimp top, with Teflon cap liner.

5. Balance: analytical, capable of accurately weighing 0.0001 gram.

6. Volumetric flasks: 5, 10, 25 and 50 mL Class A, with ground-glass stoppers.

B. INSTRUMENTS

1. Gas chromatographs

   a. Hewlett Packard 5890 and 5890 Series II GC's are used with temperature programing. VG data systems are used for measuring peak areas.

2. Purge and Trap System:

   a. (System I) O.I. Model MPM-16 (multi purging module) and an O.I. 460 sample concentrator.

   b. (System II) 2 O.I. 4551 (loop sampling module) and an O.I. 4460A sample concentrator with an O.I. SIM (STANDARD INJECTION MODULE) for addition of internal standard.

   c. (System III) Tekmar ALS (10 Sparge autosampler) and LCS-2 sample concentrator.

3. Detectors

   a. Systems I and II O.I. 4430 PID and HP FID

      1) Detector temperature Fid is 250°C PID is 230°C.

      2) Detector ranges and lamp intensity are adjusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

   b. System III - O.I. 4450 PID/FID Tandem detectors

      1) Detector temperature is 250°C.

      2) Detector ranges and lamp intensity are adusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

4. Column Rt_x-1 fused silica capillary column - 30 m x 0.53 mm ID, 3.0 um film thickness.

C. REAGENTS

1. Reagent water: water in which there are no interferents at the MDL of the parameters of interest.

   a. A Culligan water pretreatment system is used to deionize tap water. A carbon filter is used to remove organic contamination. This is followed by UV treatment using a Barnstead Organic Pure system in the VOA lab to ensure consistent volatiles removal.

2. Methanol - Purge and trap quality or equivalent.

3. Quality Control Check Sample Concentrate - Available from Macro Scientific or from another external source.

4. Working Standard Solutions

   a. Concentrations of mixtures and standards appear in Table II.

7. Internal Standard and Surrogate Standard Solution

   a. A stock solution of 1-Chloro-4-fluorobenzene is prepared by filling 10-mL volumetric flasks with about 9 milliliters of methanol, and

adding the reference material (50 uL) to the methanol.

b. The flask is diluted to volume, stoppered, and then mixed by inverting three times.

c. The stock standard solution is transferred into an amber bottle. The bottle is sealed with a mininert valve and stored at -10◦C.

d. Fluorobenzene is prepared similarly for use as a surrogate standard to be spiked in all analyses (10 uL into 5 mL).

e. Systems I and III - a working standard solution is prepared by adding the stock internal standard into methanol. The surrogate standard, is added to the same solution and this solution is spiked in all analyses. System II - a working internal standard solution is prepared in the same manner and loaded into the SIM (Standard Injection Module). A separate surrogate standard solution is prepared and spiked into the 40 mL vials before analysis.

8. Matrix Spike Solution

a. A spiking solution is prepared in methanol that contains the 12 analytes, each at 100 ug/lg using the procedures outlined in Section XII.

9. Solution Verification

a. Solutions will be validated against working standards before their initial use and within seven days before subsequent usage. The recovery of the solution must be greater than the lower warning limit on the X control chart for each control analyte.

VIII. SAMPLE HANDLING AND STORAGE

A. Samples are collected in 40-mL glass sample vials containing 200 uL of concentrated HCL as preservative to reduce pH of sample to <2. They are filled in such a manner that no air bubbles pass through the sample as the bottle is being filled. If the sample contains free or combined chlorine, add 10 mg of sodium thiosulfate to the sample. EPA method 330.4 or 330.5 may be used for the measurement of residual chlorine. The vial is sealed with a screw cap and a Teflon-faced septum in such a manner that no air bubbles are trapped in it.

B. The samples must be refrigerated at 4 $\pm$ 2 degrees from the time of collection.

C. Samples must be analyzed within 14 days.

IX. CALIBRATION

A. METHOD START-UP AND VALIDATION

1. To demonstrate the capability of the laboratory to generate valid data, the following steps need to be performed.

   a. Calibration standards are analyzed at 5 concentrations.

   b. A calibration curve is established for each compound, THC, and GRO.

   c. The average % spike recovery (R) and the standard deviation % (S) are calculated for the replicates. The calculated R and S values are compared to EPA literature and/or any other literature values available. The upper and lower control limits are calculated at $\pm$ 2 times the standard deviation. The upper and lower control limits and the average % recovery are utilized to construct control charts for the ongoing quality control.

   d. The method detection limit is calculated by analyzing seven replicates prepared in blank water at 1 to 5 times higher than the estimated detection limit.

   e. Method detection levels are calculated according to 40 CFR 136, Appendix B (July 1, 1987).

   f. The data are evaluated and, if acceptable, the method can be utilized on a routine basis. Any changes in laboratory preparation or chromatography that may effect the recovery or detection of the compounds requires that this entire section be repeated.

B. INITIAL CALIBRATION

1. Monthly Standard Preparation (See Section VII-C)

2. Instrument Calibration

   a. Initial calibration ideally takes place after new stock standards are made. This may occur at varying frequencies, depending on the compound responses.

b. Using Working Standards, a 5 point calibration curve for each compound of interest is built from the PID response at the concentrations listed in Table III.

c. The calibration curves for the individual compounds are constructed utilizing the Internal Standard calculation procedure as shown in Section IX-B-3. Retention time windows must be established as follows:

1) The retention time shift of the internal standards is verified. The retention time shift between the initial and subsequent standards must be less than 2.0%. If this is not met, continue injecting replicated standards to meet this criterion.

2) The standard deviation of the absolute retention times is calculated for each analyte of interest.

3) The standard deviations determined in 2. shall be used to determine the retention time windows for a particular run sequence. Plus or minus three times the standard deviations in 2 is applied to the retention times of each analyte of interest (from the daily calibration check). This range of retention time defines the retention time window for the compound of interest.

4) In cases where the retention time window is less than 0.01 minutes, use +/- 1.0% of the retention time of the daily calibration check standard to define the retention time window.

d. The response factor for each compound is calculated by the data system for each level of calibration. These factors define the calibration curve for each compound of interest.

e. Calibration curves for GRO and THC are built from the FID response of the appropriate standards at the concentrations listed in Table V. Response factors are calculated from the total area f the standards over the elution times in Table I, using the external standard method of quantitiation (RF = $Area_{std}/Amt_{std}$). The average from the five standard levels is used for quatitation of continuing calibration, QC and sample analyses.

3. Analysis of Calibration Data

a. Tabulate peak height or area responses against concentration for each compound and internal standard and calculate response factors (RF) for each compound by using this equation:

$$RF = \frac{As(C_{IS})}{A_{IS}(C_S)}$$

Where: A_S = response for parameter of concern
A_{IS} = response for Internal Standard
C_S = concentration of parameter of concern
C_{IS} = concentration of Internal Standard

b. If the relative standard deviation (RSD) for the response factors is <20%, the RF can be assumed to be invariant and the average RF can be used for calculations. The results can also be used to plot a calibration curve of response ratios:

$$\frac{As}{A_{IS}} \quad \text{vs. RF}$$

C. DAILY CALIBRATION

1. Standard Preparation

a. System I - Daily standards (midpoint concentrations of the calibration curve) are prepared by carefully adding 10 uL of the working standards and 12.5 uL of the internal standard solution to a 5-mL Leurlock syringe containing 5 mL of organic-free water.

b. System II - Daily standards (midpoint concentrations of the calibration curve) are prepared by carefully adding 21.5 uL of the working standards and 12.5 uL of the surrogate standard solution to a 42-mLsample vial containing organic-free water.

2. Instrument Calibration

a. After the standards have been run, and are in control, a laboratory blank is analyzed to check the analytical system for interferences.

b. The blank must contain less than the quantitation level of each analyte of interest before sample analysis can start (See Section XII).

c. After calibration has been completed and the system is free of interferences, sample analysis can start.

3. Calibration Data Analysis

a. 90% of the daily standard recoveries must be between three standard deviations of a mean recovery calculated for each compound over ten or more runs. If the system is not in control, a recalibration is performed at 5 concentration levels for the appropriate compounds.

4. Calibration Check Standards

a. A spiked solution containing the parameters to be tested is prepared in organic free water. The spike solution is made by carefully adding working standards to a 5-mL Leurlock syringe containing 5 mL of organic-free water. The results must fall in the range of 3 times the standard deviation of an average recovery calculated for each compound over ten or more runs. The limits are updated by the PACE QA staff.

X. PROCEDURE

A. LOADING SAMPLES

1. System I and III - The sample vial is opened and slowly drawn up slightly greater than 5 mL of sample. The volume is adjusted to 5 mL exactly. If a dilution is required,. the necessary sample volume is spiked into blank water to a 5 mL volume.

2. System I - A working standard is prepared by adding the stock standard into this solution is spiked in all analyses.

   System II - The original zero headspace sample vial is spiked with 10 μL of surrogate standard and placed into the autosamper tray.

3. m- and p-xylene coelute. This peak and o-xylene are added together and total xylenes are reported.

B. TRAP CONDITIONS

1. Purge 11 minutes (40 mL/minute of Helium)

Desorb 2 minutes at 180◦C
Bake approximately 15:00 minutes at 200◦C.

C. GAS CHROMATOGRAPHY

1. Detectors

a. System I O.I. 4450 PID/FID Tandem detectors

1) Detector temperature is 250°C

2) Detector ranges and lamp intensity are adusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

b. System II O.I. 4430 PID and HP FID

1) Detector temperature Fid is 250°C PID is 230°C.

2) Detector ranges and lamp intensity are adjusted to provide appropriate sensitivity at the MDL and linearity through the calibration range.

2. Column

a. Restek Rtx-1 fused silica capillary column
30m x 0.53 mm ID, 3.0 um film thickness
Column flow: ~10 mL/minute of Helium
Initial temperature: 40◦C; hold for 2 minutes
Rate: 5◦C/minute to 100◦C
Rate B: 20◦C/minute to 220◦C
Final Hold: 5 minutes

D. TROUBLESHOOTING

1. Routine maintenance that is performed does not prevent all problems associated with volatile organic analyses. Equipment malfunctions and samples with very high concentrations can cause a variety of problems that are difficult to diagnose. Each problem may require a combination of corrective actions before acceptable data may be generated.

XI. CALCULATIONS

A. Calculations are performed by the internal standard procedure utilizing 1-Chloro-4-fluorobenzene as the internal standard for the individual aromatics analyses.

B. The equations used to calculate the absolute amount of a component (y) are:

1. For a single level calibration the equations are of the form:

$$RRF_{(y)} = \frac{\text{Area (y)} * \text{Amount (I)}}{\text{Amount (y)} * \text{Area (I)}}$$

Where, y = Any calibrant peak or group of peaks
I = An Internal Standard peak
RRF = The relative response factor for peak y.
Area = The peak area of calibrant y or Internal Standard I in the standard.
Amount = The amount of y or I in the standard.

2. Then,

$$\text{Amount (y)} = \frac{\text{Area (y)} * \text{Amount (I)} * \text{Dilution Factor}}{\text{Area (I)} * \text{RRF(y)}}$$

Where, Area = The peak area or height of y or I in the sample.
Amount = The amount of I in the sample.

3. The actual concentrations of sample components are calculated by the data system using the equations of the best fit of straight line through the points of the initial calibration and zero.

4. The calibration plot for THC/GRO is constructed similarly, using the area sum for all of the components of the THC/GRO standard from the FID. The THC/GRO concentration is a comparison of the total peak area from the sample between the MTBE and naphthalene retention times to the linear plot through zero of the THC/GRO calibration standards. This concentration si calculated by the data system.

XII. QUALITY CONTROL

A. Duplicate spikes are processed approximately one in every twenty samples to monitor the performance of the gas chromatographic system. The spikes are prepared by adding 10 uL of the matrix spike solution to 5 mL of DI resulting in a concentration of 100 ug/L for each analyte (200 ug/L for m/p-xylenes). Spike results are compared to PACE control limits (which are $\pm$ 3 times the standard deviation of an average recovery calculated for each compound over 20 or more

runs). Corrective actions are taken if the recoveries fall outside the limits specified.

B. External, separate source check standards are run after each initial calibration to verify the ability to generate accurate date. Quarterly in-house standards are used to evaluate the performance of the system and the accuracy of the calibration curves. Standards are compared to PACE control limits. Corrective actions are taken if the recoveries are outside of those limits.

C. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that all glassware and reagents are interference free.

D. PRECISION AND ACCURACY DATA REVIEW

1. Replicate spiked samples are analyzed every 20 samples along with a check standard (spiked method blank) to monitor the performance of the gas chromatographic system. The data are evaluated according to the flowchart in Figure IX-3.

   a. Samples and spikes are analyzed and the data are calculated and recorded on the worksheets.

   b. The spike data are in control if 90% of the recoveries are between 3 standard deviations of an average recovery calculated for each compound over about ten runs. If the data are acceptable, QC data are recorded and the sample data are reported.

   c. If the sample spike data are out of control, the check standard is evaluated. If that is within limits, the sample spike data for the compound in question are documented as "sample spike out of control due to matrix effects, check standard is in control." QC with appropriate comments is documented and sample data are reported.

   d. If the check standard data are also out of control, analysis must cease until the problem is corrected and documented. All samples since the last in-control situation are then re-analyzed.

XIII. REFERENCES

A. "Determination of Volatile Organics in Water by Purge and Trap Method", Method 465-D, Minnesota Department of Health.

B. Federal Register, Vol. 44, No. 231, Thursday, Nov. 29, 1979.

C. Federal Register, Vol. 44, No. 233, Monday, Dec. 3, 1979.

D. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," Method 502.1, EPA #600/4-81-059.

E. Federal Register, Vol. 49, No. 209, Friday, Oct. 26, 1984.

F. 40 CFR Part 136, Appendix B, July 1, 1987.

TABLE I
Approximate Retention Times of
Analytes of Interest

	PID I	FID I
MTBE	2.04	
Benzene	3.45	
Toluene	6.36	
Ethyl benzene	9.53	
m-xylene > coelute	9.85	
p-xylene	9.85	
o-xylene	10.59	
1,3,5-Trimethyl benzene	13.23	
1,2,4-Trimethyl benzene	14.04	
Fluorobenzene (surrogate)	3.71	
Naphthalene	17.79	
1-Chloro-4-Fluorobenzene (ISTD)	8.65	
THC		1.25 - 20.05
GRO		1.95 - 17.90

TABLE II

Standard Preparation Concentration

Compound	Initial Conc. ug/mL	Final Conc. ug/mL
BTEX Calibration Check Std. (E)		
Benzene	NEAT d = 0.8787	200
Toluene	NEAT d = 0.866	200
Ethyl benzene	NEAT d = 0.866	200
m-xylene	NEAT d = 0.8684	100
p-xylene	NEAT d = 0.8104	100
o-xylene	NEAT d = 0.8801	200
1,3,5-TMB	NEAT d = 0.8761	100
1,2,4-TMB	NEAT d = 0.8637	100
BTEX Calibration Check Std. (H)		
Benzene	200	50
Toluene	200	50
Ethyl benzene	200	50
m-xylene	100	25
p-xylene	100	25
o-xylene	200	50
1,3,5-TMB	100	25
1,2,4-TMB	100	25
BTEX QC Spike (E)		
MTBE	1000	200
Benzene	1000	200
Toluene	1000	200
Ethyl benzene	1000	200
m,p,o-xylene	1000	200 (ea.)
1,3,5-TMB	1000	200
1,2,4-TMB	1000	200

TABLE II (Continued)

Standard Preparation Concentration

Compound	Initial Conc. ug/mL	Final Conc. ug/mL
BTEX QC Spike (H)		
MTBE	1000	40
Benzene	1000	40
Toluene	1000	40
Ethyl benzene	1000	40
m,p,o-xylene	1000	40 (ea.)
1,3,5-TMB	1000	40
1,2,4-TMB	1000	40
THC Calib/Spike Std. (H)		
Unleaded gas	780,000	780 ug/mL
THC Calib/Spike Std. (E)		
Unleaded gas	780,000	7800

TABLE III

Concentration of Compounds in Calibration Curve ug/L

	Level 1	Level 2	Level 3	Level 4	Level 5
Systems I and III					
Benzene	2	50	100	300	500
Toluene	2	50	100	300	500
Ethyl benzene	2	50	100	300	500
m-Xylene	2	50	100	350	500
p-Xylene	2	50	100	350	500
o-Xylene	2	50	100	300	500
1,3,5-Tri-methylbenz	2	50	100		
1,2,4-Tri-methylbenz	2	50	100		
MTBE	2	50	100	300	500
Hexane	16.5	66	132	396	660
System II					
B	2	10	50	100	200
T	2	10	50	100	200
E	2	10	50	100	200
MX	2	10	50	100	200
PX	2	10	50	100	200
OX	2	10	50	100	200
135	2	10	50	100	200
124	2	10	50	100	200
MTBE	2	10	50	100	200
Hexane	2.64	6.6	66	132	264

TABLE IV

Parameter	Storet Number	CAS Number
Benzene	34030	71-43-2
Toluene	34010	108-88-3
Ethyl benzene	4371	100-41-4
m-xylene		108-38-3
p-xylene		106-42-6
o-xylene		95-47-6
MTBE		1634-04-4
Hexane		
1,3,5-TMB		108-67-8
1,2,4-TMB		95-63-6

TABLE V

THC Calibration Curve (ug/L)

	Level 1	Level 2	Level 3	Level 4	Level 5
Systems I and III	39	195	780	3900	7800
System II	39	195	7800	3900	--

GRO Calibration Curve (ug/L)

	Level 1	Level 2	Level 3	Level 4	Level 5
Systems I and III	20	500	1000	3000	5000
System II	20	100	500	1000	2000

TABLE VI

Method Detection Limits, Quantitation Limits

Parameters	Quantitation Limit in ug/L
Benzene	1.0
Toluene	1.0
Ethyl benzene	1.0
m-xylene	1.0
p-xylene	1.0
o-xylene	1.0
1,3,5-TMB	1.0
1,2,4-TMB	1.0
MTBE	4.0

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ATTACHMENT A

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR ANALYSIS OF

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD)

AND POLYCHLORINATED DIBENZOFURANS (PCDF)

Multi-Media, Multi-Concentration

Document Number DFLM01.0

Including Revision DFLM01.1 (September 1991)

STATEMENT OF WORK

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EXHIBIT B: REPORTING AND DELIVERABLES REQUIREMENTS

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EXHIBIT D: ANALYTICAL METHODS

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EXHIBIT F: CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES

EXHIBIT G: GLOSSARY

EXHIBIT A

SUMMARY OF REQUIREMENTS

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SECTION I

GENERAL REQUIREMENTS

A. Purpose of the Statement of Work

Under the legislative authority granted to the U.S. Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA develops standardized analytical methods for the measurement of various pollutants in environmental samples from known or suspected hazardous waste sites. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) are among the pollutants that are of concern to EPA at such sites. PCDDs/PCDFs are believed to be among the most toxic organic compounds ever released into the environment.

With the advent of the Superfund program in 1980, EPA required the analyses of many more environmental samples than could possibly be handled through its own laboratories. Therefore, EPA elected to procure analytical services through commercial laboratories and established the Contract Laboratory Program (CLP) as a means of obtaining standardized analyses on a long-term firm, fixed-price basis. This Statement of Work (SOW) provides a technical and contractual framework for laboratories to apply EPA analytical methods to the analysis of PCDDs/PCDFs in environmental samples. The SOW provides not only the analytical methods to be applied, but also the specific technical and contractual requirements by which EPA will evaluate the data.

B. General Requirements

This SOW provides an analytical method for the isolation, detection and quantitative measurement of PCDDs and PCDFs in water, soil, fly ash, and chemical waste samples such as oil, sludge, and stillbottoms. There are 210 possible PCDD/PCDF isomers, and the methods were developed for the analysis of the 17 PCDDs/PCDFs that bear chlorine atoms in the 2,3,7 and 8 positions of their respective structures. These 17 compounds, termed the "2,3,7,8-substituted PCDDs/PCDFs," are those PCDDs/PCDFs that, based on structure activity relationships, are believed to pose the greatest risks to human health and the environment. The SOW also requires determination of the total concentrations of all PCDDs or PCDFs in a given level of chlorination (i.e., Total TCDD, Total PecDD, etc.), although complete chromatographic separation of all 210 PCDDs/PCDFs is not possible under the instrumental conditions described in the method.

The SOW requires the calculation of the 2378-TCDD toxicity equivalence using the procedures described in the "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs)," March 1989, (EPA 625/3-89/016). To aid in the assessment

of risks associated with exposure to these compounds, a factor is assigned to each of the 17 2,3,7,8-substituted PCDDs and PCDFs that relates the toxicity of that isomer to a concentration of the most toxic isomer, 2378-TCDD. The concentrations of any isomers that are detected in an environmental sample can then be adjusted by the toxicity equivalency factor (TEF) and summed, yielding a concentration of 2378-TCDD with an equivalent toxicity.

Because isomer specificity for all 17 2378-substituted PCDDs/PCDFs may not be achieved using a single gas chromatographic column, the SOW requires analysis of sample extracts on a second column when the TEF-adjusted concentration exceeds a specified level. This level varies by sample matrix.

The sample preparation procedures in the SOW use matrix-specific extraction techniques and a single set of cleanup techniques. The sensitivity of this method is dependent upon the level of interferents within a given sample. Interferents co-extracted from the sample may vary considerably from source to source, depending on the origin of the sample and the matrix type. PCDDs and PCDFs are often associated with other chlorinated compounds such as PCBs and polychlorinated diphenyl ethers which may occur at concentrations several orders of magnitude higher than that of the analytes of interest and may cause interference problems.

The samples to be analyzed by the Contractor are from known or suspected hazardous waste sites and may contain hazardous organic and/or inorganic materials at high concentration levels. The Contractor should be aware of the hazards associated with the handling and analysis of these samples. The Contractor is responsible for taking all necessary measures to ensure the health and safety of its employees.

The Contractor must be aware of the importance of maintaining the integrity of the data generated under the contract, as data may be used to make decisions regarding public health and environmental welfare. In addition, the data may be used in litigation against potentially responsible parties in the enforcement of Superfund legislation.

C. Applications and Limitations of the Statement of Work

This SOW is designed as part of the documentation for a contract between EPA and a commercial laboratory performing analyses in support of EPA Superfund programs. The resulting data may be used by EPA for a variety of purposes, such as determining the nature and extent of contamination at a hazardous waste site, assigning administrative priority to such sites based on the risk of exposure, determining appropriate cleanup actions, and determining when remedial actions are complete.

The methods described in this SOW are designed for the analysis of specific analytes in specific environmental matrices and over a limited concentration range. However, this SOW is not suitable for all analytical situations and should not be applied to matrices, analytes,

or concentration ranges for which it was not intended. Similarly, the contractual requirements embodied in the SOW apply only to those analyses performed by commercial laboratories through the CLP. Therefore, other organizations wishing to procure analytical services using the methods in this SOW are advised to develop a contracting mechanism that explicitly includes both the technical and contractual requirements contained in this SOW.

D. Organization of the Statement of Work

Exhibit A provides an overview of the SOW and its general requirements. Exhibit B contains a description of the reporting and deliverables requirements, in addition to the data reporting forms and the forms instructions. Exhibit C specifies the target compound list for this SOW with the contract-required quantitation limits for sample matrices. Exhibit D details the specific analytical procedures to be used with this SOW and resulting contracts. Exhibit E provides descriptions of required quality assurance/quality control (QA/QC) standard operating procedures and procedures used for the evaluation of analytical methodologies, QA/QC performance, and the reporting of data. Exhibit F contains chain-of-custody and sample documentation requirements which the Contractor shall follow. To ensure proper understanding of the terms utilized in this SOW, a glossary can be found in Exhibit G.

SECTION II

SPECIFIC REQUIREMENTS

A. Sample shipments to the Contractor's facility will be scheduled and coordinated by the EPA CLP Sample Management Office (SMO) acting on behalf of the Administrative Project Officer. The Contractor shall communicate with SMO personnel by telephone, as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed.

If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Traffic Reports not with shipment, sample and Traffic Report numbers do not correspond), the Contractor shall immediately contact SMO for resolution. The Contractor shall immediately notify SMO regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall notify SMO in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

B. Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique EPA Case number assigned by SMO. A Case signifies a group of samples collected at one site or geographical area over a finite time period and includes one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

A Case consists of one or more Sample Delivery Group(s). A Sample Delivery Group (SDG) is defined by the following, whichever is most frequent:

- Each Case of field samples received, OR
- Each 20 field samples within a Case, OR
- Each 14 calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

Samples may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples a second SDG, and all fly ash samples in a third SDG), at the discretion of the laboratory. Such assignment must be made at the time the samples are received and may <u>not</u> be made retroactively.

All data for all samples in a SDG are due concurrently to all data recipients as stipulated in the Delivery Schedule in Exhibit B, Section I. Data for all samples in a SDG must be submitted together (in one package) in the order specified in Exhibit B. The SDG number is the EPA sample number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number

shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. The SDG number is reported on all data reporting forms.

The SDG receipt date is the day the last sample in the SDG is received. Data for all samples in the SDG are due as stipulated in the Delivery Schedule in Exhibit B.

The Contractor is responsible for identifying each SDG as samples are received, through proper sample documentation (see Exhibit B) and communication with SMO personnel.

C. Each sample received by the Contractor will be labeled with an EPA sample number and will be accompanied by a Traffic Report bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition for each sample container.

The Contractor shall submit signed copies of Traffic Reports for all samples in a SDG to SMO within three calendar days following receipt of the last sample in the SDG. Traffic Reports shall be submitted in SDG sets (i.e., all Traffic Reports for a SDG shall be clipped together) with a SDG Cover Sheet containing information regarding the SDG, as specified in Exhibit B.

D. The Contractor shall use EPA Case numbers (including SDG numbers) and EPA sample numbers to identify samples received under this contract both verbally and in reports/correspondence.

E. Samples will be shipped routinely to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.

F. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

G. The Contractor shall prepare, extract, cleanup extracts, and analyze samples according to the analytical procedures outlined in Exhibit D. The Contractor shall also adhere to the QA/QC requirements specified in Exhibit D, including the analyses of calibration standards, blanks, spiked samples, duplicate analyses, etc., as specified in the exhibit.

H. EPA has provided the Contractor with forms for the reporting of data (Exhibit B). The Contractor shall be responsible for completing and returning analysis data sheets in the format specified in the Contract Performance/Delivery Schedule.

Use of formats other than those designated by EPA will be deemed as noncompliance. Such data are unacceptable. Resubmission in the specified format will be required at no additional cost to the Government.

I. The Contractor shall have sufficient gas chromatograph/mass spectrometer/data system (GC/MS/DS) capability to meet all the terms and conditions of the EPA contract. The Contractor shall maintain, at a minimum, all analytical equipment allocated for this contract at the time of contract award. (See Section III for instrumentation requirements.)

J. Certain samples may require sample reruns (reextraction and/or reanalysis) due to either problems with the sample matrix or Contractor insufficiencies. Sample reruns may be considered either as billable or nonbillable as defined in Exhibit D. For the purposes of this contract, the term "automatic rerun" shall signify only billable rerun analyses.

K. EPA may provide standards for use in analyses performed under the contract, subject to availability. However, the SOW identifies specific solutions that must be purchased from commercial sources, and will not be provided by EPA. When provided, EPA-supplied materials are intended for use only on EPA samples, and the Contractor may be asked to demonstrate during EPA on-site evaluations that separate standards are maintained for non-EPA work. The Contractor will be instructed how and where to request EPA standards at time of contract award. The Contractor is responsible for ensuring that all required standards are available at the Contractor's facility before accepting any samples from EPA.

L. The Contractor shall respond within seven days to requests from data recipients for additional information or explanations that result from the Government's inspection activities.

M. The Contractor shall preserve all sample extracts after analysis in bottles/vials with Teflon-lined septa and shall maintain stored extracts in the dark at room temperature. The Contractor is required to retain the sample extracts for 365 days after data submission. During that time, the Contractor shall submit the extracts within seven days after request, as specified in the Contract Performance/Delivery Schedule.

N. The Contractor shall adhere to chain-of-custody procedures described in Exhibit F. Documentation, as described therein, shall show that all procedures are being strictly followed. This documentation shall be reported as the Complete SDG File (see Exhibit B).

SECTION III

DETAILED TECHNICAL AND MANAGEMENT REQUIREMENTS

The Contractor shall have the following technical and management capabilities. For those technical functions that require a minimum educational degree and experience, an advanced degree in chemistry or any scientific/engineering discipline (e.g., Master's or Doctorate) does not substitute for the minimum experience requirements.

The Contractor shall notify in writing the Technical Project Officer and the Administrative Project Officer of any changes affecting key personnel listed in this section within 14 days of the change. The Contractor shall provide a detailed resume to the Technical Project Officer, Administrative Project Officer, and EMSL-LV for the replacement personnel within 14 days of the Contractor's assignment of the personnel. The resume shall include position description of titles, education (pertinent to this contract), number of years of experience (pertinent to this contract), month and year hired, previous experience and publications.

A. TECHNICAL CAPABILITY

1. Technical Functions

a. GC/MS Laboratory Supervisor

(1) Responsible for all technical efforts of the GC/MS laboratory to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience with dioxin and furan analyses, including at least one year of supervisory experience.

b. Sample Preparation Laboratory Supervisor

(1) Responsible for all technical efforts of sample preparations to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience, including at least one year of supervisory experience.

c. Quality Assurance Officer

(1) Responsible for overseeing the QA aspects of data and reporting directly to upper management to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory.

d. GC/MS Operator Qualifications

One year of experience in operating and maintaining GC/MS/DS used for selected ion monitoring (SIM) with a Bachelor's degree in chemistry or any scientific/engineering discipline, or in lieu of the Bachelor's degree, three years of experience in operating and maintaining the GC/MS and interpreting GC/MS SIM data.

e. Extract Cleanup Expert Qualifications

One year of experience in extract cleanup with a Bachelor's degree in chemistry or any scientific/engineering discipline, or in lieu of the Bachelor's degree, three years of experience in sample extraction and cleanup.

f. Extraction/Concentration Expert Qualifications

(1) Education:

Minimum of high school diploma and a college-level course in general chemistry.

(2) Experience:

Minimum of one year of experience in extraction/concentration.

g. Technical Staff Redundancy

The bidder shall have a minimum of one chemist available at any one time as a back-up technical person with the following qualifications to ensure continuous operations to accomplish the required work as specified by the EPA contract.

(1) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience: Minimum of one year in each of the following areas -

- o GC/MS operation and maintenance using selected ion monitoring.
- o Dioxin/furan analysis.
- o Sample extraction and cleanup.

2. Facilities

The adequacy of the facilities and equipment is of equal importance as the technical staff to accomplish the required work as specified by the EPA contract.

a. Sample Receipt Area

Adequate, contamination-free, well-ventilated work space provided with chemical resistant bench top for receipt and safe handling of EPA samples.

b. Storage Area

Sufficient space to maintain unused EPA sample volume for 60 days after data submission and sample extracts for 365 days after data submission. Samples must be stored in an atmosphere demonstrated to be free from all potential contaminants.

c. Sample Preparation Area

Adequate, contamination-free, well-ventilated work space provided with:

(1) Benches with chemical resistant tops, exhaust hoods.

NOTE: Standards must be prepared in a glove box or isolated area.

(2) Source of distilled or demineralized organic-free water.

(3) Analytical balance(s) located away from draft and rapid change in temperature.

3. Instrumentation

At a minimum, the Contractor shall have the following instruments operative and committed for the full duration of the contract.

a. Primary Instrument Requirements

(1) GC/MS equipped with GC to MS interface capable of extending a 60 meter by 0.32 mm ID, bonded DB-5 (or equivalent), fused silica capillary column into the MS ion source.

(2) GC/MS computer interfaced by hardware to the MS and capable of monitoring at least 18 selected ions for the duration of the chromatographic analysis.

(3) GC/MS computer equipped with mass storage device for saving all data from GC/MS analyses.

(4) GC/MS computer software capable of searching GC/MS analyses for specific ions and plotting the intensity of the ions with respect to time or scan run.

(5) Magnetic tape storage device capable of recording data for long-term, off-line storage.

b. Secondary Instrument Requirements

The Contractor shall have one back-up instrument, identical to the requirements above, in place and operational at any time. This instrument must be included in the bidder's inventory of equipment. In addition, the Contractor shall have an in-house stock of instrument parts and circuit boards to ensure continuous operation to meet contract-specified holding and turnaround times.

4. Data Handling and Packaging

The Contractor shall have reasonable capacity to submit reports and data packages as specified in Exhibit B. To complete this task, the Contractor shall be required to:

a. Provide space, tables and copy machines to meet the contract requirements.

b. Designate personnel.

B. LABORATORY MANAGEMENT CAPABILITY

The Contractor must have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for EPA contract(s) and to maintain a successful operation. To establish this capability, the Contractor shall designate personnel to carry out the following responsibilities for the EPA contract. Functions include, but are not limited to, the following:

1. Technical Staff

Responsible for all technical efforts for the EPA contract.

2. Project Manager

Responsible for overall aspects of EPA contract(s) (from sample receipt through data delivery) and the primary contact for the Administrative Project Officer and Technical Project Officer.

3. Sample Custodian

Responsible for receiving EPA samples (logging, handling and storage).

4. Quality Assurance Officer

Responsible for overseeing the QA aspects of the data and reporting directly to upper management.

5. Document Control Officer

Responsible for ensuring that all documents generated are placed in the Complete SDG File for inventory and are delivered to the appropriate EPA Region or other receiver as designated by EPA.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

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SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

The following table reiterates the contract reporting and deliverables requirements specified in the Contract Schedule and specifies the distribution that is required for each deliverable. NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Administrative Project Officer (APO) will notify the Contractor in writing of such changes when they occur.

Item	No. Copies	Delivery Schedule	Distribution (1)	(2)	(3)	(4)
A. Updated SOPs	3	60 days after contract award.		X	X	X
*B. Sample Traffic Reports (original)	1	3 days after receipt of last sample in Sample Delivery Group (SDG).**	X			
C. Sample Data Summary Package	1	45 days after receipt of last sample in SDG.	X			
***D. Sample Data Package	2	45 days after receipt of last sample in SDG.	X		X	
****E. Complete SDG File	1	45 days after receipt of last sample in SDG.	X			
*****F. Quality Assurance Plan	3	60 days after contract award and as required in Exhibit E.		As Directed		
G. GC/MS Tapes	Lot	Retain for 365 days after data submission, or submit within 7 days after receipt of written request by APO and/or EMSL-LV.		As Directed		

Item	No. Copies	Delivery Schedule	Distribution (1) (2) (3)
H. Extracts	Lot	Retain for 365 days after data submission, or submit within 7 days after receipt of written request by APO or SMO.	As Directed

Distribution:
(1) Sample Management Office (SMO)
(2) Region-Client (Technical Project Officer (TPO))
(3) Environmental Monitoring Systems Laboratory (EMSL-LV)
(4) National Enforcement Investigations Center (NEIC)

* Copy also required in the Sample Data Summary Package.

** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 14 days or less and not exceeding 20 samples. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that all samples have been delivered. (See Exhibit A for further description.)

*** Concurrent delivery required. Delivery shall be made such that all designated recipients receive the item on the same calendar day.

**** Complete SDG File will contain the original sample data package plus all of the original documents described under Section II, Part E.

***** See Exhibit E for a more detailed description.

NOTE: As specified in the Contract Schedule (G.2 Government Furnished Supplies and Materials), unless otherwise instructed by SMO, the Contractor shall dispose of unused sample volume and used sample bottles/containers no earlier than 60 days following submission of analytical data.

Distribution Addresses:

(1) USEPA Contract Laboratory Program
Sample Management Office
P.O. Box 818
Alexandria, VA 22314

For overnight delivery service, use street address:
300 North Lee Street
Alexandria, VA 22314

(2) USEPA Regions:

SMO, acting on behalf of the APO, will provide the Contractor with the list of addressees for the 10 EPA Regions. SMO will provide the

Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

(3) USEPA Environmental Monitoring Systems Laboratory
P.O. Box 93478
Las Vegas, NV 89193-3478
ATTN: Data Audit Staff

For overnight delivery service, use street address:
944 E. Harmon, Executive Center
Las Vegas, NV 89109
ATTN: Data Audit Staff

(4) USEPA National Enforcement Investigations Center (NEIC)
Attn: CLP Audit Program
Denver Federal Center Building 53
P. O. Box 25227
Denver, CO 80225

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor shall provide reports and other deliverables as specified in the Contract Schedule (Reporting Requirements and Deliverables, F.2). The required content and form of each deliverable are described in this exhibit.

All reports and documentation MUST BE:

- Legible.
- Clearly labeled and completed in accordance with instructions in this exhibit.
- Arranged in the order specified in this section.
- Paginated consecutively in ascending order starting from the SDG Narrative.

If submitted documentation does not conform to the above criteria, the Contractor shall be required to resubmit such documentation with deficiencies corrected, at no additional cost to the Government.

Whenever the Contractor is required to submit or resubmit data as a result of an onsite laboratory evaluation or through an APO/TPO action, the data must be clearly marked as ADDITIONAL DATA and must be sent to all three contractual data recipients (SMO, EMSL-LV and the Region). A cover letter shall be included which describes what data are being delivered, to which EPA Case(s) the data pertain, and who requested the data.

Whenever the Contractor is required to submit or resubmit data as a result of contract compliance screening by SMO, the data must be sent to all three contractual data recipients (SMO, EMSL-LV and the Region). In all three instances the data must be accompanied by a color-coded Cover Sheet (Laboratory Response To Results of Contract Compliance Screening) provided by SMO.

Section III of this exhibit contains forms instructions to assist the Contractor in accurately providing EPA with all required data. Section IV contains copies of the required data reporting forms in EPA-specified formats.

Descriptions of the requirements for each deliverable item cited in Reporting Requirements and Deliverables (Contract Schedule, Section F) are specified in this section. Items submitted concurrently MUST BE arranged in the order listed. Additionally, the components of each item MUST BE arranged in the order presented in this section when the item is submitted. Examples of specific data deliverables not included herein may be obtained by submitting a written request to the APO, stating the information requested and signed by the Laboratory Manager.

A. Quality Assurance Plan and Standard Operating Procedures

See Exhibits E and F for requirements.

B. Sample Traffic Reports

The original Sample Traffic Report (TR) page marked "Lab Copy for Return to SMO" shall be delivered with laboratory receipt information and signed in original Contractor signature, for each sample in the SDG. TRs shall be submitted in SDG sets (i.e., TRs for all samples in a SDG shall be clipped together) with a SDG Cover Sheet attached.

The SDG Cover Sheet shall contain the following items:

- Laboratory name.
- Contract number.
- Sample analysis price - full sample price from the EPA contract.
- Case number.
- List of EPA sample numbers of all samples in the SDG, identifying the first and last samples received and their dates of receipt (LRDs).

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the highest sample number (considering both alpha and numeric designations).

In addition, each TR must be clearly marked with the SDG number, the sample number of the first sample in the SDG (as described in the following paragraph). This information should be entered below the laboratory receipt date on the TR. In addition, the TR for the last sample received in the SDG must be clearly marked "SDG - FINAL SAMPLE."

The EPA sample number of the first sample received in the SDG is the SDG number. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. The SDG number is also reported on all data reporting form (see Section III, Form Instruction Guide).

If samples are received at the laboratory with multi-sample TRs, all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the Contractor must make the appropriate number of photocopies of the TR and submit one copy with each SDG Cover Sheet.

C. Sample Data Summary Package

One Sample Data Summary Package shall be delivered to SMO concurrently with delivery of other required sample data. The Sample Data Summary Package consists of copies of specified items from the Sample Data Package. These items are listed below and are described under Part D, Sample Data Package.

The Sample Data Summary Package shall be ordered as follows and shall be submitted separately (i.e., separated by rubber bands, clips or other means) directly preceding the Sample Data Package. Sample data forms shall be arranged in increasing EPA sample number order, considering both letters and numbers. For example, DBE400 is a lower sample number than DBF100, as E precedes F in the alphabet.

The Sample Data Summary Package shall contain data for samples in one SDG of the Case as follows:

1. SDG Narrative.

2. Completed Forms I (PCDD-1, PCDD-2 and PCDD-3) for all samples. Original and rerun sample data shall be provided on separate forms.

D. Sample Data Package

The Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, blanks, matrix spikes, and duplicate analyses. The Sample Data Package is divided into the three major units described below.

The Contractor shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Contractor may dispose of the package.

1. SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name; Case number; sample numbers in the SDG, differentiating between initial analyses and reanalyses; SDG number; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample reanalyses are submitted, the Contractor shall state in the SDG Narrative for <u>each</u> reanalysis, whether it considers the reanalysis to be billable, and if so, why.

The Contractor must also include any problems encountered, both technical and administrative, the corrective actions taken and the resolutions, and an explanation for all flagged edits (i.e., manual edits) on quantitation lists.

NOTE: If a column is used that has different first and last eluting isomers than the DB-5 column, the Contractor shall fully document, in the SDG Narrative, the order of elution of the isomers and identify the first and last eluting isomers for that particular column for the window defining mix and CC3 solution.

The SDG Narrative shall contain the following statement, <u>verbatim</u>: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by the signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature. Additionally, the SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated. All copies of the SDG Narrative shall be signed in original signature.

2. Traffic Reports

A copy of the TRs submitted in Part A for all of the samples in the SDG shall be delivered. The TRs shall be arranged in increasing EPA sample numbering order, considering <u>both</u> letters and numbers in ordering samples. Copies of the SDG Cover Sheet shall be included with the copies of the TRs.

If samples are received at the laboratory with multi-sample TRs, all the samples on one multi-sample TR may not necessarily be in the

same SDG. In this instance, the Contractor must make the appropriate number of photocopies of the TR so that a copy is submitted with each data package to which the TR applies.

In addition, in any instance where samples from more than one multi-sample TR are in the same data package, the Contractor must submit a copy of the SDG Cover Sheet with copies of the TRs.

3. PCDD/PCDF Data

a. Sample Data - in order by EPA sample number

(1) Target Compound List Results (Form I PCDD-1).

(2) Calculation of the Toxicity Equivalence (Form I PCDD-2).

(3) Second Column Confirmation Summary (Form I PCDD-3).

If the TEF is greater than the limits specified in Exhibit D, analysis on a column capable of resolving all 2378-substituted PCDDs/PCDFs is required.

(4) Selected Ion Current Profile (SICP) for each sample and each analysis of each sample. SICPs must contain the following header information:

- o EPA sample number.
- o Date and time of analysis.
- o GC/MS instrument ID.
- o Lab file ID.

(5) Total Congener Concentration Results (Form II PCDD).

b. Quality Control Data

(1) Spiked Sample Results (Form III PCDD-1) - in order by EPA sample number.

(2) Duplicate Sample Results (Form III PCDD-2) - in order by EPA sample number.

(3) Method Blank Summary (Form IV PCDD) - in order by EPA sample number assigned to the blanks.

(4) Window Defining Mix Summary (Form V PCDD-1) - in order by EPA sample number assigned to the window defining mix.

(5) Chromatographic Resolution Summary (Form V PCDD-2) - in order by EPA sample number assigned to the standard used to evaluate the column resolution.

(6) SICP for each analysis above [b.(1) - (5)]. SICPs must contain the header information described in a. (4) above.

c. Calibration Data

(1) Initial Calibration Data (Form VI PCDD-1 and Form VI PCDD-2) - in order by instrument, if more than one instrument used.

(a) PCDD/PCDF standard(s) SICPs for the initial (five-point) calibration shall be labeled as stated above.

(b) When more than one initial calibration is performed, the data must be arranged in chronological order by instrument.

(2) Continuing Calibration Data (Form VII PCDD-1 and Form VII PCDD-2) - in order by instrument, if more than one instrument is used.

(a) PCDD/PCDF standard(s) SICPs for all continuing calibrations shall be labeled as stated above.

(b) When more than one continuing calibration is performed, the data must be arranged in chronological order, by instrument.

d. Raw Quality Control Data

(1) Blank Data - in order by EPA sample number assigned to the blank. SICPs shall be submitted for each blank analyzed and labeled as above.

(2) Spiked Sample Data - in order by EPA sample number. SICPs shall be submitted for each spiked sample analyzed and labeled as above.

E. Complete SDG File

One Complete SDG File (CSF), including the original Sample Data Package, shall be delivered to the Region concurrently with delivery of the Sample Data Package to SMO and EMSL-LV. The contents of the CSF will be numbered according to the specifications described in Sections III and IV. The Document Inventory Sheet, Form DC-2, is contained in Section IV. The CSF will contain all original documents where possible. No copies will be placed in the CSF unless the originals are bound in a logbook which is maintained by the laboratory. The CSF will contain all original documents specified in Sections III and IV, and Form DC-2.

The CSF will consist of the following original documents in addition to the documents in the Sample Data Package:

1. Original Sample Data Package.

2. A completed and signed Document Inventory Sheet (Form DC-2).

3. All original shipping documents including, but not limited to, the following:

   a. EPA Chain-of-Custody Record.

   b. Airbills.

   c. EPA Traffic Reports.

   d. Sample tags (if present) sealed in plastic bags.

4. All original receiving documents including, but not limited to, the following:

   a. Form DC-1.

   b. Other receiving forms or copies of receiving logbooks.

   c. SDG Cover Sheet.

5. All original laboratory records, not already submitted in the Sample Data Package, of sample transfer, preparation and analysis including, but not limited to, the following:

   a. Original preparation and analysis forms or copies of preparation and analysis logbook pages.

   b. Internal sample and sample extract transfer chain-of-custody records.

   c. Screening records.

   d. All instrument output, including strip charts from screening activities.

6. All other original SDG-specific documents in the possession of the laboratory, including, but not limited to, the following:

   a. Telephone contact logs.

   b. Copies of personal logbook pages.

   c. All hand-written Case-specific notes.

   d. Any other Case-specific documents not covered by the above.

NOTE: All Case-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other SDG-specific documents generated after the CSF is sent to EPA, as well as copies that are altered in any fashion, are also deliverables to EPA (original to the Region, and copies to SMO and EMSL-LV).

If the laboratory does submit SDG-specific documents to EPA after submission of the CSF, the documents should be numbered as an addendum to the CSF, and a revised DC-2 Form should be submitted, or the documents should be numbered as a new CSF, and a new DC-2 Form should be submitted to the Regions only.

F. GC/MS Tapes

The Contractor must store all raw and processed GC/MS data on magnetic tape in appropriate instrument manufacturer's format. This tape must include data for samples, blanks, initial calibrations and continuing calibrations, as well as all laboratory-generated quantitation reports and SICPs required to generate the data package. The Contractor shall maintain a written reference logbook of tape files to EPA sample number, calibration data, standards and blanks. The logbook should include EPA sample numbers and standard and blank IDs, identified by Case and SDG.

The Contractor is required to retain the GC/MS tapes for 365 days after data submission. During that time, the Contractor shall submit tapes and associated logbook pages within seven days after receipt of a written request from the APO or EMSL-LV.

When submitting GC/MS tapes to EPA, the following materials must be delivered in response to the request:

1. All associated raw data files for samples, blanks, matrix spikes, initial and continuing calibration standards, and window defining mix solutions.

2. All processed data files and quantitation output files associated with the raw data files described above.

3. All associated identifications and calculation files used to generate the data submitted in the data package.

4. A copy of the Contractor's written reference logbook relating tape files to EPA sample number, calibration data, standards, blanks and matrix spikes. The logbook must include EPA sample numbers and lab file identifiers for all samples, blanks and standards, identified by Case and SDG.

The laboratory must also provide a statement attesting to the completeness of the GC/MS data tape submission, signed and dated by the Laboratory Manager. This statement must be part of a cover sheet that includes the following information relevant to the data tape submission:

1. Laboratory name.

2. Date of submission.

3. Case number.

4. SDG number.

5. GC/MS make and model number.

6. Software version.

7. Disk drive type (e.g., CDC, PRIAM).

8. File transfer method (e.g., DSD, DTD, FTP, Aquarius).

9. Names and telephone numbers of two laboratory contacts for further information regarding the submission.

G. Extracts

The Contractor shall preserve sample extracts in the dark at room temperature in bottles/vials with Teflon-lined septa. Extract bottles/vials shall be labeled with EPA sample number, Case number and SDG number. A logbook of stored extracts, listing EPA sample numbers and associated Case and SDG numbers, shall be maintained.

The Contractor is required to retain extracts for 365 days following data submission. During that time, the Contractor shall submit extracts and associated logbook pages within seven days following receipt of a written request from the APO or SMO.

SECTION III

FORM INSTRUCTION GUIDE

This section includes specific instructions for the completion of all required forms. These instructions are arranged in the following order:

A. General Information and Header Information

B. PCDD/PCDF Sample Data (Form I PCDD-1, PCDD-2 and PCDD-3)

C. PCDD/PCDF Total Congener Concentration Summary (Form II)

D. PCDD/PCDF Spiked Sample and Duplicate Sample Results (Form III PCDD-1 and PCDD-2)

E. PCDD/PCDF Method Blank Summary (Form IV)

F. PCDD/PCDF Window Defining Mix Summary, Chromatographic Resolution Summary, and Analytical Sequence (Form V PCDD-1, PCDD-2 and PCDD-3)

G. PCDD/PCDF Initial Calibration Data Summary (Form VI PCDD-1 and PCDD-2)

H. PCDD/PCDF Continuing Calibration Data Summary (Form VII PCDD-1 and PCDD-2)

I. Sample Log-In Sheet (Form DC-1)

J. Document Inventory Sheet (Form DC-2)

A. General Information and Header Information

The data reporting forms presented in Section IV have been designed in anticipation of the development of a computer-readable data format. Although a "diskette deliverable" is not a requirement at this time, the design of the data reporting forms have taken such a future requirement into consideration. Therefore, the specific length of each field on the forms is the approximate length that would be included in a data element dictionary, with exceptions made in some instances for additional space on the hardcopy forms for visual clarity.

All characters which appear on the data reporting forms presented in Section IV must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the APO. The names of the various fields and compounds (e.g., "Lab Code," "2378-TCDD") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix: (Soil/Water/Waste/Ash)" must appear, not just "Matrix"). For items appearing on the uncompleted forms (Section IV), the use of uppercase and lowercase letters is optional.

Alphabetic entries made onto the forms by the Contractor shall be in ALL UPPERCASE letters (e.g., "SOIL," not "Soil" or "soil"). If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line. However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms. The only exception would be those underscores at the bottom of a "box" that are intended as a data entry line. (For instance, on Form II, if data must be entered on the last line of the box, it will replace the underscores).

Six pieces of information are common to the header section of each data reporting form. They are Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. Except as noted below for SAS No., this information must be entered on every form and must match on every form.

The "Lab Name" shall be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

The "Lab Code" is an alpha-numeric abbreviation of up to six letters and numbers assigned by EPA to identify the laboratory and aid in data processing. This lab code shall be assigned by EPA at the time a contract is awarded and shall not be modified by the Contractor, except at the direction of EPA. If a change of name or ownership occurs at the laboratory, the lab code will remain the same unless and until the Contractor is directed by EPA to use another lab code assigned by EPA.

The "Case No." is the EPA-assigned Case number associated with the sample and reported on the Traffic Report or sample shipping paperwork.

The "Contract" is the number of the EPA contract under which the analyses were performed.

The "SDG No." is the EPA sample number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services (SAS). If samples are to be analyzed under SAS only and reported on these forms, then enter "SAS No.," and leave "Case No." blank. If samples are analyzed according to the Routine Analytical Services (IFB) protocols and have additional SAS requirements, enter both "Case No." and "SAS No." on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. NOTE: Some samples in a SDG may have a SAS No., while others do not.

The other information common to most of the forms is the "EPA Sample No." This number appears either in the upper right-hand corner of the form, or as the left column of a table summarizing data from a number of samples. When the "EPA Sample No." is entered into the triple-spaced box in the upper right-hand corner of Form I, III or IV, it should be entered on the middle line of the three lines that comprise the box.

All samples, spiked samples, duplicate samples, blanks and standards shall be identified with an EPA sample number. For field samples, spiked samples, and duplicates samples, the EPA sample number is based on the unique identifying number given in the Traffic Report or sample shipping records for that sample.

In order to facilitate data assessment, the following sample suffixes must be used:

XXXXX	-	EPA sample number
XXXXXS	-	Spiked aliquot of sample "XXXXX"
XXXXXD	-	Duplicate aliquot of sample "XXXXX"
XXXXXRE	-	Reextracted and reanalyzed aliquot of sample "XXXXX"
XXXXXDL	-	Diluted analysis of sample "XXXXX"

Form V PCDD-3 requires that all samples analyzed in a given 12-hour analytical sequence be listed, regardless of whether or not they are part of the SDG being reported, and regardless of whether or not they are EPA samples. Therefore, use "ZZZZZ" as the EPA sample number for any sample analysis not associated with the SDG being reported.

For blanks and standards, the following identification scheme must be used as the "EPA Sample No."

1. Method blanks shall be identified as DFBLK##.

2. Calibration standards shall be identified as CC1##, CC2##, CC3##, CC4## and CC5##, corresponding to the calibration solutions identified in Exhibit D.

3. The window defining mixture shall be identified as WDM##.

4. The column performance solution shall be identified as CPS##.

The "EPA Sample No." must be unique within a SDG. Therefore, the Contractor must replace the two-character "##" terminator of the identifier with one or two characters or numbers, or a combination of both, to create a unique EPA sample number for each blank and standard within the SDG. For example, possible identifiers for method blanks would be DFBLK1, DFBLK2, DFBLKA1, DFBLKB2, DFBLKAB, etc.

Several other pieces of information are common to many of the data reporting forms. These include "Matrix," "Lab Sample ID," "Lab File ID," "Instrument," and "GC Column."

For "Matrix," enter "SOIL" for a soil/sediment sample, "WATER" for an aqueous sample, and "WASTE" for a chemical waste sample, including the matrices of oily sludge, wet fuel oil, stillbottoms, oils, or other materials significantly contaminated with these matrices. Enter "ASH" for fly ash samples.

"Lab Sample ID" is an optional laboratory-generated internal identifier. Up to 12 alpha-numeric characters may be reported here. If the Contractor does not have a lab sample ID, this field may be left blank. However, if this identifier is used on any of the forms, or accompanying hardcopy data deliverables, it must be reported on all the appropriate forms.

"Lab File ID" is the laboratory-generated name of the GC/MS data system file containing information pertaining to a particular analysis. Up to 14 alpha-numeric characters may be used here.

"Instrument" is common to many of the forms, particularly those containing calibration data. The identifier used by the laboratory must include some indication of the manufacturer and/or model of the instrument, and contain additional characters or numbers that differentiate between all instruments of the same type in the laboratory. The instrument identifier must be consistent on all forms within the SDG.

"GC Column" and "ID (mm)" are common to various other forms. These two fields are to be used to identify the stationary phase of the GC column (previously called GC Column ID), and the internal diameter of the GC column in millimeters (mm). For packed columns, convert the ID from inches to millimeters as necessary, and enter in the "ID" field.

For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round

up). If the figure following the last digit to be retained equals 5, round up if the digit to be retained is odd, and round down if that digit is even.

B. PCDD/PCDF Sample Data

1. Form I PCDD-1

This form is used for tabulating and reporting the sample analysis results for target analytes. It is related to Form I PCDD-2, and for each sample for which there is a Form I PCDD-1, there must be a corresponding Form I PCDD-2.

Complete all header information according to the instructions in Part A and as follows:

Enter the "Matrix" of the sample being analyzed. The designation of matrix must reflect which one of the matrix-specific extraction procedures in Exhibit D was used for extraction of the sample.

For "Sample wt/vol," enter the number of grams (for soil) or milliliters (for water) of sample used in the first blank line, and the units, either "G" or "ML," in the second blank.

For water samples, indicate the extraction procedure used by entering "SEPF" for separatory funnel extraction or "CONT" for continuous liquid-liquid extraction in the field labeled "Water Sample Prep."

Enter the actual volume of the most concentrated sample extract, in microliters, under "Conc. Extract Volume:" This volume will typically be 100 microliters, although this volume is split into two aliquots before analysis.

Enter "GC Column," "Instrument," "Lab Sample ID," and "Lab File ID" as described in Part A.

"Date Received" is the date of sample receipt at the laboratory, as noted on the Traffic Report (i.e., the validated time of sample receipt, VTSR) for that sample. It must be entered as MM/DD/YY.

"Date Extracted" and "Date Analyzed" must also be entered as MM/DD/YY. If continuous liquid-liquid extraction procedures are used for water samples, enter the date on which the procedure was started as the "Date Extracted." If separatory funnel procedures are used for water samples, enter the date on which the procedure was completed. The "Date Analyzed" must be the date of the analysis for which the results are reported on Form I. (If the sample requires a second column confirmation and is reported on Form I PCDD-3, the "Date Analyzed" on Form I PCDD-3 must be the date of the second analysis, while the date on Form I PCDD-1 and PCDD-2 will be the date of the first analysis.)

If the sample has been diluted for analysis, enter the "Dilution Factor" as a single number, not a fraction. For example, enter "100.0" for a 1 to 100 dilution of the extract. Enter "0.1" for a concentration of 10 to 1. If the sample was not diluted, enter "1.0."

NOTE: "Dilution" refers to sample handling steps other than those outlined in Exhibit D. If the weight or volume of the sample taken for extraction is not the weight or volume specified in the protocol, this is not a dilution but is accounted for in the weight/volume term. A dilution refers specifically to the addition of clean solvent to a measured volume of the most concentrated sample extract.

The appropriate concentration units, "NG/L" for water samples or "UG/KG" for all other matrices, must be entered in the field for "CONCENTRATION UNITS:"

For each analyte detected in a sample, enter the absolute retention time of the detected peak under "PEAK RT." Enter the retention time in minutes and decimal minutes, not seconds or minutes and seconds. The retention time must be entered even if the peak did not meet all of the identification criteria in Exhibit D.

Enter the ion abundance ratio for the two m/z's (listed under "Selected Ions") in the column labeled "ION RATIO." If the ion abundance ratio falls outside the acceptance limits listed in Exhibit D, place an asterisk (*) in the column under the number (#) symbol.

For target analytes that meet all the identification criteria in Exhibit D, the Contractor shall report the concentrations detected as uncorrected for blank contaminants in the column in the lower portion of the form labeled "CONCENTRATION." Report all results to two significant figures.

Under the column labeled "Q" for qualifier, flag each result with the specific data reporting qualifiers listed below. The Contractor is encouraged to use additional flags as needed, but the definition of such flags must be explicit, must not contradict the qualifiers listed below, and must be included in the accompanying Narrative.

For reporting results to EPA, the following contract-specific qualifiers are to be used. The seven qualifiers listed below are not subject to modification by the laboratory. Up to five qualifiers may be reported on Form I for each analyte.

The seven EPA-defined qualifiers to be used are as follows:

U - Indicates compound was analyzed for but not detected. The CONCENTRATION column is left blank in this instance, and an estimated detection limit (EDL) must be calculated based on the signal-to-noise ratio, as described in Exhibit D. This

calculation takes into account the sample weight/volume extracted, the volume of the most concentrated extract, the injection volume, and dilution of the most concentrated extract prior to analysis. The calculation does not consider the percent solids content of the sample, as all results are reported on a wet weight basis.

J - Indicates an estimated value. This flag is used when the mass spectral data indicate presence of an analyte meeting all the identification criteria in Exhibit D, but the result is less than the sample quantitation limit, but greater than zero.

B - This flag is used when the analyte is found in the associated blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

E - This flag identifies analytes whose concentrations exceed the calibration range of the GC/MS instrument for that specific analysis. If one or more compounds have a response greater than full scale, except as noted in Exhibit D, the sample extract must be diluted and reanalyzed according to the specifications in Exhibit D. All such compounds with a response greater than full scale should have the concentration flagged "E" on the Form I for the original analysis. If the dilution of the extract causes any compounds identified in the first analysis to be below the calibration range in the second analysis, the results of both analyses shall be reported on separate copies of Form I. The Form I for the diluted sample shall have the "DL" suffix appended to the EPA sample number.

D - This flag indicates all compounds identified in an analysis at a secondary dilution factor. If a sample extract is reanalyzed at a higher dilution factor, as in the "E" flag above, the "DL" suffix is appended to the EPA sample number on the Form I for the diluted sample, and all concentration values reported on that Form I are flagged with the "D" flag. This flag alerts data users that any discrepancies between the concentrations reported may be due to dilution of the sample extract.

S - This flag indicates that the analyte in question is, in the opinion of the GC/MS Interpretation Specialist, a PCDD/PCDF, even though the M-[COCl]+ ion did not meet the requirement of 2.5 times signal-to-noise (see Exhibit D, Section 11.3).

H - This flag indicates that the analyte in question was quantitated using peak heights rather than peak areas for both the analyte and its internal standard (see Exhibit D, Section 11.4).

X - Other specific flags may be required to properly define the results. If used, they must be fully described, and such description must be attached to the Sample Data Summary

Package and the SDG Narrative. Begin using "X." If more than one flag is needed, use "Y" and "Z" as needed. The laboratory-defined flags are limited to the letters "X," "Y," and "Z."

The combination of flags "BU" or "UB" is expressly prohibited. Blank contaminants are flagged "B" only when they are detected in the sample associated with the blank.

If a peak detected in the sample meets all of the identification criteria except the ion abundance ratio, flag the ion ratio as indicated above, and report the "Estimated Maximum Possible Concentration" as calculated in Exhibit D under the "EMPC/EDL" column. Do not report the value of the EMPC under the column labeled "CONCENTRATION," as that column is only for analytes meeting all the identification criteria.

If an analyte was not detected in the sample, enter "U" in the qualifier column, as described above, and report the Estimated Detection Limit" as calculated in Exhibit D under the "EMPC/EDL" column. Do not report the value of the EDL if there is an entry under "CONCENTRATION." The presence of the "U" alerts the data user that the reported value is an EDL, otherwise it is assumed to be an EMPC.

The bottom portion of Form I PCDD-1 contains the fields for reporting the recoveries of the internal standard and the cleanup standard. The recoveries of these standards are crucial in evaluating the effectiveness of this isotope dilution method. For each internal standard and the cleanup standard, enter the absolute retention time of the standard in the sample in minutes and decimal minutes, as above. Report the ion abundance ratio of each of the five internal standards under the "ION RATIO" column. Flag any ion ratios that fall outside the ion ratio limits listed on the form by placing an asterisk (*) in the column under the number (#) symbol. There is no ion abundance ratio for the cleanup standard, as only one ion is monitored.

Report the percent recovery of the internal standards and the cleanup standard, calculated according to Exhibit D, under the "%REC" column. The quality control limits for recovery are listed on the form. Flag any recovery outside those limits by placing an asterisk (*) under the number (#) symbol in the recovery column. Requirements for reanalysis of samples due to poor recoveries are given in Exhibit D.

2. Form I PCDD-2, Toxicity Equivalence Summary

This page of Form I is used to report the results of the toxicity equivalence calculations for each sample analyzed. The concentration of each of the 2,3,7,8-substituted PCDD and PCDF isomers is multiplied by a toxicity equivalence factor (TEF), as described in Exhibit D, to arrive at a concentration of 2,3,7,8-TCDD with an equivalent toxicity. The total of all the toxic

equivalents determines whether or not the sample needs to be analyzed on a second GC column to more completely separate the 2378-TCDF from all other TCDD and TCDF isomers (see Exhibit D).

Complete the header information as above. The header of Form I PCDD-2 must match the header of Form I PCDD-1 for the same sample.

For each 2,3,7,8-substituted isomer positively identified in the sample, enter the concentration found in the column labeled "CONCENTRATION." If an isomer was not detected, i.e., flagged "U" on Form I PCDD-1, for the purposes of this calculation, enter 0.0 (zero) as the concentration. EMPC values are not included in the TEF calculations under this SOW.

Multiply each concentration times the TEF listed on the form for that isomer, and enter the product of the two in the column labeled "TEF-ADJUSTED CONCENTRATION." Add all 17 TEF-adjusted concentrations together, including any zeros, and enter the total on the line at the bottom of the form.

If the total TEF-adjusted concentration is greater than the values listed at the bottom of the form and in Exhibit D, then a second column confirmation analysis is required (see Exhibit D).

3. Form I PCDD-3, Second Column Confirmation Results

This page of Form I is used to report the results of all second column confirmation analyses performed. The requirements for second column confirmation are discussed above and in Exhibit D. Each time a second column confirmation is performed, the results are reported on Form I PCDD-3.

Complete the header information as above, except note that the fields for "GC Column" and "Date Analyzed" must correspond to the second column confirmation analysis, i.e., they must not match those fields in the header of Form I PCDD-1 or PCDD-2. Other fields such as "Instrument," "Dilution Factor," and "Lab File ID" may also differ and must correspond to the second column confirmation analysis.

Complete the information in the lower portion of the form in a fashion similar to that for Form I PCDD-1, but entering the results of the second column confirmation.

Enter the data on recovery of the internal standards and cleanup standard from the second column confirmation analysis in a fashion similar to that for the original analysis.

C. PCDD/PCDF Total Congener Concentration Summary (Form II)

This form is used to report the total concentration of all PCDD/PCDF isomers in a given homologue that are detected in the sample, including those isomers that do not represent the 2,3,7,8-substituted isomers of greatest toxicological concern. Because there are many isomers in each

homologue, it is necessary to indicate the number of peaks that represent isomers within the homologue. Enter the number of peaks detected in each homologue under "PEAKS." For instance, if three PeCDD peaks are detected and summed together, enter "3" under "PEAKS."

Enter the concentration of the total homologue, as calculated in Exhibit D, under "CONCENTRATION." Enter qualifiers under the "Q" column, as described above. If no isomers in a homologue were detected, enter "U" as the qualifier, and enter the lowest EDL of any of the 2,3,7,8-substituted isomers under the "EMPC/EDL" column.

If any of the peaks in a homologue meet all the identification criteria except the ion abundance ratio, then report the total concentration as an EMPC under the "EMPC/EDL" column.

D. PCDD/PCDF Spiked Sample and Duplicate Sample Results (Form III)

1. PCDD/PCDF Spiked Sample Summary (Form III PCDD-1)

This page of Form III is used to report the accuracy of the spiked sample analysis, measured as recovery of the 10 spiked analytes. Because some of the analytes may also be present in the unspiked aliquot of the sample, results for both the unspiked and spiked analyses are reported on Form III.

Complete the header information as in Part A. Enter the EPA sample number for the spiked sample aliquot in the box at the top of the form. Similarly, the lab sample ID and lab file ID must refer to the spiked sample analysis.

Enter the "Spike Added" of each of the 10 analytes in picograms (pg). In the column labeled "Spiked Sample Result," enter the concentration (or EMPC) of each analyte detected in the spiked sample aliquot. The concentration units must be those indicated at the top of the form and be appropriate to the sample matrix listed in the header. Enter the concentration (or EMPC) of each analyte detected in the original analysis of the unspiked sample aliquot. If an analyte was not detected in the unspiked aliquot, enter zero in place of the concentration, and use this value in the calculations described in Exhibit D. Calculate the recovery of each spiked analyte as described in Exhibit D, and enter this value to the nearest whole percentage point in the column labeled "%REC." Flag any recoveries outside the quality control limits listed on the form by placing an asterisk (*) in the column under the number (#) symbol.

In addition to Form III PCDD-1, a copy of Form I must be completed for the spiked sample analysis as well, following the procedures described above.

2. PCDD/PCDF Duplicate Sample Summary (Form III PCDD-2)

This page of Form III is used to report the precision of the duplicate sample analysis, measured as the relative percent

difference (RPD) between the results of the original and duplicate analyses of one sample of each matrix in each SDG. In order to allow direct comparison of the results of both the analyses, the concentration results from the original and duplicate analyses are reported on a single copy of Form III PCDD-2.

Complete the header information as described in Part A above, but enter the EPA sample number, lab sample ID, and lab file ID of the duplicate aliquot in these fields on Form III PCDD-2. Enter the concentration units.

For each target analyte, enter the results from both the analyses under the columns "Sample Concentration" and "Duplicate Concentration." These values must match those on Form I for these aliquots, except that undetected analytes (flagged "U" on Form I) are reported as zero on Form III PCDD-2. If either or both the analyses resulted in an EMPC for any analyte, enter the EMPC as the concentration, and use that value in the calculations.

Calculate the relative percent difference between the two concentrations or EMPCs, as described in Exhibit D, using zero for undetected analytes, and report this value to the nearest whole percentage point under "RPD." If the analyte was not detected in either aliquot, enter zero for both concentrations, and report the RPD as zero as well. Flag all values outside the quality control limits listed on the forms by entering an asterisk (*) under the number (#) symbol.

E. PCDD/PCDF Method Blank Summary (Form IV)

This form summarizes the samples associated with each method blank analysis. A copy of Form IV is required for each blank.

Complete the header information as described in Part A. The EPA sample number entered in the box at the top of the form shall be the number assigned to the method blank. The matrix entered on this form refers to the matrix of the associated samples, as one blank is required each time that samples of a similar matrix are extracted together. Therefore, samples of differing matrices cannot be mixed together on a single Form IV.

Summarize the samples associated with a given method blank in the box in the lower portion of the form, entering the EPA sample number, lab sample ID, lab file ID, and date of analysis of each sample. Include spiked samples and duplicate samples as well.

F. PCDD/PCDF Window Defining Mix Summary, Chromatographic Resolution Summary, and Analytical Sequence (Form V)

1. PCDD/PCDF Window Defining Mix Summary (Form V PCDD-1)

This page of Form V is used to report the results of the analysis of the window defining mixture that precedes each initial

calibration on each GC column and instrument used for analysis. The analysis of this mixture is used to document the retention time window for the PCDD/PCDF homologue.

Complete the header information as described in Part A, entering the EPA sample number of the window defining mixture injection in the box at the top of the form. The header information must correspond to the analysis of the window defining mixture.

In the box in the lower portion of the form, enter the absolute retention times of the first and last eluting isomers in each homologue. Enter the retention times in minutes and decimal minutes, not minutes and seconds, nor seconds.

NOTE: As there is only one possible octachlorinated dioxin and furan, the retention times of these analytes are not contained in the window defining mixture, and are not reported here.

2. PCDD/PCDF Chromatographic Resolution Summary (Form V PCDD-2)

This page of Form V is used to report the chromatographic resolution of selected analytes in one of two solutions, depending on the GC column. The chromatographic resolution of these analytes is crucial to evaluating the results for the PCDDs/PCDFs reported in the samples. This evaluation is made every 12 hours during which samples or standards are analyzed.

For the DB-5 (or equivalent) column, the chromatographic resolution is judged from the analysis of the CC3 standard during initial or continuing calibration. For the SP-2331 (or equivalent) column, the chromatographic resolution is judged from the analysis of the column performance solution that precedes the analysis of the CC3 standard on this column (see Exhibit D).

Complete one copy of Form V PCDD-2 for each GC column used for analysis. Complete the header information as described in Part A, entering the EPA sample number of the CC3 standard or the column performance solution in the box at the top of the form. Enter the date and time of analysis of the standard in the header.

Calculate the chromatographic resolution for the GC column identified in the header according to the procedures in Exhibit D. For the DB-5 (or equivalent) column, enter only the results from the CC3 analysis. For the SP-2331 (or equivalent) column, enter only the results from the column performance solution analysis.

The GC column chosen for the confirmation analysis must meet the resolution criteria for the other specified column. If the Contractor chooses a single column for analysis that is designed such that a second column confirmation analysis is not required, then the Contractor must demonstrate that the resolution criteria for both of the specified columns have been met (see Exhibit D).

3. PCDD/PCDF Analytical Sequence (Form V PCDD-3)

This page of Form V is used to report the sequence of analyses, including the analysis of the window defining mixture, the calibration standards, blanks, samples, duplicates, and spiked samples. One copy of Form V PCDD-2 is required for each 12-hour period during which samples, blanks, standards, etc. associated with the SDG are analyzed.

Complete the header information as described in Part A. Enter the inclusive dates and times of the analyses of the first and last initial calibration standards in the fields for "Init. Calib. Date(s)" and "Init. Calib. Times." Dates must be in the format MM/DD/YY, and all times are expressed as HHMM, in military time (i.e., a 24-hour clock).

In the box in the lower portion of the form, enter the EPA sample number, lab sample ID, lab file ID, and date and time of analysis of all standards, samples, blanks, duplicates, spiked samples, dilutions, reanalyses, etc. All analyses in the 12-hour period must be listed on Form V. If analysis is not associated with the SDG being reported, enter the EPA sample number as "ZZZZZ," as described in Part A. The 12-hour sequence must end with the analysis of the appropriate calibration standard, as described in Exhibit D. In order to meet the requirements of the 12-hour sequence, the standard must be injected within 12 hours of the injection of the standard that began the sequence (CC3 on the DB-5, and the column performance solution on the SP-2331).

If the analytical sequence includes the analysis of the initial calibration standards, these standards and the window defining mix must be included on that copy of Form V, identified by the EPA sample numbers described in Part A. A copy of the analytical sequence that includes these initial calibration standards and the window defining mix must be submitted with each data package to which the initial calibration applies, but the Case number and SAS number must match those of each data package in which these initial calibration data are reported.

G. PCDD/PCDF Initial Calibration Data Summary (Form VI)

1. PCDD/PCDF Initial Calibration Response Factor Summary (Form VI PCDD-1)

This form is used to summarize the response factors for each target analyte, internal standard and cleanup standard calculated from the initial calibration. Complete the header information as described in Part A. Enter the inclusive initial calibration date(s) and times, as described for Form V PCDD-2. One copy of Form VI PCDD-1 must be completed for each initial calibration, for each instrument and GC column used for analysis of samples, and must be accompanied by a corresponding Form VI PCDD-2.

Enter the relative response factors (RRF) determined from the analysis of each of the calibration standards (CC1 through CC5). Enter RRF values to three decimal places. Calculate the mean RRF, as described in Exhibit D, and enter in the column "MEAN RRF." Calculate the relative standard deviation as a percentage of the mean (%RSD), and enter under "%RSD." Note that seven of the native analytes and the cleanup standard occur only in the CC3 standard, and therefore, %RSD calculations are not possible and are not reported on this form. However, for these analytes, enter the single point RRF as the "MEAN RRF." Also note that as the recovery standards are used to determine the RRFs of the internal standards, no RRF values can be calculated for the recovery standards, and therefore, they do not appear on Form VI PCDD-1.

All initial calibrations must meet the quality control limits for %RSD listed on the form.

2. PCDD/PCDF Initial Calibration Ion Abundance Ratio Summary (Form VI PCDD-2)

This page of Form VI is used to report the ion abundance ratios for each of the initial calibration standards. Because the ratio of the abundances of the two ions monitored for each analyte is crucial to the identification of these analytes, the ion abundance ratios must meet the quality control limits.

For each native analyte, internal standard and recovery standard, the two ions monitored for each analyte are listed in the column labeled "Selected Ions." Calculate the ratio of the abundances of these two ions according to the procedures in Exhibit D, and enter the ion abundance ratio of each analyte in each of the initial calibration standards to two decimal places.

Compare the ion abundance ratios to the quality control limits shown on the form, and flag any analyte which did not meet these limits in one or more of the standards.

Note that the cleanup standard does not appear on Form VI PCDD-2, as only one ion is monitored for this analyte, and therefore, no ion abundance ratio can be calculated.

One copy of Form VI PCDD-2 must be completed for each initial calibration, for each instrument and GC column used for analysis of samples, and must accompany a corresponding copy of Form VI PCDD-1.

H. PCDD/PCDF Continuing Calibration Data Summary

1. PCDD/PCDF Continuing Calibration Summary (Form VII PCDD-1)

This page of Form VII is used to summarize the results of the continuing calibration that must occur in each 12-hour analytical sequence. The form is used to report the RRF values and ion abundance ratios of each analyte in the CC3 standard, and to compare these values to the initial calibration data reported on

Form VI. One copy of Form VII PCDD-1 must be completed for each continuing calibration performed, and must be accompanied by a corresponding copy of Form VII PCDD-2.

Complete the header information as described in Part A. The date and time of analysis and lab file ID in the header must correspond to the analysis of the CC3 standard. Enter the date of the associated initial calibration in the field for "Init. Calib. Date(s):" If the calendar date changed during the initial calibration, enter the inclusive dates of the first and last standards in the associated initial calibration in the fields for "Init. Calib. Date(s)."

For each of the native analytes, internal standards, and the cleanup standard, enter the relative response factor (RRF) determined from the analysis of the continuing calibration standard in the column labeled "RRF." Enter the mean RRF for each analyte from the associated initial calibration, in the column labeled "MEAN RRF." For the seven native analytes and the cleanup standard that undergo only a single-point calibration, enter the CC3 RRF from the initial calibration, which is also entered as the mean RRF on Form VI. The values reported in this column must match those reported on the Form VI for the associated initial calibration. Calculate the percent difference (%D) between the RRF and the mean RRF for each analyte, and report under "%D." If the percent difference exceeds the quality control limits shown on the form (±30%), flag that analyte by placing an asterisk (*) in the "RRF FLAG" column. Report the ion abundance ratio of each analyte under the "ION RATIO" column. Flag any ion ratio that fails outside the quality control limits shown on the form by placing as asterisk (*) in the "ION FLAG" column.

Note that because only one ion is monitored for the cleanup standard, no ion ratio is determined for this analyte. For the recovery standards, relative response factors are not calculated or reported on Form VII, but the ion abundance ratios for these standards must be reported on Form VII.

2. PCDD/PCDF Continuing Calibration Summary (Form VII PCDD-2)

This page of Form VII is used to summarize the absolute and relative retention times of the analytes in the continuing calibration standard that must be analyzed in each 12-hour analytical sequence. Absolute retention times and relative retention times are critical to the identification of PCDDs/PCDFs by this method. One copy of Form VII PCDD-2 must be completed for each continuing calibration performed and must be accompanied by a corresponding copy of Form VII PCDD-1.

Complete the header information as described in Part A. The date and time of analysis and lab file ID in the header must correspond to the analysis of the CC3 standard. Enter the date of the associated initial calibration in the field for "Init. Calib. Date(s):" If the calendar date changed during the initial

calibration, enter the inclusive dates of the analyses of the first and last standards in the associated initial calibration in the fields for "Init. Calib. Date(s)."

For each of the native analytes and the cleanup standard, enter the relative retention time (RRT) and absolute retention time (RT) of the analyte in the calibration standard. RRT is calculated according to the procedures in Exhibit D, as the RT of the native analyte divided by the RT of appropriate internal standard. For the internal standards and recovery standards, report the only the absolute retention times. Enter all RTs in minutes and decimal minutes. RRTs are reported to two decimal places.

I. Sample Log-In Sheet (Form DC-1)

This form is used to document the receipt and inspection of sample containers and samples. One original of Form DC-1 is required for each sample shipping container. If the samples in a single sample shipping container must be assigned to more than one SDG, the original Form DC-1 shall be placed with the deliverables for the SDG of the lowest Arabic number, and a copy of Form DC-1 must be placed with the deliverables for the other SDG(s). The copies should be identified as "copy(ies)," and the location of the original should be noted on the copies.

Sign and date the airbill (if present). Examine the shipping container and record the presence/absence of custody seals and their condition (e.g., intact, broken) in item 1 of Form DC-1. Record the custody seal numbers in item 2.

Open the container, remove the enclosed sample documentation, and record the presence/absence of chain-of-custody record(s), SMO forms (e.g., Traffic Reports, Packing Lists), and airbills or airbill stickers in items 3-5. Specify if there is an airbill present or an airbill sticker in item 5. Record the airbill or sticker number in item 6.

Remove the samples from the shipping container(s), examine the samples and the sample tags (if present), and record the condition of the sample bottles (e.g., intact, broken, leaking) and presence of absence of sample tags in items 7 and 8.

Review the sample shipping documents and complete the header information described in Instruction A. Compare the information recorded on all the documents and samples and circle the appropriate answer in item 9.

If there are no problems observed during receipt, sign and date (include time) Form DC-1, the chain-of-custody record, and Traffic Report, and write the sample numbers on Form DC-1. Record the appropriate sample tags and assigned laboratory numbers if applicable. The log-in date should be recorded at the top of Form DC-1 and the date and time of cooler receipt at the laboratory should be recorded in items 10 and 11. Record the fraction designation (if appropriate) and the specific area dasignation (e.g., refrigerator number) in the Sample Transfer block located in the bottom left corner of Form DC-1. Sign and date the Sample Transfer block. Cross out unused columns and spaces.

If there are problems observed during receipt or an answer marked with an asterisk (e.g., "absent*") was circled, contact SMO and document the contact as well as resolution of the problem on a CLP Communication Log. Following resolution, sign and date the forms as specified in the preceding paragraph and note, where appropriate, the resolution of the problem.

J. CSF Inventory Sheet (Form DC-2)

This form is used to record the inventory of the CSF purge documents and count of documents in the original Sample Data Package that is sent to the Region.

Organize all EPA-CSF documents as described in Section II and Section III. Assemble the documents in the order specified on Form DC-2 and Section II and III, and stamp each page with a consecutive number. (Do not number the DC-2 form.) Inventory the CSF by reviewing the document numbers and recording page number ranges in the columns provided in the Form DC-2. If there are no documents for a specific document type, enter "NA" in the empty space.

Certain laboratory-specific documents related to the CSF may not fit into a clearly defined category. The laboratory should review Form DC-2 to determine if it is most appropriate to place them under item 5, 6, 7, or 8. Item 10 should be used if there is no appropriate previous item. These types of documents should be described or listed in the blanks under each appropriate item.

SECTION IV

DATA REPORTING FORMS

1DFA
PCDD/PCDF SAMPLE DATA SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SELECTED IONS	PEAK RT	ION RATIO	#	CONCENTRATION	Q	EMPC/EDL
2378-TCDD	320/322						
2378-TCDF	304/306						
12378-PeCDF	340/342						
12378-PeCDD	356/358						
23478-PeCDF	340/342						
123478-HxCDF	374/376						
123678-HxCDF	374/376						
123478-HxCDD	390/392						
123678-HxCDD	390/392						
123789-HxCDD	390/392						
234678-HxCDF	374/376						
123789-HxCDF	374/376						
1234678-HpCDF	408/410						
1234678-HpCDD	424/426						
1234789-HpCDF	408/410						
OCDD	458/460						
OCDF	442/444						

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis.

INTERNAL STANDARD	SELECTED IONS	PEAK RT	ION RATIO	#	ION RATIO LIMITS	% REC	#	RECOVERY LIMITS
13C-2378-TCDF	316/318				0.65-0.89			25-150
13C-2378-TCDD	332/334				0.65-0.89			25-150
13C-123678-HxCDD	402/404				1.05-1.43			25-150
13C-1234678-HpCDF	420/422				0.88-1.20			25-150
13C-OCDD	470/472				0.76-1.01			25-150
37Cl-2378-TCDD	328/NA		NA		NA			25-150

Column to be used to flag values outside QC limits

1DFB

PCDD/PCDF TOXICITY EQUIVALENCE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	CONCENTRATION	TEF	TEF-ADJUSTED CONCENTRATION
2378-TCDD		x 1.0 =	
2378-TCDF		x 0.1 =	
12378-PeCDF		x 0.05 =	
12378-PeCDD		x 0.5 =	
23478-PeCDF		x 0.5 =	
123478-HxCDF		x 0.1 =	
123678-HxCDF		x 0.1 =	
123478-HxCDD		x 0.1 =	
123678-HxCDD		x 0.1 =	
123789-HxCDD		x 0.1 =	
234678-HxCDF		x 0.1 =	
123789-HxCDF		x 0.1 =	
1234678-HpCDF		x 0.01 =	
1234678-HpCDD		x 0.01 =	
1234789-HpCDF		x 0.01 =	
OCDD		x 0.001 =	
OCDF		x 0.001 =	
		Total =	

NOTE: Do <u>not</u> include EMPC or EDL values in the TEF-adjusted Concentration.

If the Total Toxic Equivalent Concentration of the sample is greater than 7 ng/L for an aqueous sample, greater than 0.7 ug/Kg for any solid matrix, or greater than 7 ug/Kg for a chemical waste sample, then second column confirmation of the results may be required.

1DFC

PCDD/PCDF SECOND COLUMN CONFIRMATION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SELECTED IONS	PEAK RT	ION RATIO	#	CONCENTRATION	Q	EMPC/EDL
2378-TCDD	320/322						
2378-TCDF	304/306						
12378-PeCDF	340/342						
12378-PeCDD	356/358						
23478-PeCDF	340/342						
123478-HxCDF	374/376						
123678-HxCDF	374/376						
123478-HxCDD	390/392						
123678-HxCDD	390/392						
123789-HxCDD	390/392						
234678-HxCDF	374/376						
123789-HxCDF	374/376						
1234678-HpCDF	408/410						
1234678-HpCDD	424/426						
1234789-HpCDF	408/410						
OCDD	458/460						
OCDF	442/444						

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis.

INTERNAL STANDARD	SELECTED IONS	PEAK RT	ION RATIO	#	ION RATIO LIMITS	% REC	#	RECOVERY LIMITS
13C-2378-TCDF	316/318				0.65-0.89			25-150
13C-2378-TCDD	332/334				0.65-0.89			25-150
13C-123678-HxCDD	402/404				1.05-1.43			25-150
13C-1234678-HpCDF	420/422				0.88-1.20			25-150
13C-OCDD	470/472				0.76-1.01			25-150
37Cl-2378-TCDD	328/NA		NA		NA			25-150

Column to be used to flag values outside QC limits

2DF

PCDD/PCDF TOTAL HOMOLOGUE CONCENTRATION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

HOMOLOGUE	PEAKS	CONCENTRATION	Q	EMPC/EDL
DIOXINS				
Total TCDD_____	_____	_____	_____	_____
Total PeCDD____	_____	_____	_____	_____
Total HxCDD____	_____	_____	_____	_____
Total HpCDD____	_____	_____	_____	_____
FURANS				
Total TCDF_____	_____	_____	_____	_____
Total PeCDF____	_____	_____	_____	_____
Total HxCDF____	_____	_____	_____	_____
Total HpCDF____	_____	_____	_____	_____
_____	_____	_____	_____	_____

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis. The total congener concentrations do not affect the TEF calculations.

3DFA

PCDD/PCDF SPIKED SAMPLE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash)

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SPIKE ADDED (PG)	SPIKED SAMPLE CONCENTRATION	SAMPLE CONCENTRATION	% REC #	QC LIMITS
2378-TCDD					50-150
2378-TCDF					50-150
12378-PeCDF					50-150
12378-PeCDD					50-150
123678-HxCDF					50-150
123678-HxCDD					50-150
1234678-HpCDF					50-150
1234678-HpCDD					50-150
OCDD					50-150
OCDF					

If an analyte is not detected in the unspiked sample, enter 0 (zero) as the "SAMPLE CONCENTRATION."

Column to be used to flag values outside QC limits.

QC limits are advisory.

3DFB

PCDD/PCDF DUPLICATE SAMPLE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash)

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SAMPLE CONCENTRATION	DUPLICATE CONCENTRATION	RPD	#	QC LIMITS
2378-TCDD					50
2378-TCDF					50
12378-PeCDF					50
12378-PeCDD					50
23478-PeCDF					50
123478-HxCDF					50
123678-HxCDF					50
123478-HxCDD					50
123678-HxCDD					50
123789-HxCDD					50
234678-HxCDF					50
123789-HxCDF					50
1234678-HpCDF					50
1234678-HpCDD					50
1234789-HpCDF					50
OCDD					50
OCDF					50
					50

If an analyte is not detected in either analysis, enter 0 (zero) as the concentration.

Column to be used to flag values outside QC limits.

QC limits are advisory

4DF

PCDD/PCDF METHOD BLANK SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Extracted: _____

Date Analyzed: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, SPIKES, AND DUPLICATES:

EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED

5DFA

PCDD/PCDF WINDOW DEFINING MIX SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Lab File ID: _____

Instrument ID: _____ Date Analyzed: _____

Time Analyzed: _____

CONGENER	RT FIRST ELUTING	RT LAST ELUTING
TCDD		
TCDF		
PeCDD		
PeCDF		
HxCDD		
HxCDF		
HpCDD		
HpCDF		

5DFB

PCDD/PCDF CHROMATOGRAPHIC RESOLUTION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Lab File ID: _____

Instrument ID: _____ Date Analyzed: _____

Time Analyzed: _____

Percent Valley determination for DB-5 (or equivalent) column -
For the CC3 standard beginning the 12-hour period:

13C-2378-TCDD/13C-1234-TCDD: _____

123478-HxCDD/123678-HxCDD: _____

QC LIMITS:

Percent Valley between the TCDD isomers must be less than or equal to 25%

Percent Valley between the HxCDD isomers must be less than or equal to 50%

Percent Valley Determination for SP-2331 (or equivalent) Column -
For the Column Performance Solution beginning the 12-hour period:

1478-TCDD/2378-TCDD: _____

2378-TCDD/(1237/1238)-TCDD: _____

QC LIMITS:

Percent Valley between the TCDD isomers must be less than or equal to 25%.

5DFC
PCDD/PCDF ANALYTICAL SEQUENCE SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ _____

Init. Calib. Times: _____ _____

THE ANALYTICAL SEQUENCE OF STANDARDS, SAMPLES, BLANKS, SPIKES, AND DUPLICATES IS AS FOLLOWS:

EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED

6DFA

PCDD/PCDF INITIAL CALIBRATION RESPONSE FACTOR SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ - _____

Init. Calib. Times: _____ _____

NATIVE ANALYTES VS. INTERNAL STDS.	RRF (N) CC1	CC2	CC3	CC4	CC5	MEAN RRF	%RSD
2378-TCDD							
2378-TCDF							
12378-PeCDF							
12378-PeCDD							
23478-PeCDF							
123478-HxCDF							
123678-HxCDF							
123478-HxCDD							
123678-HxCDD							
123789-HxCDD							
234678-HxCDF							
123789-HxCDF							
1234678-HpCDF							
1234678-HpCDD							
1234789-HpCDF							
OCDD							
OCDF							
INTERNAL STANDARDS VS. RECOVERY STDS.							
13C-2378-TCDD							
13C-2378-TCDF							
13C-123678-HxCDD							
13C-1234678-HpCDF							
13C-OCDD							
37Cl-2378-TCDD							

A single point calibration is performed for seven of the native analytes and the cleanup standard. Therefore, no %RSD is reported for these compounds.

QC Limits: %RSD must be less than or equal to 15.0%.

6DFB

PCDD/PCDF INITIAL CALIBRATION ION ABUNDANCE RATIO SUMMARY

Lab Name:_____ Contract:_____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ _____

Init. Calib. Times: _____ _____

NATIVE ANALYTES	SELECTED IONS	ION ABUNDANCE RATIO CC1	CC2	CC3	CC4	CC5	FLAG	QC LIMITS
2378-TCDD	320/322							0.65-0.89
2378-TCDF	304/306							0.65-0.89
12378-PeCDF	340/342							1.24-1.86
12378-PeCDD	356/358							1.24-1.86
23478-PeCDF	340/342							1.24-1.86
123478-HxCDF	374/376							1.05-1.43
123678-HxCDF	374/376							1.05-1.43
123478-HxCDD	390/392							1.05-1.43
123678-HxCDD	390/392							1.05-1.43
123789-HxCDD	390/392							1.05-1.43
234678-HxCDF	374/376							1.05-1.43
123789-HxCDF	374/376							1.05-1.43
1234678-HpCDF	408/410							0.88-1.20
1234678-HpCDD	424/426							0.88-1.20
1234789-HpCDF	408/410							0.88-1.20
OCDD	458/460							0.76-1.02
OCDF	442/444							0.76-1.02
INTERNAL STANDARDS								
13C-2378-TCDD	332/334							0.65-0.89
13C-2378-TCDF	316/318							0.65-0.89
13C-123678-HxCDD	402/404							1.05-1.43
13C-1234678-HpCDF	420/422							0.88-1.20
13C-OCDD	470/472							0.76-1.02
RECOVERY STANDARDS								
13C-1234-TCDD	332/334							0.65-0.89
13C-123789-HxCDD	402/404							1.05-1.43

QC limits represent ± 15% window around the theoretical ion abundance ratio.

A single point calibration is performed for seven of the native analytes and the cleanup standard.

The laboratory must flag any analyte in any calibration solution which does not meet the ion abundance ratio QC limit by placing an asterisk in the fl column.

7DFA

PCDD/PCDF CONTINUING CALIBRATION SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Date Analyzed: _____ Time Analyzed: _____

Lab File ID: _____ Init. Calib. Date(s): _____ _____

NATIVE ANALYTES	SELECTED IONS	RRF	MEAN RRF	%D	RRF FLAG	ION RATIO	ION FLAG	QC LIMITS
2378-TCDD	320/322							0.65-0.89
2378-TCDF	304/306							0.65-0.89
12378-PeCDF	340/342							1.24-1.86
12378-PeCDD	356/358							1.24-1.86
23478-PeCDF	340/342							1.24-1.86
123478-HxCDF	374/376							1.05-1.43
123678-HxCDF	374/376							1.05-1.43
123478-HxCDD	390/392							1.05-1.43
123678-HxCDD	390/392							1.05-1.43
123789-HxCDD	390/392							1.05-1.43
234678-HxCDF	374/376							1.05-1.43
123789-HxCDF	374/376							1.05-1.43
1234678-HpCDF	408/410							0.88-1.20
1234678-HpCDD	424/426							0.88-1.20
1234789-HpCDF	408/410							0.88-1.20
OCDD	458/460							0.76-1.02
OCDF	442/444							0.76-1.02
INTERNAL STANDARDS VS. RECOVERY STDS.								
13C-2378-TCDD	332/334							0.65-0.89
13C-2378-TCDF	316/318							0.65-0.89
13C-123678-HxCDD	402/404							1.05-1.43
13C-1234678-HpCDF	420/422							0.88-1.20
13C-OCDD	470/472							0.76-1.02
37Cl-2378-TCDD	328/NA					NA	NA	NA
RECOVERY STANDARDS								
13C-1234-TCDD	332/334	NA	NA	NA	NA			0.65-0.89
13C-123789-HxCDD	402/404	NA	NA	NA	NA			1.05-1.43

QC limits shown are for ion abundance ratios. Maximum %D for RRF is ± 30.0% The laboratory must flag any analyte which does not meet criteria for %D or ion abundance ratio by placing an asterisk in the appropriate flag column.

7DFB

PCDD/PCDF CONTINUING CALIBRATION RETENTION TIME SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Date Analyzed: _____ Time Analyzed: _____

Lab File ID: _____ Init. Calib. Date(s): _____ _____

NATIVE ANALYTES	RRT	RT
2378-TCDD		
2378-TCDF		
12378-PeCDF		
12378-PeCDD		
23478-PeCDF		
123478-HxCDF		
123678-HxCDF		
123478-HxCDD		
123678-HxCDD		
123789-HxCDD		
234678-HxCDF		
123789-HxCDF		
1234678-HpCDF		
1234678-HpCDD		
1234789-HpCDF		
OCDD		
OCDF		
INTERNAL STANDARDS VS. RECOVERY STDS.		
13C-2378-TCDD	NA	
13C-2378-TCDF	NA	
13C-123678-HxCDD	NA	
13C-1234678-HpCDF	NA	
13C-OCDD	NA	
37Cl-2378-TCDD		
RECOVERY STANDARDS		
13C-1234-TCDD	NA	
13C-123789-HxCDD	NA	

RRT = (RT of analyte)/(RT of appropriate internal standard)

SAMPLE LOG-IN SHEET

Lab Name	Page _____ of _____
Received By *(Print Name)*	Log-in Date
Received By *(Signature)*	
Case Number	Sample Delivery Group No. / SAS Number

Remarks:

1. Custody Seal(s) — Present/Absent* Intact/Broken
2. Custody Seal Nos.: _____ _____
3. Chain-of-Custody Records — Present/Absent*
4. Traffic Reports or Packing Lists — Present/Absent*
5. Airbill — Airbill/Sticker Present/Absent*
6. Airbill No.: _____ _____
7. Sample Tags — Present/Absent*
   Sample Tag Numbers — Listed/Not Listed on Chain-of-Custody
8. Sample Condition: — Intact/Broken*/Leaking
9. Does information on custody records, traffic reports, and sample tags agree? — Yes/No*
10. Date Received at Lab: _____
11. Time Received: _____

EPA Sample #	Corresponding Sample Tag #	Corresponding Assigned Lab #	Remarks: Condition of Sample Shipment, etc.

Sample Transfer

Fraction	Fraction
Area #	Area #
By	By
On	On

* Contact SMO and attach record of resolution.

Received By	Logbook No.
Date	Logbook Page No.

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET

LABORATORY NAME _____ CITY/STATE _____

CASE NO. _____ SDG NO. _____ SDG NOS. TO FOLLOW _____ _____ _____ SAS NO. _____

CONTRACT NO. _____ SOW NO. _____

All documents delivered in the complete SDG file must be original documents where possible. (REFERENCE EXHIBIT B, SECTION II and SECTION III.)

	PAGE NOs FROM	TO	CHECK LAB	EPA
1. Inventory Sheet (Form DC-2) (Do not number)				
2. SDG Narrative				
3. Traffic Report				
4. PCDD/PCDF Data				
a. Sample Data				
TCL Results (Form I PCDD-1)				
Calculation of the Toxicity Equivalence (Form I PCDD-2)				
Second Column Confirmation Summary (Form I PCDD-3)				
Selected Ion Current Profile (SICP) for each sample and each analysis of each sample				
Total Congener Concentration Results (Form II PCDD)				
b. Quality Control Data				
Spiked Sample Results (Form III PCDD-1)				
Duplicate Sample Results (Form III PCDD-2)				
Method Blank Summary (Form IV PCDD)				
Window Defining Mix Summary (Form V PCDD-1)				
Chromatographic Resolution Summary (Form V PCDD-2)				
SICP for each QC analysis				
c. Calibration Data				
Initial Calibration Data (Form VI PCDD-1 and Form VI PCDD-2) and PCDD/PCDF standard(s) SICPs for the initial (five-point) calibration				
Continuing Calibration Data (Form VII PCDD-1 and Form VII PCDD-2) and PCDD/PCDF standard(s) SICPs for all continuing calibrations				
d. Raw Quality Control Data				
Blank Data and SICPs for each blank analyzed				
Spiked Sample Data and SICPs for each spiked sample analyzed				

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET (Cont.)

CASE NO. _____ SDG NO. _____ SDG NOS. TO FOLLOW _____ _____ _____ SAS NO. _____

	PAGE NOs FROM	TO	CHECK LAB	EPA
5. Miscellaneous Data				
Original preparation and analysis forms or copies of preparation and analysis logbook pages	___	___	___	___
Internal sample and sample extract transfer chain-of-custody records	___	___	___	___
Screening records	___	___	___	___
All instrument output, including strip charts from screening activities (describe or list)	___	___	___	___
_____	___	___	___	___
_____	___	___	___	___
6. EPA Shipping/Receiving Documents				
Airbills (No. of shipments ___)	___	___	___	___
Chain-of-Custody Records	___	___	___	___
Sample Tags	___	___	___	___
Sample Log-In Sheet (Lab & DCl)	___	___	___	___
SDG Cover Sheet	___	___	___	___
Miscellaneous Shipping/Receiving Records (describe or list)	___	___	___	___
_____	___	___	___	___
_____	___	___	___	___
Internal Lab Sample Transfer Records and Tracking Sheets (describe or list)				
_____	___	___	___	___
_____	___	___	___	___
Other Records (describe or list)				
Telephone Communication Log	___	___	___	___
_____	___	___	___	___
_____	___	___	___	___

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET (Cont.)

CASE NO. _____ SDG NO. _____ SDG NOS. TO FOLLOW _____ _____ _____ SAS NO. _____

9. Comments: _____

Completed by:
(CLP Lab) _____ (Signature) _____ (Printed Name/Title) _____ (Date)

dited by:
(EPA) _____ (Signature) _____ (Printed Name/Title) _____ (Date)

EXHIBIT C

TARGET COMPOUND LIST (TCL) AND
CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)

NOTE: The values in these tables are quantitation limits, not absolute detection limits. The amount of material necessary to produce a detector response that can be identified and reliably quantified is greater than that needed to be simply detected above the background noise. The quantitation limits in these tables are set at the concentrations in the sample equivalent to the concentration of the lowest calibration standard analyzed for each analyte.

Specific quantitation limits are highly matrix-dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

The CRQL values listed on the following pages are based on the analysis of samples according to the specifications given in Exhibit D. All CRQL values are reported on a wet weight basis, as are sample data produced using the specifications in Exhibit D.

TARGET COMPOUND LIST (TCL) AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)

PCDD/PCDF	CAS Number	Quantitation Limits[1] Water (ng/L)	Soil (ug/Kg)	Fly Ash (ug/Kg)	Chemical Waste[2] (ug/Kg)
2378-TCDD	1746-01-6	10	1.0	1.0	10
2378-TCDF	51207-31-9	10	1.0	1.0	10
12378-PeCDF	57117-41-6	25	2.5	2.5	25
12378-PeCDD	40321-76-4	25	2.5	2.5	25
23478-PeCDF	57117-31-4	25	2.5	2.5	25
123478-HxCDF	70648-26-9	25	2.5	2.5	25
123678-HxCDF	57117-44-9	25	2.5	2.5	25
123478-HxCDD	39227-28-6	25	2.5	2.5	25
123678-HxCDD	57653-85-7	25	2.5	2.5	25
123789-HxCDD	19408-74-3	25	2.5	2.5	25
234678-HxCDF	60851-34-5	25	2.5	2.5	25
123789-HxCDF	72918-21-9	25	2.5	2.5	25
1234678-HpCDF	67562-39-4	25	2.5	2.5	25
1234678-HpCDD	35822-46-9	25	2.5	2.5	25
1234789-HpCDF	55673-89-7	25	2.5	2.5	25
OCDD	3268-87-9	50	5.0	5.0	50
OCDF	39001-02-0	50	5.0	5.0	50

1 All CRQL values listed here are based on the wet weight of the sample.

2 Chemical waste includes the matrices of oils, stillbottoms, oily sludge, wet fuel oil, oil-laced soil, and surface water heavily contaminated with these matrices.

In addition, data are reported for the total concentration of all detected PCDDs or PCDFs in the following homologues. However, because the number of non-2,3,7,8-substituted isomers that might be detected in a sample is unpredictable, it is not possible to assign CRQL values to the total homologue concentrations.

Homologue	CAS Number	Number of Possible Isomers	Number of 2,3,7,8-Substituted Isomers
Total TCDD	41903-57-5	22	1
Total TCDF	55722-27-5	38	1
Total PeCDD	36088-22-9	14	1
Total PeCDF	30402-15-4	28	2
Total HxCDD	34465-4608	10	3
Total HxCDF	55684-94-1	16	4
Total HpCDD	37871-00-4	2	1
Total HpCDF	38998-75-3	4	2

There is only one isomer in both the OCDD and OCDF homologues, hence the total concentration is the same as the 2,3,7,8-substituted concentration listed on the previous page.

TCDD - Tetrachlorinated dibenzo-*p*-dioxin
TCDF - Tetrachlorinated dibenzofuran
PeCDD - Pentachlorinated dibenzo-*p*-dioxin
PeCDF - Pentachlorinated dibenzofuran
HxCDD - Hexachlorinated dibenzo-*p*-dioxin
HxCDF - Hexachlorinated dibenzofuran
HpCDD - Heptachlorinated dibenzo-*p*-dioxin
HpCDF - Heptachlorinated dibenzofuran
OCDD - Octachlorinated dibenzo-*p*-dioxin
OCDF - Octachlorinated dibenzofuran

EXHIBIT D

ANALYTICAL METHODS

Table of Contents

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1. Scope and Application

1.1 This method is appropriate for the detection and quantitative measurement of 2378-tetrachlorinated dibenzo-*p*-dioxin (2378-TCDD), 2378-tetrachlorinated dibenzofuran (2378-TCDF), and the 2,3,7,8-substituted penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soil, fly ash, and chemical waste samples including stillbottom, fuel oil, and sludge matrices. The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS) on sample extracts that have been subjected to specified cleanup procedures. The calibration range is dependent on the compound and the sample size. The sample size varies by sample matrix. The Contract Required Quantitation Limits (CRQLs) for each matrix and compound are listed in Exhibit C. The upper limit of the calibration range for each compound is 20 times the CRQL. Samples in which any target compound is found above the calibration range must be diluted and reanalyzed.

1.2 The protocol requires the calculation of the 2378-TCDD toxicity equivalence according to the procedures given in the U.S. Environmental Protection Agency "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016). This procedure recognized that structure-activity relationships exist between the chemical structure of a particular PCDD/PCDF "and its ability to elicit a biological/toxic response in various in vivo and in vitro test systems." Of the 210 possible chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans, the 17 isomers that bear chlorine atoms in the 2,3,7 and 8 positions of their respective structures are the compounds of greatest concern. To aid in the assessment of risks to human health and the environment, a factor is assigned to each of these 17 2,3,7,8-substituted PCDDs and PCDFs that relates the toxicity of that isomer to a concentration of the most toxic isomer, 2378-TCDD. These factors are called TEFs. The concentrations of any of the 17 isomers that are detected in an environmental sample can then be adjusted by the TEF and summed, yielding a concentration of 2378-TCDD with an equivalent toxicity.

1.3 If the toxicity equivalence is less than 0.7 parts per billion (ppb) for a soil or fly ash sample, less than 7 parts-per-trillion (ppt) for an aqueous sample, or less than 7 ppb for a chemical waste, no further analysis is required. If the toxicity equivalence is greater than or equal to 0.7 ppb (soil or fly ash), 7 ppt (aqueous), or 7 ppb (chemical waste), analysis on a column capable of resolving all 2,3,7,8-substituted PCDDs/PCDFs is required.

For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an "Estimated Maximum Possible Concentration" (see Section 15.7), regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

1.4 This method is also capable of determining the total concentration of all PCDDs/PCDFs in a given level of chlorination (i.e., Total TCDD, Total PeCDF, etc.), although complete chromatographic separation of all 210 possible PCDDs/PCDFs is not possible under the instrumental conditions described here. The "Total" concentrations are not assigned TEF values in the February 1989 TEF procedure, and therefore are not included in the toxicity equivalence calculations.

1.5 The qualitative identification criteria (see Section 11) include requirements for retention times, simultaneous detection of three ions per compound, and limits on the ratio of the abundances of the two most intense ions produced by each compound. In instances where a signal is detected that meets all of the qualitative identification criteria except the ion abundance ratio, the method requires calculation of an "Estimated Maximum Possible Concentration" (EMPC). The presence of interferences that coelute with the compounds of interest may cause the ion abundance ratio to fall outside the limits for qualitative identification and would also affect the quantitative results. The EMPC is a worst case estimate of the sample concentration that the signal would represent if it did meet all the identification criteria (see Section 15.7). Because of the quantitative uncertainty associated with the EMPC values, they are not included in the TEF calculations performed in the method.

1.6 The data that result from these analyses are reported based on the wet weight of the sample. However, for solid matrices such as soil/sediments, the percent solid content of the sample is also reported, if needed by the data user. The percent solids content of fly ash samples is not reported because the fly ash is treated with an aqueous acid solution prior to extraction.

1.7 This method is designed for use only by analysts experienced with residue analysis and skilled in HRGC/LRMS.

1.8 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure of personnel to materials known or believed to contain PCDDs/PCDFs.

2. Summary of Method

2.1 Soil/Sediment Extraction

For the purposes of this method, a soil/sediment sample is defined as a portion of wet soil/sediment which does not contain oil, but which may contain other solids such as stones, vegetation, etc. The sample should not contain an obvious liquid phase (see Section 8.4). A 10 g aliquot of the soil/sediment sample is spiked with the internal standard solution and extracted with toluene in a combination of a Soxhlet extractor and a Dean Stark water separator (SDS).

2.2 Water Extraction

For the purposes of this method, a water sample is defined as a single phase system that is primarily clear water but may contain very small

amounts of floating, suspended and settled particulate matter. Multiple phases should not be present (see Section 8.4). Approximately 1 L of the water sample is spiked with the internal standard solution and filtered to separate the aqueous and particulate fractions. The filtered aqueous fraction is extracted with methylene chloride using a separatory funnel or continuous liquid-liquid extractor. The particulate fraction is extracted with toluene in a SDS extractor. The extracts of the two fractions are then combined for cleanup.

2.3 Fly Ash Extraction

For the purposes of this method, a fly ash sample is defined as a solid matrix from an incineration or other combustion process which may contain water and other solids. It should not contain an obvious liquid phase. A 10 g aliquot of the fly ash is washed with dilute hydrochloric acid, spiked with the internal standard solution, and extracted with toluene in a SDS extractor.

2.4 Chemical Waste Sample Extraction

For the purposes of this method, a chemical waste sample includes sample matrices of oils, stillbottoms, oily sludge, oil-laced soil, and surface water heavily contaminated with the matrices listed above (see Section 8.2). Internal standards are added in the concentrations listed in Table 4 to a 1 or 10 g aliquot of chemical waste. Wet fuel oil and oily sludge samples, showing signs of water, are spiked with the internal standard solution, fitted with a reflux condenser and a Dean Stark water separator to remove the water, and extracted with toluene. Stillbottom samples are spiked with the internal standard solution, refluxed with toluene, and filtered.

2.5 Cleanup and Analysis

Immediately prior to cleanup, all extracts are spiked with a ^{37}Cl-2378-TCDD standard. Because it is added after extraction, the recovery of this standard may be used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various cleanup procedures. The extracts are subjected to an acid-base washing treatment and dried. Following a solvent exchange step, the extract is cleaned up by column chromatographic procedures, including silica gel, acid alumina, and carbon on celite columns, to eliminate sample components that may interfere with the detection and measurement of PCDDs/PCDFs. The extracts are concentrated and the solvent is exchanged to tridecane. The recovery standards are added to an aliquot (50 uL) of the extract and the aliquot is reduced to the final volume of 50 uL. The remaining 50 uL of extract is retained in the event that dilutions or reanalyses are required. One or two uL of the concentrated aliquot containing the recovery standards are injected onto a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS) (see Paragraph 4.1.1).

The identification of PCDD/PCDF isomers is based on the simultaneous detection of the two most abundant ions in the molecular ion regions and the M-COCl ion. In addition, the identification of OCDD and five

of the 2,3,7,8-substituted isomers, for which a ^{13}C-labeled standard is available in the internal standard and recovery standard solutions, is based on their exact retention time (-1 to 3 seconds from the respective internal or recovery standard signal). The 2,3,7,8-substituted isomers for which ^{13}C-labeled standards are not available in the sample extracts are identified by the relative retention times of the isomer in the daily standard as compared to the appropriate internal standard.

The identification of all other PCDD/PCDF isomers is based on their retention times falling within their respective PCDD/PCDF retention time windows as established by a window defining mix. Confirmation of all PCDDs/PCDFs is based on a comparison of the ratio of the integrated ion abundance of the molecular ion species to the theoretical ion abundance ratio.

The PCDDs/PCDFs are quantitated by comparing the MS response of the detected analyte relative to the MS response of the appropriate ^{13}C-labeled internal standard (Table 2). The responses of both the ions monitored for each analyte are used for quantitation. The labeled internal standards are added prior to sample extraction. Thus, the quantitative results for the native analytes are corrected for the recovery of the internal standards, based on the assumption that losses of the internal standards during sample preparation and analysis are equal to the losses of the unlabeled PCDDs/PCDFs.

2.6 The recovery of the internal standards is determined by comparing the MS response of the internal standard to the MS response of the appropriate recovery standard (Table 2). The recovery standards are also isotopically labeled compounds, and are added to each sample extract and blank aliquot just prior to injection.

Because the ability to quantify the concentrations of the unlabeled analytes and the precision of the measurements are related to the recovery of the internal standards, upper and lower limits are placed on the percent recovery of the internal standards (see Paragraphs 15.5.2 and 17.1.1).

2.7 If the concentration of any PCDD/PCDF exceeds the calibration range of the instrument, a dilution must be performed to bring that concentration within range. Additional recovery standard solution is added to the diluted sample extract immediately prior to reanalysis (see Section 10.4).

If the MS response of any internal standard in the diluted sample is less than 10% of its MS response in the continuing calibration standard, the unlabeled PCDD/PCDF concentrations in the sample are estimated using the MS responses of the recovery standards (see Paragraph 15.3). The purpose of this requirement is to ensure that there is an adequate MS response for quantitation.

2.8 In order to provide information on recovery of the analytes of interest from the sample matrix, the laboratory must prepare a second aliquot of one sample of each matrix in each Sample Delivery Group (SDG) and spike

it with the analytes at concencrations specified in Section 13. This aliquot is analyzed and the recovery of the spiked analytes is determined.

2.9 In order to provide information on the precision of the analysis in the sample matrix, the laboratory must perform a duplicate analysis on one sample of each matrix in each SDG. The samples to be analyzed in duplicate may be specified by the Region in advance; however, if no samples are so specified, the laboratory must select a sample of each matrix for duplicate analyses. The precision of the analysis is determined as the relative percent difference of the concentrations as specified in Section 14.

2.10 Due to a variety of situations that may occur during contract performance, the laboratory shall be required to reextract and reanalyze certain samples or groups of samples. As used hereafter, except in the case of dilutions, the term "rerun" shall indicate sample reextraction, cleanup and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed (see Section 10.4).

When the rerun is required due to matrix effects, interferences or other problems encountered, the Government will pay the Contractor for the reruns. Such reruns shall be billable and accountable under the specified contract allotment of automatic reruns. When the rerun is required due to Contractor materials, equipment or instrumentation problems or lack of Contractor adherence to specified contract procedures, the rerun shall not be billable nor accountable under the terms of this contract. The Contractor's failure to perform any of the sample reruns specified herein, either billable or nonbillable, shall be construed as Contractor nonperformance and may result in the termination of the contract for default. Specific requirements for reextraction and reanalysis are given in Section 17.

NOTE: A contaminated method blank is the only circumstance that may require more than one rerun per sample.

3. Interferences

3.1 Any compound that yields ions listed in Table 5 and also elutes within the retention time window of the corresponding homologue is a potential interference. PCDDs/PCDFs are often associated with other chlorinated compounds such as polychlorinated biphenyls (PCBs) and polychlorinated diphenyl ethers (PCDPEs). These compounds may be found at concentrations several orders of magnitude higher than that of the analytes of interest and may otherwise interfere with the analysis of PCDDs/PCDFs. Therefore, the retention time of the target analytes must be verified using reference standards and compared to retention time windows established during the calibration. While the cleanup procedures specified in this method are designed to minimize these interferences, some samples may ultimately require additional cleanup steps to achieve the detection limits.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause

misinterpretation of chromatographic data. All of these materials shall be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

NOTE: Because of the possibility of contamination, analysts should avoid using PVC gloves. However, latex gloves may be adequate.

3.3 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be necessary.

3.4 High resolution capillary columns are used to resolve as many PCDD/PCDF isomers as possible. No single column is known to resolve all 210 of the isomers. The columns employed by the laboratory in these analyses must be capable of resolving the 17 2,3,7,8-substituted PCDDs/PCDFs sufficiently to meet the method specifications (see Section 7.1).

4. Apparatus and Equipment

Brand names and catalog numbers are for illustrative purposes only and do not imply an endorsement by EPA. Equivalency of materials from other suppliers may be demonstrated by performing analyses that meet the specifications of this method.

4.1 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

4.1.1 The GC shall be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port shall be designed for capillary columns; a splitless or an on-column injection technique is recommended. A 2 uL injection volume is assumed throughout this method; however, with some GC injection ports, other volumes may be more appropriate. A 1 uL injection volume may be used if adequate sensitivity and precision can be demonstrated.

NOTE: The injection volume for all sample extracts, blanks, quality control (QC) samples and calibration solutions shall be the same.

4.1.2 Mass spectral data shall be obtained using a low resolution instrument that utilizes 70 volts (nominal) electron energy in the electron impact mode. The system shall be capable of selected ion monitoring (SIM) for at least 18 ions per cycle, with a cycle time of 1 second or less. Minimum integration time for SIM is 25 milliseconds per m/z. The integration time used to analyze samples shall be identical to the time used to analyze the initial and continuing calibration solutions and QC samples. Total data acquisition time per cycle (18 ions) must not exceed 1 second.

4.1.3 An interfaced data system is required to acquire, store, reduce and output mass spectral data.

4.1.4 GC/MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.1.5 The Contractor shall use a magnetic media storage device capable of recording data suitable for long-term off-line storage. The Contractor shall record all raw GC/MS data acquired during the entire contract period on magnetic media in appropriate instrument manufacturer format.

4.2 GC Column

Fused silica capillary columns are required. The columns shall demonstrate the required separation of all 2378-specific isomers whether a dual column or a single column analysis is chosen. Column operating conditions shall be evaluated at the beginning and end of each 12-hour period during which samples or concentration calibration solutions are analyzed (see Section 7.4).

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column. In order to determine the concentration of the individual 2,3,7,8-substituted isomers, if the toxicity equivalence is greater than 0.7 ppb (solids), 7 ppt (aqueous), or 7 ppb (chemical waste), the sample extract shall be reanalyzed on a 60 m SP-2330 or SP-2331 (or equivalent) GC column.

For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an Estimated Maximum Possible Concentration (see Section 15.7), regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

Analysis on a single column is acceptable if the required separation of all the 2378-specific isomers is demonstrated and the minimum acceptance criteria outlined in Sections 7.1, 7.2 and 7.3 are met. See Section 11 for the specifications for the analysis of the 2378-specific isomers using both dual columns and single columns.

4.3 Miscellaneous Equipment

The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

4.3.1 Nitrogen evaporation apparatus (N-Evap* Analytical Evaporator Model 111. Organomation Association Inc., Northborough, MA, or equivalent).

4.3.2 Balance capable of accurately weighing ± 0.01 g.

4.3.3 Water bath. Equipped with concentric ring cover and temperature controlled within ± 2°C.

4.3.4 Stainless steel (or glass) pan large enough to hold contents of 1-pint sample containers.

4.3.5 Glove box. For use in preparing standards from neat materials and in handling soil/sediment samples containing fine particulates that may pose a risk of exposure.

4.3.6 Rotary evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10 or equivalent.

4.3.7 Centrifuge. Capable of operating at 400 x G with a 250-300 mL capacity.

4.3.8 Drying oven.

4.3.9 Vacuum oven. Capable of drying solvent-washed solid reagents at 110°C.

4.3.10 Mechanical shaker. A magnetic stirrer, wrist-action or platform-type shaker, that produces vigorous agitation. Used for pre-treatment of fly ash samples.

4.4 Glassware

4.4.1 Extraction jars. Amber glass with Teflon-lined screw cap; minimum capacity of approximately 200 mL; must be compatible with mechanical shaker to be used.

4.4.2 Kuderna-Danish (KD) Apparatus. 500 mL evaporating flask, 10 mL graduated concentrator tubes with ground glass stoppers, three ball macro-Synder column.

4.4.3 Disposable Pasteur pipets, 150 mm long x 5 mm ID.

4.4.4 Disposable serological pipets, 10 mL for preparation of the carbon column specified in Section 9.10.

4.4.5 Vials. 0.3 mL and 2 mL amber borosilicate glass with conical shaped reservoir and screw caps lined with Teflon-faced silicone disks.

4.4.6 Funnels. Glass; appropriate size to accommodate filter paper (12.5 cm).

4.4.7 Chromatography Columns. 300 mm x 10.5 mm glass chromatographic column fitted with Teflon stopcock.

4.4.8 Soxhlet Apparatus, 500 mL flask, all glass. Complete with glass extractor body, condenser, glass extraction thimbles, heating mantle, and variable transformer for heat control.

NOTE: Extraction thimbles must be of sufficient size to hold 100 g of sand, 5 g of silica gel, and at least 10 g of solid sample, with room to mix the sand and sample in the thimble.

4.4.9 Dean Stark Water Separator Apparatus, with a Teflon stopcock. Must fit between Soxhlet extractor body and condenser.

4.4.10 Concentrator tubes. 15 mL conical centrifuge tubes.

4.4.11 Separatory funnels. 125 mL and 2 L separatory funnels with a Teflon stopcock.

4.4.12 Continuous Liquid-Liquid Extractor. 1 L sample capacity, suitable for use with heavier than water solvents.

4.4.13 Boiling chips. Teflon boiling chips washed with hexane prior to use.

4.4.14 Buchner funnel. 15 cm.

4.4.15 Filtration flask. For use with Buchner funnel, 1 L capacity.

4.5 Glassware Cleaning Procedures

Reuse of glassware should be minimized to avoid the risk of using contaminated glassware. All glassware that is reused shall be scrupulously cleaned as soon as possible after use, applying the following procedure.

4.5.1 Rinse glassware with the last solvent used in it.

4.5.2 Wash with hot water containing detergent.

4.5.3 Rinse with copious amounts of tap water and several portions of distilled water. Drain dry.

4.5.4 Rinse with high purity acetone & hexane.

4.5.5 After glassware is dry, store inverted or capped with aluminum foil in a clean environment.

Do not bake reusable glassware as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered, but should be minimized, as repeated baking may cause active sites on the glass surface that will irreversibly adsorb PCDDs/PCDFs.

CAUTION: The analysis for PCDDs/PCDFs in water samples is for much lower concentrations than in soil/sediment, fly ash, or chemical waste samples. Extreme care must be taken to prevent cross-contamination between soil/sediment, fly ash, chemical waste and water samples. Therefore, it is strongly recommended that separate glassware be reserved for analyzing water samples.

4.6 Preextraction of Glassware

It is required that all glassware be rinsed or preextracted with solvent immediately before use. The SDS apparatus and continuous liquid-liquid extractors must be preextracted for approximately three hours immediately prior to use. The pooled waste solvent for a set of extractions may be concentrated and analyzed as a method of demonstrating that the glassware was free of contamination.

It is recommended that each piece of reusable glassware be numbered in such a fashion that the laboratory can associate all reusable glassware with the processing of a particular sample. This procedure will assist the laboratory in tracking down possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

5. Reagents and Consumable Materials

Brand names and catalog numbers are for illustrative purposes only and do not imply an endorsement by EPA. Equivalency of materials from other suppliers may be demonstrated by performing analyses that meet the specifications of this method.

5.1 Solvents. High purity, distilled-in-glass: hexane, methanol, methylene chloride, toluene, isooctane, cyclohexane, acetone, tridecane (or nonane).

5.2 Filters

5.2.1 Filter paper. Whatman No. 1 or equivalent.

5.2.2 Glass fiber filter. 15 cm, for use with Buchner funnel.

5.2.3 0.45 micron, Millipore or equivalent, PTFE or other material compatible with toluene. Rinse with toluene.

5.3 White quartz sand. 60/70 mesh, for use in the SDS extractor. Bake at 450°C for 4 hours minimum.

5.4 Glass wool, silanized. Extract with methylene chloride and hexane before use.

5.5 Sodium Sulfate. Granular, anhydrous. Before use, heat to 400°C in a shallow tray for approximately 4 hours, cool in a desiccator, and store in a glass jar.

5.6 Potassium Hydroxide. ACS grade, prepare a 20% (w/v) solution in distilled water.

5.7 Sulfuric Acid, concentrated. ACS grade, specific gravity 1.84.

5.8 Sodium Chloride. ACS grade, prepare a 5% (w/v) solution in distilled water.

5.9 Hydrochloric Acid, concentrated. ACS grade, specific gravity 1.17. Prepare a 1N solution in distilled water for pretreatment of fly ash samples.

5.10 Column Chromatography Reagents

5.10.1 Alumina, acidic AG4, Bio Rad Laboratories (catalogue #132-1240) or equivalent. Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil-covered glass container for 24 hours at 190°C.

5.10.2 Charcoal Carbon. Active carbon AX-21 (Anderson Development Company, Adrian, MI, or equivalent), prewashed with methanol and dried in vacuo at 110°C.

5.10.3 Celite 545 (Supelco or equivalent).

5.10.4 Silica gel. High purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil-covered glass container for 24 hours at 190°C.

5.10.5 Silica gel impregnated with 2% (w/w) sodium hydroxide. Add 1 part by weight of 1 M NaOH solution to 2 parts silica gel (extracted and activated) in a screw-cap bottle and mix with a glass rod until free of lumps.

5.10.6 Silica gel impregnated with 40% (w/w) sulfuric acid. Add 2 parts by weight concentrated sulfuric acid to 3 parts silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw-cap glass bottle.

5.11 Calibration Solutions (Table 3)

Five tridecane (or nonane) solutions (CC1-CC5) containing 10 unlabeled and 7 carbon-labeled PCDDs/PCDFs at known concentrations which are used to calibrate the instrument. One of these five solutions (CC3) is used as the continuing calibration solution and contains 7 additional unlabeled 2,3,7,8-substituted isomers that are commercially supplied (see Paragraph 7.3.2.1). The concentration ranges are homologue-dependent with the lowest concentrations associated with tetra- and pentachlorinated dioxins and furans (0.1-2.0 ng/uL), and the higher concentrations associated with the hexa- through octachlorinated homologues (0.5-10.0 ng/uL). Depending on the availability of materials, the Environmental Monitoring Systems Laboratory (EMSL-LV) will provide these solutions, with the exception of the additional 2,3,7,8-substituted isomers for the CC3 solution.

5.12 Internal Standard Solution (Table 4)

The solution contains the five internal standards in tridecane (or nonane) at the nominal concentrations listed in Table 4. Depending on the availability of materials, EMSL-LV will provide the solution. Mix 10 uL with 1.0 mL of acetone before adding to each sample and blank.

5.13 Recovery Standard Solution

The hexane solution contains the recovery standards, $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD, at concentrations of 5.0 ng/uL, in a solvent other than tridecane or nonane (see Section 10.2). Depending upon the availability of materials, EMSL-LV will provide the solution.

5.14 Continuing Calibration Solution

This solution contains standards to be used for identification and quantitation of target analytes. In order to have all 2,3,7,8-substituted isomers and the cleanup standard present for quantitation purposes, a commercially supplied supplemental standard and the cleanup standard solution are combined with the EPA-supplied CC4 solution to produce the CC3 solution (see Paragraph 7.4.1). This solution is identified in Table 3.

5.15 Window Defining Mix

This solution is to be obtained by the laboratory through commercial vendors. The solution contains the first and last eluting isomer of each homologue (see Table 9) and is used to verify that the switching times between the descriptors have been appropriately set.

The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture. However, these standards and other isomers may be added to the mixture listed in Table 7 at the discretion of the laboratory, so long as the additional contents of the mixture are clearly specified in every SDG Narrative.

If the laboratory employs a GC column that has a different elution order than those specified here, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the window defining mix used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those listed in Table 9.

EMSL-LV does not supply the window defining mix (see Table 9).

5.16 Supplemental Calibration Solution

This solution contains seven 2,3,7,8-substituted PCDD/PCDF isomers to be added to the CC4 solution to produce the CC3 solution that is used for identification and quantitation of target analytes. EMSL-LV does not supply this solution (see Table 10).

5.17 Cleanup Standard

This solution contains $^{37}Cl_4$-2378-TCDD at a concentration of 5 ng/uL (5 ug/mL) in tridecane (or nonane) and is added to all sample extracts prior to cleanup. The solution may be added at this concentration or

diluted into a larger volume of solvent (see Paragraph 9.7.1). The recovery of this compound is used to judge the efficiency of the cleanup procedures.

5.18 Matrix Spiking Standard

This solution contains 10 of the 2,3,7,8-substituted isomers, at the concentrations listed in Table 11 in tridecane (or nonane), and is used to prepare the spiked sample aliquot (see Section 13). Dilute 10 uL of this standard to 1.0 mL with acetone and add to the aliquot chosen for spiking.

5.19 Column Performance Solution

The laboratory must obtain this solution through commercial vendors. The solution contains 2378-TCDD and the other TCDD isomers (1478-TCDD and the 1237/1238-TCDD pair) that elute closest to 2378-TCDD on the SP-2331 (or equivalent) column. The solution is used to verify the chromatographic resolution of the SP-2331 (or equivalent) GC column. The concentrations of these isomers should be approximately 0.5 ng/uL in tridecane (or nonane).

If the laboratory employs a GC column that has a different elution order than those specified here, the laboratory must ensure that the isomers eluting closest to 2378-TCDD are represented in the column performance solution.

EMSL-LV does <u>not</u> supply the column performance solution.

6. <u>Mass Calibration</u>

Mass calibration of the MS is recommended prior to analyzing the calibration solutions, blanks, samples and QC samples. It is recommended that the instrument be tuned to greater sensitivity in the high mass range in order to achieve better response for the later eluting compounds. Optimum results using FC-43 for mass calibration may be achieved by scanning from 222-510 amu every one second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode. Under these conditions, m/z 414 and m/z 502 should be 30-50% of m/z 264 (base peak).

7. <u>Retention Time Windows and Calibration of Target Analytes</u>

Prior to the calibration of the GC/MS system, it is necessary to establish the appropriate switching times for the SIM descriptors (see Table 7) and to verify the chromatographic resolution. The switching times are determined by the analysis of the window defining mix, containing the first and last eluting isomers in each homologue (see Table 9). Chromatographic resolution is verified by the analysis of one of two solutions, depending on the GC column used for analysis.

Two types of calibration procedures, initial and continuing, are required. The initial calibration is required before any samples are analyzed for PCDDs/PCDFs, and intermittently throughout sample

analysis, as dictated by the results of the continuing calibration (see Section 7.4). The continuing calibration is required at the beginning of each 12-hour time period during which samples are analyzed.

Samples shall not be analyzed until acceptable descriptor switching times, chromatographic resolution, and calibrations, as described in Sections 7.1, 7.2, 7.3 and 7.4, are achieved and documented. The sequence of analyses is shown in Table 13.

7.1 Window Defining Mix

The window defining mix shall be analyzed before any calibration standards in order to evaluate the descriptor switching times. The commercially available mix (see Section 5.15) contains the first and last eluting isomers in each homologue. Mixes are available for various columns. The mix for the DB-5 (or equivalent) column may not be appropriate for the SP-2331 or other columns.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third descriptor, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor.

The descriptor switching times are set such that the isomers that elute from the GC during a given retention time window will also be those isomers for which the ions are monitored. For the homologues that overlap between descriptors, the laboratory may use discretion in setting the switching times. However, do not set descriptor switching times such that a change in descriptors occurs at or near the expected retention time of any of the 2,3,7,8-substituted isomers.

The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture. However, these standards and other isomers may be added to the mixture listed in Table 7 at the discretion of the laboratory, so long as the additional contents of the mixture are clearly specified in every SDG Narrative.

7.1.1 Analyze a 2 uL aliquot of the window defining mix, using the GC column conditions in Table 1.

7.1.2 Adjust the descriptor switching times and the GC column conditions as needed to ensure that the isomers elute in the appropriate ion descriptors (see Table 7).

7.1.3 The window defining mix must be analyzed at the following frequency:

7.1.3.1 Before initial calibration on each instrument and GC column used for analysis.

7.1.3.2 Each time a new initial calibration is performed, regardless of reason.

7.1.3.3 Each time adjustments or instrument maintenance activities are performed that may affect retention times.

7.1.3.4 Any time the retention time of either the $^{13}C_{12}$-1234-TCDD or $^{13}C_{12}$-123789-HxCDD recovery standards in any analysis varies by more than 10 seconds from its retention time in the most recent continuing calibration standard (see Paragraphs 7.3.2.3, 7.5.2.1 and 11.1.4)

7.1.4 If the laboratory employs a GC column that has a different elution order than those columns specified here, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the window defining mix used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those listed in Table 9.

7.1.5 Analysis on a single GC column (as opposed to situations requiring a second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and SP-2331 (or equivalent) columns are met (see Paragraphs 7.3.2.1 and 7.2.3).

7.2 Chromatographic Resolution

7.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 standard during both the initial and continuing calibration procedures (see Paragraphs 7.3.2.1 and 7.4.2).

7.2.2 For analyses on a SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially available column performance mixture (see Section 5.19) that contains the TCDD isomers that elute most closely with 2378-TCDD on this GC column (1478-TCDD and the 1237/1238-TCDD pair).

Analyze a 2 uL aliquot of this solution, using the column operating conditions and descriptor switching times previously established.

Note: The column performance mixture may be combined with the window defining mix into a single solution, provided that the combined solution contains the isomers needed to determine that the criteria for both analyses can be met.

7.2.3 GC Resolution Criteria for SP-2331 or Equivalent Column. The chromatographic peak separation between unlabeled 2378-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of ≤ 25 percent, where:

Valley = (x/y)(100).
y = the peak height of any TCDD isomer.
x = the distinction from the baseline to the bottom of the valley between adjacent peaks, measured as shown in Figure 5.

The resolution criteria must be evaluated using measurements made on the selected ion current profile (SICP) for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

Further analyses may not proceed until the GC resolution criteria have been met.

7.2.4 If the laboratory uses a GC column other than those specified here, the laboratory must ensure that the isomers eluting closest to 2378-TCDD on that column are used to evaluate GC column resolution. The chromatographic peak separation between unlabeled 2378-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of ≤ 25 percent.

7.2.5 Analysis on a single GC column (as opposed to situations requiring a second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for <u>both</u> the DB-5 and SP-2331 (or equivalent) columns are met (see Paragraphs 7.3.2.1 and 7.2.3).

7.3 Initial Calibration

Once the window defining mix has been analyzed and the descriptor switching times have been verified (and after the analysis of the column performance solution if using a GC column other than DB-5), the five concentration calibration solutions (CC1-CC5), described in Table 3, shall be analyzed prior to any sample analysis. The CC1, CC2, CC4 and CC5 solutions shall be used as provided by EPA. The CC3 solution is prepared by combining CC4 solution, the supplemental calibration solution, and the internal, cleanup, and recovery standard solutions as described in Paragraph 7.4.1.

7.3.1 Analyze a 2 uL (see Paragraph 4.1.1) aliquot of each of the five concentration calibration solutions, beginning with CC3 solution (see Paragraph 7.4.1). The following MS/DS conditions shall be used:

7.3.1.1 Acquire SIM data for each of the ions listed in Table 5 including the ions to monitor interfering compounds. See Table 7 for the recommended MS descriptors.

7.3.1.2 The total cycle time for data acquisition must be less than one second. Acquire at least five data points for each ion during the elution of the GC peak.

7.3.2 The Contractor shall not proceed with the sample analysis until an acceptable initial calibration has been performed and documented according to the following criteria: GC resolution, ion abundance ratios, retention times, and instrument sensitivity.

7.3.2.1 GC Resolution Criteria for DB-5 or Equivalent Column. The chromatographic peak separation between the $^{13}C_{12}$-2378-TCDD peak and $^{13}C_{12}$-1234-TCDD isomers shall be resolved with a valley of $\leq$ 25 percent, in all calibration standards, where:

Valley = (x/y)(100).
y = the peak height of $^{13}C_{12}$-2378-TCDD.
x = measured using the $^{13}C_{12}$-1234-TCDD peak as shown in Figure 5.

In addition, the chromatographic peak separation between the 123478-HxCDD and 123678-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50 percent, calculated in a similar fashion as above.

The resolution criteria must be evaluated using measurements made on the SICP for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

7.3.2.2 The relative ion abundance criteria for PCDDs/PCDFs listed in Table 6 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions. The lower and upper limits of the ion abundance ratios represent a $\pm$ 15 percent window around the theoretical abundance ratio for each pair of selected ions. The ^{37}Cl-2378-TCDD cleanup standard contains no ^{35}Cl, thus the ion abundance ratio criterion does not apply to this compound.

7.3.2.3 For all calibration solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix analysis. In addition, the absolute retention times of the recovery standards, $^{13}C_{12}$-

1234-TCDD and $^{13}C_{12}$-123678-HxCDD, shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard.

7.3.2.4 MS Sensitivity. For all calibration solutions, including the CC1 solution, the signal-to-noise ratio (S/N) must be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10 for the internal standard and recovery standard ions.

7.3.3 Calculate the relative response factors (RRFs) for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) (see Table 8), according to the formulae below. For the seven unlabeled analytes and the $^{37}Cl_4$-2378-TCDD cleanup standard that are found only in the CC3 solution, only one RRF is calculated for each analyte. For the other 10 unlabeled analytes, calculate the RRF of each analyte in each calibration standard.

Calculate the RRFs for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}) (see Table 8), in each calibration standard, according to the following formulae:

$$RRF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

where:

A_n^1 and A_n^2 - integrated areas of the two quantitation ions of the isomer of interest (Table 5).

A_{is}^1 and A_{is}^2 - integrated areas of the two quantitation ions of the appropriate internal standard (Table 5).

A_{rs}^1 and A_{rs}^2 - integrated areas of the two quantitation ions of the appropriate recovery standard (Table 5).

Q_n - quantity of unlabeled PCDD/PCDF analyte injected (ng).

Q_{is} - quantity of appropriate internal standard injected (ng).

Q_{rs} - quantity of appropriate recovery standard injected (ng).

For quantitations involving the use of peak heights instead of peak areas, see Section 11.4.

There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

The RRF_n and RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is} and Q_{rs} must be the same.

NOTE: This protocol is based on the assumption that if the 10 unlabeled 2,3,7,8-substituted isomers provided in the EPA standard solutions meet linearity criteria, then the seven additional 2,3,7,8-substituted isomers and the cleanup standard in the CC3 solution may be assumed to have a sufficiently linear response to be used for quantitation. These eight RRFs cannot be used to determine percent relative standard deviation, but <u>are</u> used for percent difference determinations (as described in Paragraph 7.4.6.4) and quantitation of target analytes.

7.3.4 Calculate the relative response factors for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}) where:

$$RRF_{rs} = RRF_n \times RRF_{is}$$

This relative response factor is necessary when the sample is diluted to the extent that the MS response of the internal standard is less than 10 percent of its MS response in the continuing calibration standard (see Section 15.3).

7.3.5 Relative Response Factor Criteria. Calculate the mean RRF and percent relative standard deviation (%RSD) of the five RRFs (CC1-CC5) for each unlabeled PCDD/PCDF and labeled internal standards present in all five concentration calibration solutions.

No mean RRF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean RRF}} \times 100$$

The %RSD of the five RRFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards must not exceed 15.0 percent.

7.3.6 The response factors to be used for determining the total homologue concentrations are described in Section 15.2.

7.3.7 If any of the requirements listed in Paragraphs 7.3.2 or 7.3.5 are not met, the Contractor is responsible for taking corrective action before sample analyses are performed. The following suggestions may be useful:

7.3.7.1 Check and adjust the GC and/or MS operating conditions.

7.3.7.2 Replace the GC column.

7.3.7.3 Adjust the MS for greater or lesser resolution using FC-43 (see Section 6).

7.3.7.4 Recalibrate the mass scale.

Once the corrective actions have been completed, the Contractor must perform a new initial calibration that does meet all the QC requirements, beginning with analysis of the window defining mix, before sample analyses may proceed.

7.4 Continuing Calibration

The continuing calibration consists of two parts: evaluation of the chromatographic resolution and verification of the RRF values to be used for quantitation. At the beginning of each 12-hour period, the chromatographic resolution is verified in the same fashion as in the initial calibration: through the analysis of the CC3 solution on the DB-5 (or equivalent) column or through the analysis of the column performance solution on the SP-2331 (or equivalent) column.

NOTE: The 12-hour time period is defined as beginning with the injection of the CC3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12-hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be injected within 12:00 hours of the CC3 solution or the column performance solution.

7.4.1 Prepare the CC3 solution by combining the following volumes of the solutions listed in Section 5:

500 uL	CC4 Solution
125 uL	Supplemental Calibration Solution
50 uL	Internal Standard Solution
50 uL	Recovery Standard Solution
50 uL	Cleanup Standard Solution
225 uL	Tridecane (or nonane)

to yield a final volume of 1.0 mL at the concentrations specified for the CC3 solution in Table 3.

7.4.2 For the DB-5 (or equivalent) column, begin the 12-hour period by analyzing the CC3 solution. Inject a 2 uL aliquot of the continuing calibration solution (CC3) into the GC/MS. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the continuing calibration solution (see Paragraph 7.3.1). Evaluate the chromatographic resolution using the QC criteria in Paragraph 7.3.2.1.

7.4.3 For the SP-2331 (or equivalent) column, or other columns with different elution orders, begin the 12-hour period by analyzing a 2 uL aliquot of the appropriate column performance solution. Evaluate the chromatographic resolution using the QC criteria in Paragraph 7.2.3 or 7.2.4. If this solution meets the QC criteria, proceed with the analysis of a 2 uL aliquot of the CC3 solution. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the continuing calibration solution (see Paragraph 7.3.1).

7.4.4 Calculate the RRFs for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) and the response factors for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}), according to the following formulae:

$$RRF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

A_n^1, A_n^2, A_{is}^1, A_{is}^2, A_{rs}^1, A_{rs}^2, Q_n, Q_{is} and Q_{rs} are defined in Paragraph 7.3.3.

There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

The RRF_n and RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is} and Q_{rs} must be the same.

7.4.5 Calculate the RRFs for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}), where $RRF_{rs} = RRF_n \times RRF_{is}$. This relative response factor is necessary for calculations when the sample is diluted (see Section 15.3).

7.4.6 Continuing Calibration Criteria. The Contractor shall not proceed with sample analysis until an acceptable continuing

calibration has been performed and documented according to the following criteria: GC resolution, ion abundance ratios, retention times, instrument sensitivity, and response factors.

7.4.6.1 GC Column Resolution Criteria. The chromatographic resolution on the DB-5 (or equivalent) column must meet the QC criteria in Paragraph 7.3.2.1. The chromatographic resolution on the SP-2331 (or equivalent) column must meet the QC criteria in Paragraph 7.2.3. In addition, the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50 percent.

7.4.6.2 Ion Abundance Criteria. The relative ion abundances listed in Table 6 shall be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

7.4.6.3 Instrument Sensitivity Criteria. For the CC3 solution, the S/N ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

7.4.6.4 Response Factor Criteria. The measured RRFs of each analyte and internal standard in the CC3 solution must be within $\pm$ 30.0 percent of the mean RRFs established during initial calibration for the EPA-supplied standards and within $\pm$ 30.0 percent of the single point RRFs established during initial calibration for the supplemental calibration standards and the cleanup standards.

$$\% \text{ Difference} = \frac{(RRF_i - RRF_c)}{RRF_i} \times 100$$

where:

RRF_i = Relative response factor established during initial calibration.

RRF_c = Relative response factor established during continuing calibration.

7.4.7 If any of the criteria listed in Paragraph 7.4.6 are not met, the Contractor must take corrective actions and reanalyze the continuing calibration standard (CC3). If the criteria in Paragraph 7.4.6 <u>are</u> met after the corrective action, then sample analysis may begin, as described in Section 10.

If the criteria in Paragraph 7.4.6 are <u>not</u> met after the corrective action, then the Contractor must perform a new initial calibration, beginning with the analysis of the window

defining mix. This new initial calibration must meet all of the QC criteria in Sections 7.1, 7.2 and 7.3 before sample analysis may begin.

7.5 Instrument Sensitivity Check

In order to demonstrate that the GC/MS/DS system has retained adequate sensitivity during the course of sample analyses, the Contractor must analyze the lowest of the standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

7.5.1 Analyze a 2 uL aliquot of the CC1 solution, using the identical instrumental conditions used for analysis of samples and standards.

7.5.2 The CC1 solution analyzed at the end of the 12-hour period must meet the following QC criteria:

7.5.2.1 Retention Time Criteria. The absolute retention time of the recovery standards, $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123678-HxCDD, shall not change by more than 10 seconds between the initial CC3 analysis and the ending CC1 analysis. If the retention times of either of these standards changes by more than $\pm$ 10 seconds, the Contractor must adjust the switching times of the descriptors and analyze the window defining mix before proceeding with further analyses.

7.5.2.2 All the analytes in the CC1 solution must meet the ion abundance ratio criteria in Table 6.

7.5.2.3 Instrument Sensitivity Criteria. For the CC1 solution, the S/N ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10.0 for the labeled internal and recovery standards.

7.5.3 If the analysis of the CC1 solution at the end of the 12-hour period fails either the ion abundance ratio or S/N criteria above, the Contractor must:

7.5.3.1 Take corrective action.

7.5.3.2 Perform a new initial calibration, beginning with the analysis of the window defining mix.

7.5.3.3 Start a new analytical sequence (see Table 13).

7.5.3.4 Reanalyze all samples originally analyzed in the preceding 12-hour time period in which:

7.5.3.4.1 No PCDDs/PCDFs were detected.

7.5.4.3.2 Neither 2378-TCDD or 2378-TCDF were detected, even if other PCDDs or PCDFs were detected.

7.5.4.3.3 Any 2,3,7,8-substituted PCDD or PCDF is reported as an Estimated Maximum Possible Concentration (see Section 15.7).

These reanalyses are necessary because poor S/N ratios indicate a loss of sensitivity that could lead to false negative results, underestimation of concentrations, or could cause ion abundance ratios to fall outside the QC limits.

8. Sample Homogenization, Preservation and Handling

8.1 Homogenization

Although sampling personnel will attempt to collect homogeneous samples, the Contractor shall examine each sample and determine if the sample needs phase separation or mixing. The extent to which phase separation or mixing is required will depend on the sample type.

The Contractor is responsible for taking a representative sample aliquot from the phase or phases to be analyzed. This responsibility entails efforts to make the sample phase as homogeneous as possible. Stirring is recommended when possible.

8.2 Sample Types

8.2.1 For the purpose of this method, a chemical waste sample includes the sample matrices of oils, oily sludge, stillbottom, oil-laced soil, and surface water heavily contaminated with any of the above matrices. The sample may contain particulates and an obvious non-aqueous liquid phase.

8.2.2 For the purpose of this method, a soil/sediment sample is defined as a single phase solid system composed of soil or sediment. The sample may contain stones and vegetation, but should not contain an obvious aqueous or non-aqueous liquid phase.

CAUTION: Finely divided soils contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing the analytes. Such samples should be handled in a confined environment (e.g., a closed hood or a glove box).

8.2.3 For the purpose of this method, a water sample is defined as a single phase system, the primary component of which is water.

The sample may include floating, suspended and settled particulate matter in quantities that do not cause severe problems with filtration or extraction.

8.3 Sample Preservation

8.3.1 Water Samples. Each water sample received will consist of at least two 1-liter (or quart) amber glass bottles. Store at 4 ± 2°C from collection until extraction. Do not freeze. After a portion of the sample is removed for analysis, the unused portion of the sample is stored at 4 ± 2°C in a locked, limited access area for at least 60 days from the date of data submission.

8.3.2 Soil/Fly Ash/Chemical Waste Samples. Each soil/fly ash/chemical waste sample received will be contained in a 1-pint glass jar surrounded by vermiculite in a sealed metal paint can. Until a portion is removed for analysis, the sealed sample must be stored in a locked, limited access area at room temperature. Do not freeze. After a portion is removed for analysis, the unused portion of the sample is returned to its original container and stored at room temperature for at least 60 days from the date of data submission.

8.3.3 To minimize the potential for photodecomposition, all samples must be protected from light from the time of receipt until extraction.

8.4 Sample Handling and Preextraction Treatment

8.4.1 If a soil/sediment sample contains an obvious aqueous liquid phase, decant or centrifuge the sample to separate the phases (see Paragraph 8.4.7).

8.4.2 If a soil/sediment sample does not contain an obvious liquid phase, homogenize the sample by careful stirring with a clean glass rod or spatula.

8.4.3 If a soil/sediment sample contains an obvious non-aqueous liquid phase, or contains more than two phases (i.e. non-aqueous liquid/aqueous liquid/solid), contact the Sample Management Office (SMO) in order to determine which phase(s) should be analyzed.

8.4.4 All water samples are filtered prior to extraction, and the filtered liquid and the particulates are extracted separately (see Section 9.5). If a water sample contains significant amounts of suspended particulates, centrifuge the sample and decant the water from the particulates before filtering (Paragraph 8.4.7).

8.4.5 If a water sample contains an obvious non-aqueous liquid phase or a non-particulate solid phase, contact SMO in order to determine which phase(s) should be analyzed.

8.4.6 If a water sample does not contain significant amounts of suspended particulates, homogenize the sample by carefully shaking the capped sample bottle.

8.4.7 Centrifugation. If centrifugation of a sample is necessary, place the entire sample in a suitable centrifuge bottle(s) with a 250-300 mL capacity, and centrifuge for 30 minutes at 400 x G. Decant the liquid phase into a clean container. Remove the solid phase by careful pouring or using a clean spatula or glass rod. Proceed with the analysis of the appropriate phase or phases.

CAUTION: A phase that is not analyzed may contain PCDDs/PCDFs and should be handled and disposed of appropriately.

9. Extraction Procedures

Four types of extraction procedures are employed in these analyses depending on the sample matrix. Chemical waste samples are extracted by refluxing with a Dean Stark water separator. Fly ash samples and soil/sediment samples are extracted in a combination of a Soxhlet extractor and a Dean Stark water separator. Water samples are filtered and then the filtrate is extracted using either a separatory funnel procedure or a continuous liquid-liquid extraction procedure. The filtered particulates are extracted in a combination of a Soxhlet extractor and a Dean Stark water separator.

9.1 Chemical Waste Sample Extraction

9.1.1 Assemble a flask (50 mL or 125 mL, see below), a Dean Stark trap, and a condenser, and preextract with toluene for three hours. Preextraction will ensure that the glassware is as clean as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

9.1.2 Oily Sludge/Wet Fuel Oil. Weigh about 1 g of sample to two decimal places into a tared preextracted 125-mL flask. Add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample in the flask. Attach the preextracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

Continue refluxing the sample until all the water has been removed. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 9.6.

9.1.3 Stillbottom/Oil. Weigh about 1 g of sample to two decimal places into a tared preextracted 50-mL flask. Add 1 mL of the

acetone-diluted internal standard solution (see Section 5.12) to the sample in the flask. Attach the preextracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 9.6.

9.1.4 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.2 Soxhlet-Dean Stark (SDS) Apparatus

The combination of a Soxhlet extractor and a Dean Stark moisture trap is used for the removal of water and extraction of PCDDs/PCDFs from samples of fly ash, soil/sediment, and the particulate fraction of water samples. The combination consists of a Soxhlet extractor body with a Dean Stark moisture trap fitted between the extractor and the condenser (see Figure 4).

Procedures for the use of this apparatus were developed by the Dow Chemical Company and have been tested by the EPA Industrial Technology Division, Office of Water Regulations and Standards. Those tests indicate that based on the recovery of labeled analytes, the extraction by SDS apparatus is as good, or better, than extraction by Soxhlet alone.

For soil/sediment samples, the results of these analyses are reported based on the <u>wet weight</u> of the sample. However, use of the SDS apparatus allows the water content of a sample to be determined from the same aliquot of sample that is also extracted for analysis. The amount of water evolved from the sample during extraction is used to approximate the percent solids content of the sample. The percent solids data may be employed by the data user to approximate the dry weight concentrations. The percent solids determination does <u>not</u> apply to the extraction of particulates from the filtration of water samples or to the extraction of fly ash samples which are treated with an HCl solution prior to extraction.

Further, as described here, the SDS apparatus allows the extraction of sample matrices containing water <u>without</u> the addition of drying agents such as sodium sulfate. The use of sodium sulfate during extraction may be responsible for the loss of analytes, through adsorption onto carbon particles produced by baking this reagent at high temperatures in order to remove organic contaminants, and by trapping analytes in pores in the sodium sulfate as moisture is adsorbed.

The following procedures apply to all uses of the SDS apparatus for extracting matrices covered by this protocol.

NOTE: It may be necessary to wrap portions of the SDS apparatus with aluminum foil or glass wool to obtain proper operation.

9.2.1 Refer to Section 4.5 for detailed instructions on cleaning glassware such as the SDS apparatus. In particular, do not bake the components of the SDS apparatus as part of routine cleaning, as repeated baking of glassware can cause active sites on the glass surface that will adsorb PCDDs/PCDFs and other analytes. All glass parts of the SDS apparatus, including the thimbles, must be preextracted with toluene for approximately three hours immediately prior to use. Preextraction will ensure that the glassware is as clean as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

9.2.2 The extraction of soil/sediment, fly ash, and particulates from water samples will require the use of a Soxhlet thimble. Prior to preextraction, prepare the thimble by adding 5 g of 70/230 mesh silica gel to the thimble to produce a thin layer in the bottom of the thimble. This layer will trap fine particles in the thimble. Add 80-100 g of quartz sand on top of the silica gel, and place the thimble in the extractor.

9.2.3 After preextraction for three hours, allow the apparatus to cool and remove the thimble. Mix the appropriate weight of sample with the sand in the thimble, being careful not to disturb the silica gel layer.

If the sample aliquot to be extracted contains large lumps or is otherwise not easily mixed in the thimble, the sand and sample may be mixed in another container. Transfer approximately 2/3 of the sand from the thimble to a clean container, being careful not to disturb the silica gel layer when transferring the sand. Thoroughly mix the sand and the sample with a clean spatula, and transfer the sand/sample mixture to the thimble.

If a sample with particularly high moisture content is to be extracted, it may be helpful to leave a small conical depression in the material in the thimble. This procedure will allow the water to drain through the thimble more quickly during the early hours of the extraction. As the moisture is removed during the first few hours of extraction, the depression will collapse, and the sample will be uniformly extracted.

9.3 Fly Ash Sample Extraction

9.3.1 Weigh about 10 g of the fly ash to two decimal places, and transfer to an extraction jar (Paragraph 4.4.1). Add 1 mL of the acetone-diluted internal standard solution (Section 5.12) to the sample.

9.3.2 Add 150 mL of 1 N HCl to the fly ash sample in the jar. Seal the jar with the Teflon-lined screw cap, place on a mechanical shaker, and shake for three hours at room temperature.

9.3.3 Rinse a Whatman #1 (or equivalent) filter paper with toluene, and then filter the sample through the filter paper in a Buchner funnel into a 1 L receiving flask. Wash the fly ash with approximately 500 mL distilled water.

9.3.4 Mix the fly ash with the sand in a preextracted thimble, and place the filter paper on top of the sand. Place the thimble in a SDS extractor, add 200 mL toluene, and extract for 16 hours.

The solvent must cycle completely through the system 5-10 times per hour. Cool and filter the toluene extract through a rinsed glass fiber filter into a 500 mL round-bottom flask. Rinse the filter with 10 mL of toluene. Concentrate the extract as described in Section 9.6.

NOTE: A blank must be analyzed using a piece of filter paper handled in the same manner as the fly ash sample.

9.3.5 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.4 Soil/Sediment Sample Extraction

NOTE: Extremely wet samples may require centrifugation to remove standing water before extraction (see Paragraph 8.4.7).

9.4.1 Weigh about 10 grams of the soil to two decimal places and transfer to a preextracted thimble (see Paragraph 9.2.2). Mix the sample with the quartz sand, and add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample/sand mixture. Add small portions of the solution at several sites on the surface of the sample/sand mixture.

9.4.2 Place the thimble in the SDS apparatus. Add 200 to 250 mL toluene to the SDS apparatus, and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour.

9.4.3 Estimate the percent solids content of the soil/sediment sample by measuring the volume of water evolved during the SDS

extraction procedure. For extremely wet samples, the Dean Stark trap may need to be drained one or more times during the 16-hour extraction. Collect the water from the trap, and measure its volume to the nearest 0.1 mL. Assume a density of 1.0 g/mL, and calculate the percent solids content according to the formula below:

$$\text{Percent Solids} = \frac{\text{(Wet weight of sample - Weight of water)}}{\text{Wet weight of sample}} \times 100$$

9.4.4 Concentrate this extract as described in Section 9.6.

9.4.5 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.5 Water Sample Extraction

9.5.1 Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1-L sample bottle for determination of the exact sample volume. Add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample bottle. Cap the bottle, and mix the sample by gently shaking for 30 seconds. Filter the sample through a 0.45 micron filter that has been rinsed with toluene.

NOTE: Reagent water used as a blank must also be filtered in a similar fashion and subjected to the same cleanup and analysis as the water samples.

If the total dissolved and suspended solids contents are too much to filter through the 0.45 micron filter, centrifuge the sample, decant, and then filter the aqueous phase (see Paragraph 8.4.7). Combine the solids from the centrifuge bottle(s), the particulate on the filter and the filter itself, and proceed with the SDS extraction in Paragraph 9.5.4.

9.5.2 The filtered aqueous sample is poured into a 2-L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the Contractor shall employ mechanical techniques to complete the phase separation (i.e., glass stirring rod). Drain the methylene chloride extract into a 500-mL KD concentrator (mounted with a 10-mL concentrator tube) by passing the extract through a funnel packed with a glass wool plug and half-filled with anhydrous sodium sulfate. Extract the water sample two more times using 60 mL of fresh methylene

chloride each time. Drain each extract through the funnel into the KD concentrator. After the third extraction, rinse the sodium sulfate with at least 30 mL of fresh methylene chloride. Concentrate this extract as described in Section 9.6.

9.5.3 A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. The following procedure is used for a continuous liquid-liquid extractor.

Preextract the continuous liquid-liquid extractor for three hours with methylene chloride and reagent water. Filter the sample as in Paragraph 9.5.1. Allow the extractor to cool, discard the methylene chloride, and add the filtered aqueous sample to the continuous liquid-liquid extractor. Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds.

Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask and sufficient reagent water to ensure proper operation. Extract for 16 hours. Allow to cool, then detach the flask and dry the sample by running it through a rinsed funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate into a 500 mL KD flask. Proceed to Section 9.6.

9.5.4 Combine the filtered particulate portion of the sample with the quartz sand in the extraction thimble. Add the filter on top of the particulate/sand mixture, and place the thimble into a preextracted SDS apparatus.

Add 200 to 250 mL of toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour. Concentrate this extract as described in Section 9.6.

9.5.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1-L graduated cylinder. Record the sample volume to the nearest 5 mL.

9.5.6 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.6 Macro-Concentration Procedures (All Matrices)

Prior to cleanup, extracts from all matrices must be concentrated to approximately 10 mL. In addition, the concentrated extracts from the

aqueous filtrate and the filtered particulates must be combined prior to cleanup. Two procedures may be used for macro-concentration, Kuderna-Danish (K-D) or rotary evaporator. Concentration of toluene by K-D requires the use of a heating mantle, as toluene boils above the temperature of a water bath. The two procedures are described in general terms below.

9.6.1 Concentration by K-D

9.6.1.1 Add one or two clean boiling chips to the round bottom flask from the SDS extractor or the reflux flask. Attach a three-ball macro Snyder column.

9.6.1.2 Pre-wet the column by adding approximately 1 mL of toluene through the top. Place the round bottom flask in a heating mantle and apply heat as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

9.6.2 Concentration by Rotary Evaporator

9.6.2.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for contamination check if necessary. Between samples, three 2-3 mL aliquots of toluene should be rinsed down the feed tube into a waste beaker.

9.6.2.2 Attach the round bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

9.6.2.3 Lower the flask into the water bath and adjust the speed of rotation and the temperature as required to complete the concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: If the rate of concentration is too fast, analyte loss may occur.

9.6.2.4 When the liquid in the concentration flask has reached an apparent volume of 2 mL, remove the flask from the water bath, and stop the rotation. Slowly and carefully, admit air into the system. Be sure

not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of hexane.

9.6.3 Extracts of Chemical Waste, Fly Ash, and Soil/Sediment Samples

9.6.3.1 For chemical waste, fly ash, and soil/sediment samples, the extract must be concentrated to approximately 10 mL prior to acid-base washing treatment. Concentrate the extract by either of the two procedures listed above.

9.6.3.2 Transfer the concentrated extract to a 125 mL separatory funnel. Rinse the flask with toluene and add the rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 9.7.

9.6.4 Extracts of Aqueous Filtrates

9.6.4.1 Extracts of the aqueous filtrate of water samples are in methylene chloride which is concentrated to approximately 10 mL by K-D or rotary evaporator prior to combining with the toluene extract of the particulates. If using K-D, the methylene chloride can be concentrated in a water bath instead of a heating mantle.

9.6.4.2 Combine the extract of the filtrate with the extract of the particulates as described in Section 9.6.

9.6.5 Extracts of Particulates from Aqueous Samples

9.6.5.1 If the extract is from the particulates from an aqueous sample, it must be concentrated to approximately 10 mL by either K-D or rotary evaporator, and combined with the concentrated extract of the filtrate (Paragraph 9.6.4.1) prior to acid-base washing treatment.

9.6.5.2 Assemble a glass funnel filled approximately one-half full with sodium sulfate such that the funnel will drain into the K-D concentrator or round bottom flask from Paragraph 9.6.4.1 containing the concentrated methylene chloride extract of the filtrate. (You may use the same funnel from Paragraph 9.5.2 or 9.5.3.) Pour the concentrated toluene extract of the particulates through the sodium sulfate into the K-D concentrator or round bottom flask. Rinse the flask from the particulate extract with three 15-20 mL volumes of hexane, and pour each rinse through the sodium sulfate into the K-D concentrator or round bottom flask.

9.6.5.3 Concentrate the combined extract to approximately 10 mL (the volume of the toluene) by either K-D or rotary evaporator.

9.6.5.4 Transfer the concentrated combined extract to a 125 mL separatory funnel. Rinse the concentrator with three 5 mL volumes of hexane, and add each rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 9.7.

9.7 Extract Cleanup Procedures (All Matrices)

9.7.1 Prior to cleanup, all extracts are spiked with the $^{37}Cl_4$-2378-TCDD cleanup standard (Section 5.17). The recovery of this standard is used to monitor the efficiency of the cleanup procedures. Spike 5 uL of the cleanup standard (or a larger volume of diluted solution containing 25 ng of $^{37}Cl_4$-2378-TCDD) into each separatory funnel containing an extract, resulting in a concentration of 0.25 ng/uL in the final extract analyzed by GC/MS.

9.7.2 Partition the concentrated extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard the acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

CAUTION: Concentrated sulfuric acid is hazardous and should be handled with care.

9.7.3 Partition the concentrated extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

9.7.4 Partition the concentrated extract against 40 mL of 20 percent (w/v) potassium hydroxide (KOH). Shake for two minutes. Remove and discard the base layer (bottom). Repeat the base washes until color is not visible in the bottom layer (perform base washes a maximum of four times). Strong base (KOH) is known to degrade certain PCDDs/PCDFs; therefore, contact time should be minimized.

9.7.5 Partition the concentrated extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring it through a funnel containing a rinsed filter half-filled with anhydrous sodium sulfate. Collect the extract in an appropriate size (100-250 mL) round bottom flask. Wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel and combine the extracts. Concentrate the extracts to 1.0 mL using the procedures described in Section 9.8.

9.8 Micro-Concentration of Extracts

Prior to column chromatographic cleanup procedures, the extracts from all matrices must be concentrated to approximately 1.0 mL. This concentration may be accomplished using either K-D or rotary evaporator, followed by nitrogen evaporation.

9.8.1 Concentrate the extracts to approximately 1 mL, using the procedures in Paragraph 9.6.1 or 9.6.2.

9.8.2 When the liquid in the concentration flask has reached an apparent volume of 1 mL, transfer the extract to a conical centrifuge tube using three 2-3 mL rinses of hexane.

9.8.3 Transfer the centrifuge tube containing the sample extract to a nitrogen evaporation device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

NOTE: A large vortex in the solvent may cause analyte loss.

9.8.4 Lower the tube into a 45°C water bath and continue concentrating. When the volume of the liquid is approximately 100 uL, add 2-3 mL of the hexane and continue concentration to a final volume of 1.0 mL. Proceed with column chromatography as described in Section 9.9.

9.9 Silica Gel and Alumina Column Chromatographic Procedure

9.9.1 Column 1. Insert a glass wool plug onto the bottom of a gravity column (1 cm x 30 cm glass column) fitted with a Teflon stopcock. Add 1 g silica gel and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 1 g silica gel, 4 g sulfuric acid-impregnated silica gel, and 2 g silica gel (see Section 5.10). Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed.

9.9.2 Column 2. Insert a glass wool plug onto the bottom of a gravity column (1 cm x 30 cm glass column) fitted with a Teflon stopcock. Add 6 g of the activated acid alumina (see Paragraph 5.10.1). Tap the top of the column gently.

Check each new batch of silica gel and alumina and maintain the results of the analyses on file for examination during EPA on-site evaluations. To accomplish this, combine 50 uL of the continuing calibration solution (CC3) with 950 uL of hexane. Process this solution through both columns in the same manner as a sample extract (Paragraphs 9.9.3 through 9.9.9). Concentrate the continuing calibration solution to a final volume of 50 uL. Proceed to Section 10. If the recovery of any of the analytes is less than 80%, the batch of alumina or silica gel must not be used.

9.9.3 Add hexane to each column until the packing is free of air bubbles. A small positive pressure (5 psi) of clean dry nitrogen may be used if needed. Check the columns for channeling. If channeling is present, discard the column.

CAUTION: Do not tap a wetted column.

9.9.4 Assemble the two columns such that the eluate from Column 1 (silica gel) drains directly into Column 2 (alumina).

9.9.5 Apply the hexane solution from Paragraph 9.8.4 to the top of the silica gel column. Rinse the vial with enough hexane (1-2 mL) to complete the quantitative transfer of the sample to the surface of the silica.

9.9.6 Using 90 mL of hexane, elute the extract from Column 1 directly onto Column 2 which contains the alumina.

CAUTION: Do not allow the alumina column to run dry.

9.9.7 Add 20 mL of hexane to Column 2, and elute until the hexane level is just below the top of the alumina. Do not discard the eluted hexane, but collect in a separate flask and store it for later use, as it may be useful in determining where the labeled analytes are being lost if recoveries are less than 50 percent.

9.9.8 Add 20 mL of 20% methylene chloride/80% hexane (v/v) to Column 2 and collect the eluate.

9.9.9 Concentrate the extract to approximately 2 to 3 mL using the procedures in Section 9.8.

CAUTION: Do not concentrate the eluate to dryness. The sample is now ready to be transferred to the carbon column.

9.10 Carbon Column Chromatographic Procedure

9.10.1 Thoroughly mix 5.35 g active carbon AX-21 and 62.0 g Celite 545 to produce a 7.9% w/w mixture. Activate the mixture at 130°C for six hours, and store in a desiccator.

Check each new batch of the Carbon/Celite and maintain the results from the analyses for examination during EPA on-site evaluations. To accomplish this, add 50 uL of the continuing calibration solution to 950 uL of hexane. Process the spiked solution in the same manner as a sample extract (Paragraphs 9.10.2 through 9.10.6). Concentrate the continuing calibration solution to 50 uL and proceed with Section 9.10. If the recovery of any of the analytes is less than 80%, this batch of Carbon/Celite mixture may not be used.

9.10.2 Prepare a 4-inch glass column by cutting off each end of a 10-mL disposable serological pipet. Fire polish both ends and

flare if desired. Insert a glass wool plug at one end of the column, and pack it with 1 g of the Carbon/Celite mixture. Insert an additional glass wool plug in the other end.

CAUTION: It is very important that the column be packed properly to ensure that carbon fines are not carried into the eluate. PCDDs/PCDFs will adhere to the carbon fines and greatly reduce recovery. If carbon fines are carried into the eluate in Paragraph 9.10.5, filter the eluate using a 0.45 micron filter (pre-rinsed with toluene), then proceed to Section 9.11.

9.10.3 Rinse the column with:

9.10.3.1 4 mL Toluene.

9.10.3.2 2 mL of Methylene Chloride/Methanol/Toluene (75:20:5 v/v).

9.10.3.3 4 mL of Cyclohexane/Methylene Chloride (50:50 v/v).

Discard all the column rinsates.

9.10.4 While the column is still wet, transfer the concentrated eluate from Paragraph 9.9.9 to the prepared carbon column. Rinse the eluate container with two 0.5 mL portions of hexane and transfer the rinses to the AX-21 carbon column. Elute the column with the following sequence of solvents.

9.10.4.1 10 mL of Cyclohexane/Methylene Chloride (50:50 v/v).

9.10.4.2 5 mL of Methylene Chloride/Methanol/Toluene (75:20:5 v/v).

NOTE: The above two eluates may be collected, combined and used as a check on column efficiency.

9.10.5 Once the solvents have eluted through the column, turn the column over, elute the PCDD/PCDF fraction with 20 mL of toluene, and collect the eluate.

9.11 Final Concentration

9.11.1 Evaporate the toluene fraction from Paragraph 9.10.5 to approximately 1.0 mL in a rotary evaporator (see Section 9.8). Transfer the extract to a 2.0 mL conical vial using a toluene rinse.

CAUTION: Do <u>not</u> evaporate the sample extract to dryness.

9.11.2 Add 100 uL tridecane (or nonane) to the extract and reduce the volume to 100 uL using a gentle stream of clean dry nitrogen.

The final extract volume should be 100 uL of tridecane (or nonane). Seal the vial and store the sample extract in the dark at ambient temperature until just prior to GC/MS analysis.

10. GC/MS Analysis

10.1 Remove the extract of the sample or blank from storage. Gently swirl the solvent on the lower portion of the vial to ensure complete dissolution of the PCDDs/PCDFs.

10.2 Transfer a 50 uL aliquot of the extract to a 0.3 mL vial, and add sufficient recovery standard solution to yield a concentration of 0.5 ng/uL in a 50 uL volume. Reduce the volume of the extract back down to 50 uL using a gentle stream of dry nitrogen.

Inject a 2 uL aliquot of the extract into the GC/MS instrument (see Paragraph 4.1.1). Reseal the vial from Paragraph 9.11.2, containing the original concentrated extract.

10.3 Analyze the extract by GC/MS, and monitor all of the ions listed in Table 7. The same MS parameters used to analyze the calibration solutions shall be used for the sample extracts.

10.4 Dilutions

10.4.1 If the concentration of any PCDD/PCDF in the sample has exceeded the calibration range or the detector has been saturated, a dilution shall be performed.

An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

10.4.2 Dilutions are performed using an aliquot of the original extract, of which approximately 50 uL remain from Paragraph 9.11.2. Remove an appropriate size aliquot from the vial and add it to a sufficient volume of tridecane (or nonane) in a clean 0.3 mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/uL (1.0 ng/uL ^{13}C-OCDD). Reduce the volume of the extract back down to 50 uL using a gentle stream of dry nitrogen.

10.4.3 The dilution factor is defined as the total volume of the sample aliquot and clean solvent divided by the volume of the sample aliquot that was diluted.

10.4.4 Inject 2 uL of the diluted sample extract into the GC/MS, and analyze according to Section 10.3.

10.4.5 Diluted samples in which the MS response of any internal standard is $\geq$ 10% of the MS response of that internal standard in the most recent continuing calibration standard are quantified using the internal standards.

Diluted samples in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standard are quantified using the recovery standards (see Section 15.3).

11. Identification Criteria

For a gas chromatographic peak to be unambiguously identified as a PCDD or PCDF, it must meet all of the following criteria.

11.1 Retention Times

Retention times are required for all chromatograms; scan numbers are optional. Retention times shall either be printed at the apex of each peak on the chromatogram, or each peak shall be unambiguously labeled with an identifier that refers to the quantitation report. The chromatogram, the quantitation report, or a combination of both shall contain the retention time of each peak and its area.

11.1.1 In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

11.1.2 In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is not available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the continuing calibration. The RRT is calculated as follows:

$$RRT = \frac{\text{retention time of analyte}}{\text{retention time of corresponding internal standard}}$$

11.1.3 For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue (see Section 7.1).

11.1.4 In order to assure that retention time shifts do not adversely affect the identification of PCDDs/PCDFs, the absolute retention times of the two recovery standards added to every sample extract immediately prior to analysis may not shift by more than ± 10 seconds from their retention times in the continuing calibration standard (see Paragraph 17.1.4).

11.2 Peak Identification

All of the specified ions listed in Table 5 for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M-[COCl]+ ions

for the analytes must maximize simultaneously (± 2 seconds). This requirement also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

11.3 Signal-To-Noise Ratio

The integrated ion current for each analyte ion listed in Table 5 must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10.0 times background noise and must not have saturated the detector. However, if the M-[COCl]+ ion does not meet the 2.5 times S/N requirement but meets all the other criteria listed in Section 11 and, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, the peak may be reported as positive and the data flagged on Form I. See the instructions in Exhibit B for Form I.

11.4 Ion Abundance Ratios

The relative ion abundance criteria listed in Table 6 for native analytes and internal standards must be met using peak areas to calculate ratios.

11.4.1 If interferences are present and ion abundance ratios are not met using peaks areas, but all other qualitative identification criteria <u>are</u> met (RT, S/N, presence of all three ions), then the Contractor may use peak heights to evaluate the ion ratio.

11.4.2 If, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, then report the ion abundance ratios determined using peak heights, <u>quantitate</u> the peaks using peak heights rather than areas for both the target analyte and the internal standard, and flag the data on Form I.

11.5 Polychlorinated Diphenyl Ether (PCDPE) Interferences

The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time (▪ 2 seconds) in the corresponding PCDPE channel (see Table 5). If a PCDPE is detected, it shall be documented in the SDG Narrative, and an Estimated Maximum Possible Concentration (EMPC) shall be calculated for this GC peak according to Section 15.7, regardless of the ion abundance ratio, and reported on Form I.

12. <u>Method Blanks</u>

12.1 A minimum of one blank per matrix shall be analyzed with each SDG. If samples of the same matrix are extracted in different episodes (i.e., different shifts or days), one blank per matrix must be prepared for each episode. When water samples in a SDG are extracted using both the separatory funnel and continuous liquid-liquid extraction procedures, at least one blank must be prepared by each procedure.

12.2 Method Blank Criteria

12.2.1 Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than 5 percent of the signal of the appropriate internal standard quantitation ion.

12.2.2 A peak that meets identification criteria as a PCDD/PCDF in the method blank must not exceed 2 percent of the signal of the appropriate internal standard.

12.2.3 If the method blank extracted along with a group of samples is contaminated per Paragraph 12.2.1 or 12.2.2, then the associated positive samples and any samples containing peaks that do not meet all of the identification criteria in Section 11 must be rerun.

12.2.4 If all the criteria listed above are not met, check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any more samples are extracted and before any positive samples are reextracted.

12.2.5 Test each new lot of reagents or solvents by using them to prepare a method blank and analyze it according the procedures in this exhibit. If new lots of reagents or solvents contain interfering contaminants, purify or discard them. Maintain records of all such blanks on file for examination during EPA on-site evaluations.

13. Spiked Sample Analysis

In order to provide data on the accuracy of the analytical method, the laboratory is required to prepare and analyze a spiked sample for each matrix being analyzed. For each SDG, the laboratory must prepare a spiked sample for all of the following matrix types that occur in the SDG:

- Water
- Soil/Sediment
- Chemical Waste
- Fly Ash

If a matrix is not represented in a SDG, then no spiked sample is required for that matrix. If the Region or samplers have identified a particular sample to be used for the spike, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for spiking, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

13.1 Prepare the spiked sample aliquot by taking the same weight (or volume) of the representative matrix as is indicated in Sections 9.1 to 9.5 and placing it in a clean container of suitable size.

13.2 Add 1.0 mL of the spiking solution in Section 5.18 and Table 11 to the aliquot. Manually mix the sample to distribute the spiking solution, and let the aliquot equilibrate for one hour.

13.3 Prepare and extract the spiked sample aliquot in the same fashion as is used for field samples, and carry the aliquot through the entire analytical procedure including cleanup.

13.4 Calculate the concentration of each analyte according to the procedures in Section 15.

13.5 Calculate the recovery of each spiked analyte, using the following equation:

$$R_{spike} = \frac{\text{Amount found - Amount in unspiked sample}}{\text{Amount spiked}} \times 100$$

where the recovery (R) is expressed as a percentage

13.6 The recovery of each spiked analyte must be in the range of 50-150 percent. If the recovery of any analyte falls outside this range, the laboratory must recheck all calculations, and confirm that the spiking solutions were added and were at the correct concentrations, but no further action is necessary by the laboratory at this time. Recovery limits for these analytes will be developed at a later date.

14. Duplicate Sample Analysis

In order to provide data on the precision of the analytical method, the laboratory is required to prepare and analyze a duplicate of one sample for each matrix being analyzed. For each SDG, the laboratory must prepare a duplicate sample for all of the following matrix types that occur in the SDG:

- Water
- Soil/Sediment
- Chemical Waste
- Fly Ash

If a matrix is not represented in a SDG, then no duplicate sample is required for that matrix. If the Region or samplers have identified a particular sample to be used for the duplicate, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for use as the duplicate, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

14.1 Prepare the duplicate sample aliquot by taking the same weight (or volume) of the representative matrix as is indicated in Sections 9.1 to 9.5 and carrying it through the entire analytical procedure including extraction, cleanup and analysis.

14.2 Calculate the concentration of each analyte detected in the duplicate sample according the procedures in Section 15.

14.3 Calculate the precision of each detected analyte in the original and duplicate analyses, expressed as the Relative Percent Difference (RPD), according to the following equation:

$$RPD = \frac{|\text{Sample Result - Duplicate Result}|}{(\text{Sample Result + Duplicate Result})/2} \times 100$$

14.4 The RPD of any detected analyte must be less than or equal to 50 percent. If the RPD of any detected analyte falls above this limit, the laboratory must recheck all calculations, but no further action is necessary by the laboratory at this time. RPD limits for these analytes will be developed at a later date.

15. Calculations

15.1 For GC peaks that have met all the identification criteria outlined in Section 11, calculate the concentration of the individual PCDD or PCDF isomers using the following formulae:

ALL MATRICES OTHER THAN WATER

$$C_n \text{ (ug/kg)} = \frac{Q_{is} \times (A_n^1 + A_n^2)}{W \times (A_{is}^1 + A_{is}^2) \times RRF_n}$$

WATER

$$C_n \text{ (ng/L)} = \frac{Q_{is} \times (A_n^1 + A_n^2)}{V \times (A_{is}^1 + A_{is}^2) \times RRF_n}$$

Where:

A_n^1 and A_n^2 - integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest (Table 5).

A_{is}^1 and A_{is}^2 - integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard (Table 5).

NOTE: In instances where peak heights are used to evaluate ion abundance ratios due to interferences (see Section 11.4), substitute peak heights for areas in the formulae above.

W - weight of sample extracted, in grams.

V - volume of sample extracted, in liters.

Q_{is} - quantity (ng) of the appropriate internal standard added to the sample prior to extraction.

RRF_n - calculated relative response factor from continuing calibration (see Section 7.3).

For solids matrices, the units of ng/g that result from the formula above are equivalent to ug/Kg. Using isotope dilution techniques for quantitation, the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Q_{is}.

15.1.1 For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD and TCDF), the RRF of the 2,3,7,8-substituted isomer from the continuing calibration (see Paragraph 7.3.2.3) will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-substituted isomers.

15.1.2 For homologues that contain more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF and HpCDF), the RRF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RRF determined for that isomer during the continuing calibration (see Paragraph 7.3.2.3).

15.1.3 For homologues that contain one or more non-2,3,7,8-substituted isomers, the RRF used to calculate the concentration of these isomers will be the lowest of the RRFs determined during the continuing calibration (see Paragraph 7.3.2.3) for the 2,3,7,8-substituted isomers in that homologue. This RRF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

NOTE: The relative response factors of given isomers within any homologue may be different. However, for the purposes of these calculations, it will be assumed that every non-2,3,7,8-substituted isomer for a given homologue has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, the 2,3,7,8-substituted isomer with the lowest RRF was chosen as representative of each homologue. All relative response factor calculations for the non-2378-substituted isomers in a given homologue are based on that isomer.

15.2 In addition to the concentrations of specific isomers, the total homologue concentrations are also reported. Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:

Total concentration - sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.

The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately. The total number of GC peaks included in the total homologue concentration must be specified (see Exhibit B).

15.3 If the area of any internal standard in a diluted sample is less than 10 percent of the area of that internal standard in the continuing calibration standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard, using the formulae that follow. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. While use of a smaller aliquot of the sample might require smaller dilutions and therefore yield a larger area for the internal standard in the diluted extract, this practice leads to other concerns about the homogeneity of the sample and the representativeness of the aliquot taken for extraction.

ALL MATRICES OTHER THAN WATER

$$C_n \text{ (ug/kg)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{W \times (A_{rs}^1 + A_{rs}^2) \times RRF_{rs}}$$

WATER

$$C_n \text{ (ng/L)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{V \times (A_{rs}^1 + A_{rs}^2) \times RRF_{rs}}$$

D = dilution factor (see Paragraph 10.4.3).

A_n^1, A_n^2, A_{rs}^1, A_{rs}^2, Q_{rs}, RRF_{rs}, W and V are defined in Paragraphs 7.3.3 and 7.3.4 and Section 15.1.

15.4 Report results for soil/sediment, fly ash, and chemical waste samples in micrograms per kilograms (ug/kg) and water samples in nanograms per liter (ng/L), as described in Exhibit B.

15.5 Calculate the percent recovery for each internal standard and the cleanup standard in the sample extract, R_{is}, using the formula:

$$R_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times RRF_{is} \times Q_{is}} \times 100\%$$

A_{is}^1, A_{is}^2, A_{rs}^1, A_{rs}^2, Q_{is}, Q_{rs} and RRF_{is} are defined in Paragraph 7.3.3 and Section 15.1.

NOTE: When calculating the recovery of the $^{37}Cl_4$-2378-TCDD cleanup standard, only one m/z is monitored for this standard;

therefore, only one peak area will be used in the numerator of this formula. Use both peak areas of the $^{13}C_{12}$-1234-TCDD recovery standard in the denominator.

15.5.1 The $^{13}C_{12}$-1234-TCDD is used to quantitate the tetra internal standards and the cleanup standard, and $^{13}C_{12}$-123789-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards (see Table 8).

15.5.2 If the original sample, prior to any dilutions, has any internal standard with a percent recovery of less than 25% or greater than 150%, reextraction and reanalysis of that sample is required (see Section 17).

15.6 Sample Specific Estimated Detection Limit

The sample specific Estimated Detection Limit (EDL) is the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc.

An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.

Use the formulae below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level (H_x) is determined by measuring the height of the noise at the expected retention times of both the quantitation ions of the particular 2,3,7,8-substituted isomer. The expected retention time is determined from the most recent analysis of the CC3 standard on the same GC/MS system.

ALL MATRICES OTHER THAN WATER

$$\text{EDL (ug/kg)} = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{W \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

WATER

$$\text{EDL (ng/L)} = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{V \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

Where:

H_x^1 and H_x^2 = Peak heights of the noise for both of the quantitation ions of the 2,3,7,8-substituted isomer of interest.

H_{is}^1 and H_{is}^2 - Peak heights of both the quantitation ions of the appropriate internal standards.

D - dilution factor (see Paragraph 10.4.3).

Q_{is}, RRF_n, W and V are defined in Paragraph 7.3.3 and Section 15.1.

15.7 Estimated Maximum Possible Concentration

An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that are characterized by a response with a S/N of at least 2.5 for both the quantitation ions, but that do not meet all the identification criteria in Section 11.

Calculate the EMPC according to the following formulae:

ALL MATRICES OTHER THAN WATER

$$\text{EMPC (ug/L)} = \frac{(A_x^1 + A_x^2) \times Q_{is} \times D}{(A_{is}^1 + A_{is}^2) \times RRF_n \times W}$$

WATER

$$\text{EMPC (ng/L)} = \frac{(A_x^1 + A_x^2) \times Q_{is} \times D}{(A_{is}^1 + A_{is}^2) \times RRF_n \times V}$$

Where:

A_x^1 and A_x^2 - areas of both quantitation ions.

A_{is}^1, A_{is}^2, Q_{is}, RRF, D, W, and V are defined in Paragraph 7.3.3 and 10.4.3 and Section 15.1.

15.8 Toxicity Equivalency Factor (TEF) Calculation

The 2378-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2378-TCDD toxicity equivalency factor (TEF) to each of the 17 2,3,7,8-substituted PCDDs/PCDFs shown in Table 11 ("Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016)). The 2378-TCDD toxicity equivalence of the PCDDs/PCDFs present in the sample is calculated by summing the product of the TEF and the concentration for each of the compounds listed in Table 11.

The exclusion of homologues such as mono-, di-, tri- and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less than the toxicity of the compounds listed in Table 11. Hence, only the 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2378-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

When calculating the 2378-TCDD toxicity equivalence of a sample, the Contractor shall include only those 2,3,7,8-substituted isomers that were detected in the sample and met all of the qualitative identification criteria in Section 11. Do not include EMPC or EDL values in the TEF calculations. Further instructions regarding the calculation of the 2378-TCDD toxicity equivalence may be found in Exhibit B.

The 2378-TCDD toxicity equivalence of a sample is used in Sections 16 and 17 of this procedure to determine when second column confirmation or reextractions and reanalyses may be required.

16. Isomer Specificity

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column alone. Historically, problems have been associated with the separation of 2378-TCDD from 1237-TCDD and 1268-TCDD, and separation of 2378-TCDF from 2347-TCDF. Because of the toxicologic concern associated with 2378-TCDD and 2378-TCDF, additional analyses may be required for some samples, as described below.

16.1 If the toxicity equivalence calculated in Section 15 is greater than 0.7 ppb (soil/sediment or fly ash), 7 ppb (chemical waste), or 7 ppt (aqueous), better isomer specificity is required than can be achieved on the DB-5 column. The Contractor may utilize either of the two options listed below to achieve adequate isomer specificity.

16.1.1 The sample extract may be reanalyzed on a 60 m SP-2330 or SP-2331 (or equivalent) GC column in order to achieve better GC resolution, and therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.

16.1.2 The sample extract may be analyzed on a single GC column capable of resolving all 2,3,7,8-substituted PCDDs/PCDFs from other isomers, but not necessarily resolving all the non-2,3,7,8-substituted isomers from one another.

Regardless of GC column used, for a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF isomer, it must meet the ion abundance, signal-to-noise, and retention time criteria listed in Section 11. In addition, when using any GC column other than those specified here (DB-5, SP-2330 or SP-2331), the Contractor shall clearly document, in the SDG Narrative, the elution order of all the analytes of interest on any such column.

16.2 For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an EMPC, regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

17. Required Sample Reruns

Due to a variety of situations that may occur during contract performance, the laboratory shall be required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" shall indicate sample reextraction, cleanup and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed.

When the rerun is required due to matrix effects, interferences, or other problems encountered, the Government will pay the Contractor for the reruns. Such reruns shall be billable and accountable under the specified contract allotment of automatic reruns. When the rerun is required due to Contractor materials, equipment or instrumentation problems, or lack of Contractor adherence to specified contract procedures, the rerun shall not be billable nor accountable under the terms of this contract.

17.1 The following sample reruns may be billable as such under the contract, as defined below.

17.1.1 If the original sample has a percent recovery of any internal standard or the cleanup standard outside of the range of 25-150 percent, then reextraction and reanalysis are required.

NOTE: This rerun is billable only if the Contractor can demonstrate that the internal standards or cleanup standard were added to the original sample in accordance with contract specifications, and that the same standards are out of criteria in the reextraction and reanalysis.

17.1.2 If the internal standards are not present with at least a 10/1 S/N ratio at their respective m/z's (316, 318, 332, 334, 402, 404, 420, 422, 470 and 472), then reextraction and reanalysis are required. If the $^{37}Cl_4$-2378-TCDD is not present with at least a 10/1 S/N ratio at m/z 328, then reextraction and reanalysis are required.

NOTE: This rerun is billable only if the Contractor can demonstrate that the internal standards or cleanup standard were added to the original sample in accordance with contract specifications, and that the same standards are out of criteria in the reextraction and reanalysis.

17.1.3 If any of the internal standard ion abundance ratios as specified in Table 6 are outside the contract specified control

limits, the Contractor must reanalyze the sample extract on a second GC column with different elution characteristics, as discussed in Section 16. No reextraction is required for such an analysis. This reanalysis is only billable if the same internal standard ion abundance ratios are outside the control limits on the second column, indicating matrix effects may have occurred.

17.1.4 If the absolute retention time of either the $^{13}C_{12}$-1234-TCDD or $^{13}C_{12}$-123789-HxCDD recovery standard in a sample extract shifts by greater than 10 seconds from the retention time of that standard in the continuing calibration standard, then the sample extract must be reanalyzed after the Contractor has investigated the cause of the retention time shift and taken corrective action. No reextraction is required for such an analysis. This reanalysis is only billable if the same recovery standard retention time shifts by greater than 10 seconds in the second analysis, indicating matrix effects may have occurred.

17.2 If the calculated concentration of the unlabeled PCDDs/PCDFs exceeded the initial calibration range, the sample extract shall be diluted and reanalyzed (see Section 10.4). Such sample dilutions are billable under the contract.

NOTE: Only one dilution shall be billable per sample and only as an additional analysis with no extraction.

17.3 The following sample reruns shall be performed at the Contractor's expense and shall not be billable under the terms of the contract.

17.3.1 All positive samples associated with a contaminated method blank and any samples which contain peaks that do not meet all of the qualitative identification criteria in Section 11 associated with a contaminated method blank must be reextracted and reanalyzed. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than five percent of the signal of the appropriate internal standard quantitation ion. A peak that meets identification criteria in the method blank must not exceed two percent of the signal of the appropriate internal standard.

17.3.2 If the chromatographic peak separation between $^{13}C_{12}$-2378-TCDD and $^{13}C_{12}$-1234-TCDD is not resolved with a valley of $\leq$ 25% on the DB-5 (or equivalent) column, or 2378-TCDD is not resolved from the closest eluting isomer with a valley of $\leq$ 25% on the SP-2331 (or equivalent) column, then the Contractor shall adjust the GC/MS operating conditions and rerun the affected sample. This criterion applies to sample analyses. If this criterion is not met for a calibration standard, all associated samples must be rerun.

17.3.3 If a false positive is reported for a blind QC sample submitted by the Region, the Contractor shall reextract and reanalyze the entire SDG upon notification by SMO.

17.3.4 If the analysis results for a blind QC sample do not fall within the acceptance windows established by EPA, the Contractor shall reextract and reanalyze the entire SDG upon notification by SMO.

17.4 A native spike and duplicate shall be performed for each group of samples reextracted and reanalyzed under Section 17.3.

17.4.1 If a concurrent PCDD/PCDF SDG is being processed, the native spike and duplicate from that SDG may be shared with the rerun samples if the total number of samples does not exceed 20. The native spike and duplicate data shall be reported in the data packages for both SDGs, but are only billable once, under the original SDG for which they were prepared. If the total number of samples exceeds 20, an additional native spike and duplicate must be analyzed.

17.4.2 If no other PCDD/PCDF SDG is being processed at the time of reanalysis, the native spike and duplicate shall be chosen from the SDG for which the rerun samples are required. The native spike and duplicate analyses are only billable in instances where one or more of the associated rerun samples are also billable.

TABLE 1. SUGGESTED OPERATING CONDITIONS FOR A DB-5 (OR EQUIVALENT) COLUMN

Stationary Phase	DB-5 (or equivalent)
Film Thickness	0.25 um
Column Dimensions	60 m x 0.32 mm
Helium Linear Velocity	35 - 40 cm/sec at 240°C
Initial Temperature	170°C
Initial Time	10 minutes
Temperature Program	increase to 320°C at 8°/minute
Hold Time	until OCDF elutes
Total Time	40-45 minutes

TABLE 2. 2378-TCDD TOXICITY EQUIVALENCY FACTORS (TEFs) FOR PCDDs/PCDFs

Analyte	TEF
2378-TCDD	1.00
2378-TCDF	0.10
12378-PeCDF	0.05
12378-PeCDD	0.50
23478-PeCDF	0.50
123478-HxCDF	0.10
123678-HxCDF	0.10
123478-HxCDD	0.10
123678-HxCDD	0.10
123789-HxCDD	0.10
234678-HxCDF	0.10
1234678-HpCDF	0.01
1234678-HpCDD	0.01
1234789-HpCDF	0.01
OCDD	0.001
OCDF	0.001

Reference: "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs)," March 1989, (EPA 625/3-89/016)

TABLE 3. CONCENTRATION CALIBRATION SOLUTIONS

Analyte	CC1	CC2	CC3	CC4	CC5
2378-TCDD	0.1	0.25	0.5	1.0	2.0
2378-TCDF	0.1	0.25	0.5	1.0	2.0
12378-PeCDF	0.1	0.25	0.5	1.0	2.0
12378-PeCDD	0.1	0.25	0.5	1.0	2.0
*23478-PeCDF	---	---	0.5	---	---
*123478-HxCDF	---	---	1.25	---	---
123678-HxCDF	0.25	0.625	1.25	2.5	5.0
*123478-HxCDD	---	---	1.25	---	---
123678-HxCDD	0.25	0.625	1.25	2.5	5.0
*123789-HxCDD	---	---	1.25	---	---
*234678-HxCDF	---	---	1.25	---	---
*123789-HxCDF	---	---	1.25	---	---
*1234789-HpCDF	---	---	1.25	---	---
1234678-HpCDF	0.25	0.625	1.25	2.5	5.0
1234678-HpCDD	0.25	0.625	1.25	2.5	5.0
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
$^{13}C_{12}$-2378-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-2378-TCDF	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-123678-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1234678-HpCDF	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-OCDD	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-1234-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-123789-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{37}Cl_4$-2378-TCDD	---	---	0.25	---	---

All concentrations are in ng/uL.

*Supplemental commercial standard. Do not perform %RSD calculations on these analytes. (See Paragraph 7.4.1 for CC3 standard preparation.)

TABLE 4. INTERNAL STANDARD, RECOVERY STANDARD, AND CLEANUP STANDARD SOLUTIONS

INTERNAL STANDARD SOLUTION

Internal Standards	Concentration
$^{13}C_{12}$-2378-TCDD	5 ng/uL
$^{13}C_{12}$-2378-TCDF	5 ng/uL
$^{13}C_{12}$-123678-HxCDD	5 ng/uL
$^{13}C_{12}$-1234678-HpCDF	10 ng/uL
$^{13}C_{12}$-OCDD	10 ng/uL

RECOVERY STANDARD SOLUTION

Recovery Standards	Concentration
$^{13}C_{12}$-1234-TCDD	5 ng/uL
$^{13}C_{12}$-123789-HxCDD	5 ng/uL

CLEANUP STANDARD SOLUTION

Cleanup Standards	Concentration
$^{37}Cl_4$-2378-TCDD	5 ng/uL

TABLE 5. IONS SPECIFIED FOR SELECTED ION MONITORING FOR PCDDs/PCDFs

Analyte	Quantitation Ions		M-[COCl]$^+$
TCDD	320	322	259
PeCDD	356	358	293
HxCDD	390	392	327
HpCDD	424	426	361
OCDD	458	460	395
TCDF	304	306	243
PeCDF	340	342	277
HxCDF	374	376	311
HpCDF	408	410	345
OCDF	442	444	379
Internal Standards			
$^{13}C_{12}$-2378-TCDD	332	334	---
$^{13}C_{12}$-123678-HxCDD	402	404	---
$^{13}C_{12}$-OCDD	470	472	---
$^{13}C_{12}$-2378-TCDF	316	318	---
$^{13}C_{12}$-1234678-HPCDF	420	422	---
Recovery Standards			
$^{13}C_{12}$-1234-TCDD	332	334	---
$^{13}C_{12}$-123789-HxCDD	402	404	---
Cleanup Standard			
^{37}C14-2378-TCDD	328	(1)	263
Polychlorinated diphenyl ethers			
HxCDPE	376	---	---
HpCDPE	410	---	---
OCDPE	446	---	---
NCDPE	480	---	---
DCDPE	514	---	---

(1) There is only one quantitation ion monitored for the cleanup standard.

TABLE 6. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDDs/PCDFs

Analyte	Selected Ions	Theoretical Ion Abundance	Control Limits
TCDD	320/322	0.77	0.65 - 0.89
PeCDD	356/358	1.55	1.24 - 1.86
HxCDD	390/392	1.24	1.05 - 1.43
HpCDD	424/426	1.04	0.88 - 1.20
OCDD	458/460	0.89	0.76 - 1.02
TCDF	304/306	0.77	0.65 - 0.89
PeCDF	340/342	1.55	1.24 - 1.86
HxCDF	374/376	1.24	1.05 - 1.43
HpCDF	408/410	1.04	0.88 - 1.20
OCDF	442/444	0.89	0.76 - 1.02
Internal Standards			
$^{13}C_{12}$-1234-TCDD	332/334	0.77	0.65 - 0.89
$^{13}C_{12}$-123678-HxCDD	402/404	1.24	1.05 - 1.43
$^{13}C_{12}$-OCDD	470/472	0.89	0.76 - 1.01
$^{13}C_{12}$-2378-TCDF	316/318	0.77	0.65 - 0.89
$^{13}C_{12}$-1234678-HPCDF	420/422	1.04	0.88 - 1.20
Recovery Standards			
$^{13}C_{12}$-1234-TCDD	332/334	0.77	0.65 - 0.89
$^{13}C_{12}$-123789-HxCDD	402/404	1.24	1.05 - 1.43

TABLE 7. RECOMMENDED SELECTED ION MONITORING DESCRIPTORS

Descriptor 1	Descriptor 2	Descriptor 3	Descriptor 4
243	277	311	345
259	293	327	361
277	311	345	379
293	327	361	395
304	338	374	408
306	340	376	410
316	342	390	420
318	354	392	422
320	356	402	424
322	358	404	426
328	374	408	442
332	376	410	444
334	390	420	458
340	392	422	460
342	402	424	470
356	404	426	472
358	410	446	480
376	446	480	514

The ions at m/z 376 (HxCDPE), 410 (HpCDPE), 446 (OCDPE), 480 (NCDPE) and 514 (DCDPE) represent the polychlorinated diphenyl ethers.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third descriptor, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor.

NOTE: The descriptors used by the laboratory must be documented, and this information must be available for examination during the EPA on-site evaluations.

TABLE 8. RELATIONSHIP OF INTERNAL STANDARDS TO ANALYTES, AND RELATIONSHIP OF RECOVERY STANDARDS TO ANALYTES, INTERNAL STANDARDS AND CLEANUP STANDARD

INTERNAL STANDARDS VS. ANALYTES

$^{13}C_{12}$-TCDD	$^{13}C_{12}$-HxCDD	$^{13}C_{12}$-OCDD	$^{13}C_{12}$-TCDF	$^{13}C_{12}$-HpCDF
TCDD	HxCDD	OCDD	TCDF	HxCDF
PeCDD	HpCDD	OCDF	PeCDF	HpCDF

RECOVERY STANDARDS VS. ANALYTES, INTERNAL STANDARDS AND CLEANUP STANDARD

$^{13}C_{12}$-1234-TCDD	$^{13}C_{12}$-123789-HxCDD
TCDD	HxCDD
TCDF	HxCDF
PeCDD	HpCDD
PeCDF	HpCDF
	OCDD
	OCDF
$^{13}C_{12}$-2378-TCDD	$^{13}C_{12}$-123678-HxCDD
$^{13}C_{12}$-2378-TCDF	$^{13}C_{12}$-1234678-HpCDF
$^{37}Cl_4$-2378-TCDD	$^{13}C_{12}$-OCDD

TABLE 9. PCDD/PCDF ISOMERS IN THE WINDOW DEFINING MIX FOR A 60 M DB-5 (OR EQUIVALENT) COLUMN

Homologue	First Eluted	Last Eluted	Approximate Concentration
TCDD	1368-	1289-	0.5
TCDF	1368-	1289-	0.5
PeCDD	12479-	12389-	0.5
PeCDF	13468-	12389-	0.5
HxCDD	124679-	123467-	1.25
HxCDF	123468-	123489-	1.25
HpCDD	1234679-	1234678-	1.25
HpCDF	1234678-	1234789-	1.25

TABLE 10. SUPPLEMENTAL CALIBRATION SOLUTION

Analyte	Concentration (ng/uL)
23478-PeCDF	4
123789-HxCDD	10
123478-HxCDD	10
123478-HxCDF	10
123789-HxCDF	10
234678-HxCDF	10
1234789-HpCDF	10

The supplemental calibration solution is commercially supplied and is used for preparation of the CC3 solution. (See Paragraph 7.4.1 for CC3 preparation.)

TABLE 11. MATRIX SPIKING SOLUTION

Analyte	Concentration (ng/uL)
2378-TCDD	2.5
2378-TCDF	2.5
12378-PeCDF	6.25
12378-PeCDD	6.25
123678-HxCDF	6.25
123678-HxCDD	6.25
1234678-HpCDF	6.25
1234678-HpCDD	6.25
OCDD	12.5
OCDF	12.5

This solution is prepared in tridecane (or nonane) and diluted with acetone prior to use (see Section 5.18).

TABLE 12. COLUMN PERFORMANCE SOLUTION FOR A SP-2331 (QR EQUIVALENT) COLUMN

Isomer	Approximate Concentrations (ng/uL)
1478-TCDD	0.5
2378-TCDD	0.5
1237/1238-TCDD	0.5

The commercially supplied column performance solution may be combined with the window defining mix, provided that the combined soultion contains the isomers needed to determine that the criteria for both analyses can be met (see Paragraph 7.2.2).

TABLE 13. EXAMPLE ANALYTICAL SEQUENCES

Time	Analysis
	Window Defining Mix
	Column Performance Solution (SP-2331)
Hour 0	CC3
	CC1 (Initial Calibration)
	CC2
	CC4
	CC5
	Blanks and Samples
	o
	o
	o
	o
Hour 12	CC1
	Column Performance Solution (SP-2331)
Hour 0	CC3
	Blanks and Samples
	o
	o
	o
	o
Hour 12	CC1
	Column Performance Solution (SP-2331)
Hour 0	CC3
	Blanks and Samples
	o
	o
	o
	etc.
	CC1 (whenever the sequence does end)

NOTE: Matrix spike and duplicate samples may be analyzed in place of any "sample" listed above.

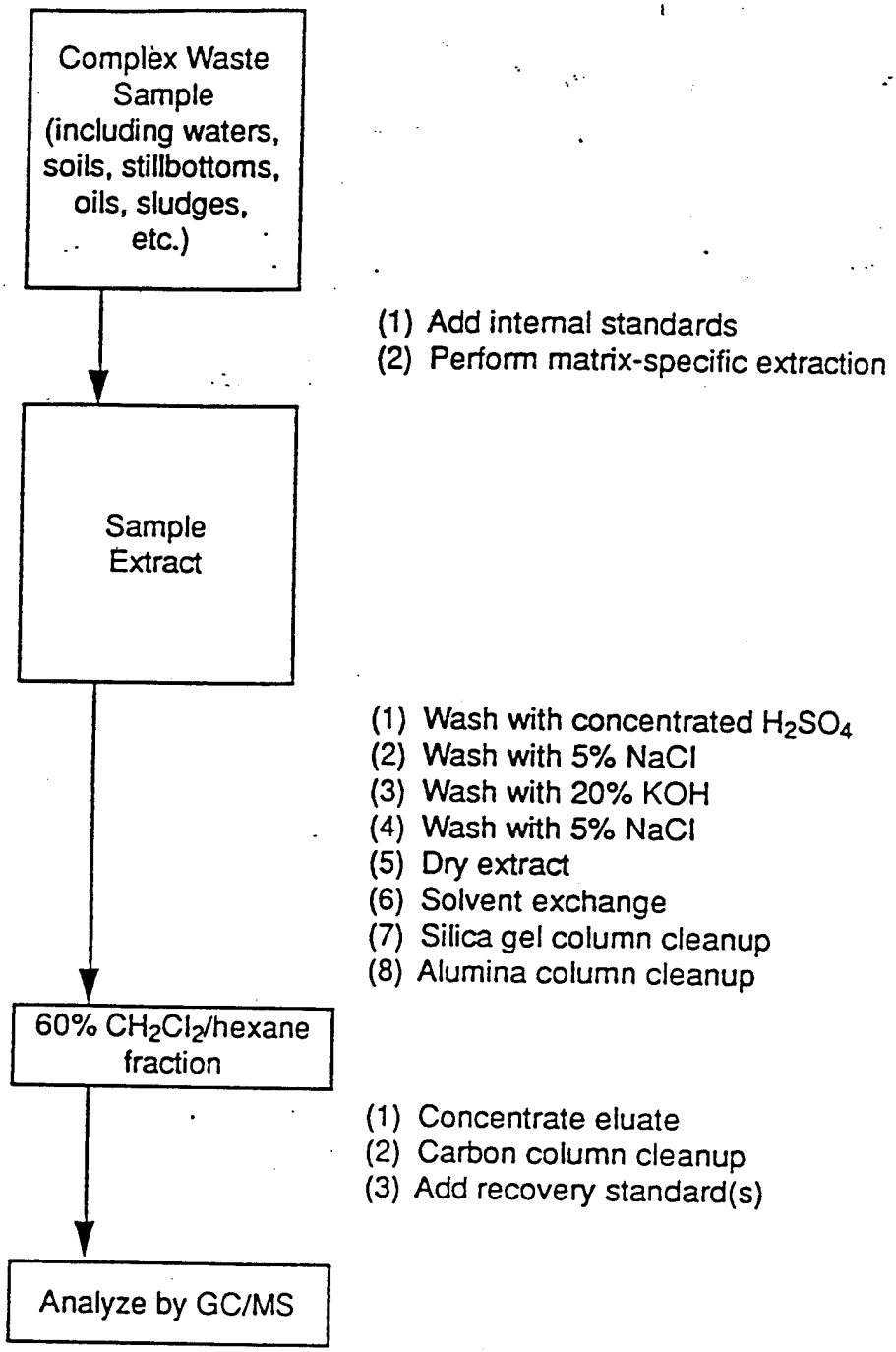
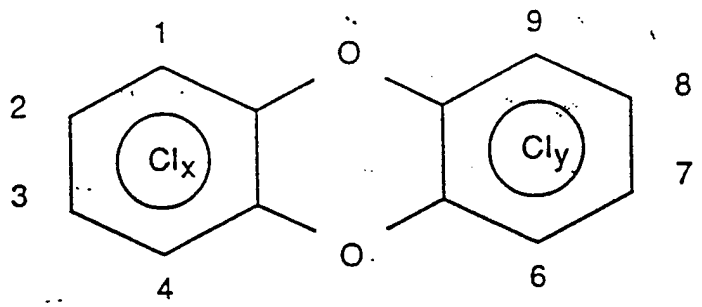
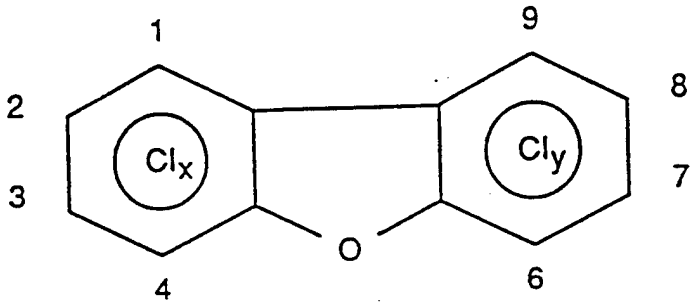


Figure 1: **Flow Chart for Sample Extraction and Cleanup for the Analysis of PCDDs and PCDFs in Complex Waste Samples**



Polychlorinated Dibenzo-*p*-Dioxin

where $x + y \leq 8$



Polychlorinated Dibenzofuran

Figure 2: General Structures of PCDDs and PCDFs

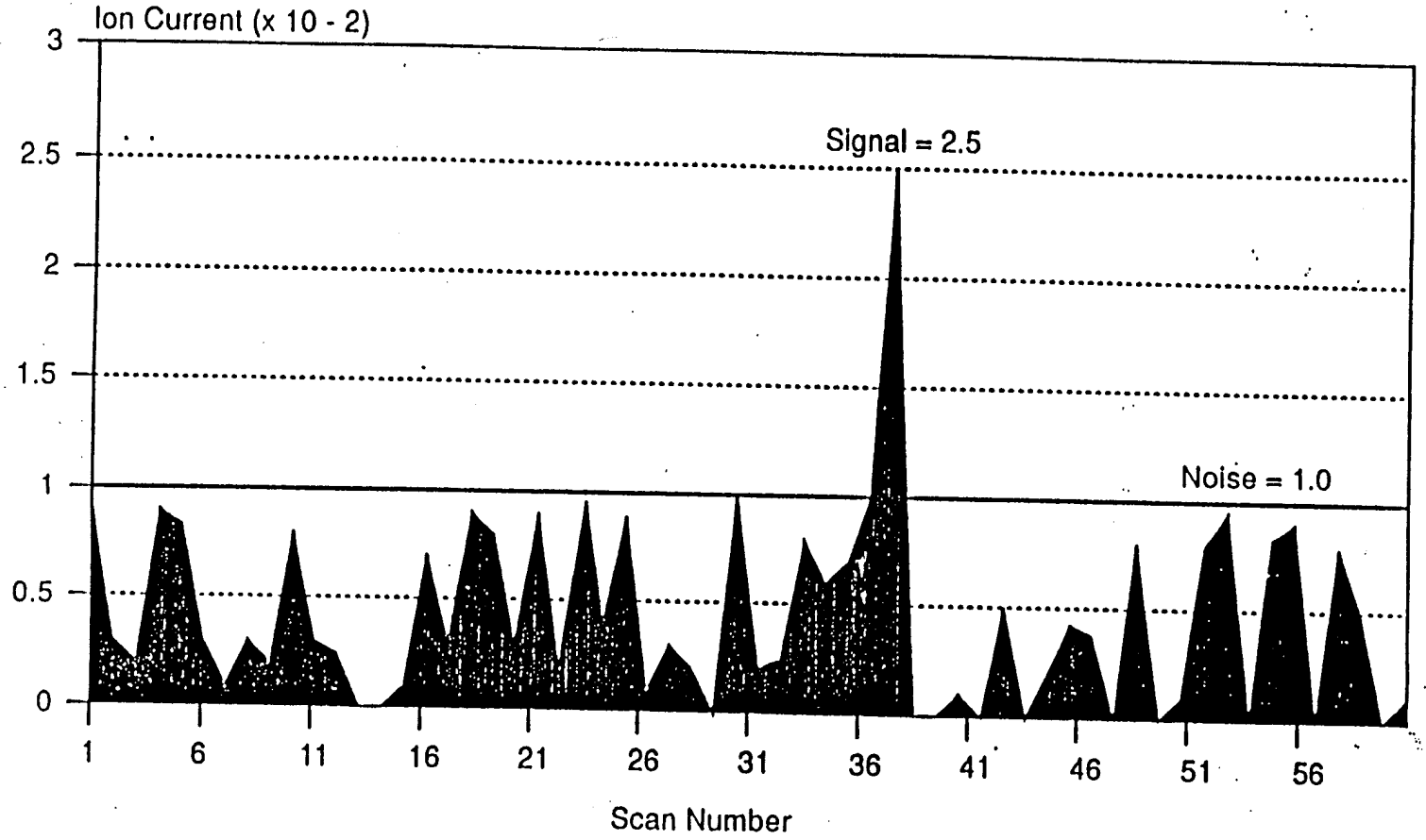


Figure 3: Measurement of Signal-To-Noise Ratio

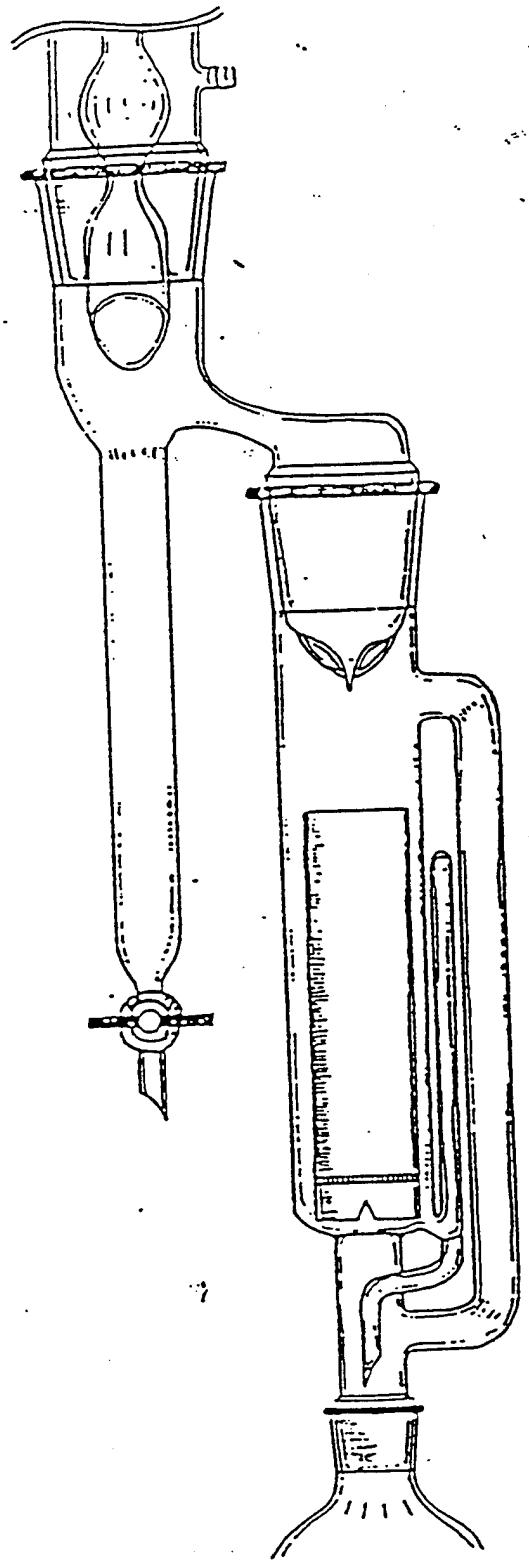


Figure 4: Soxhlet/Dean-Stark Extractor

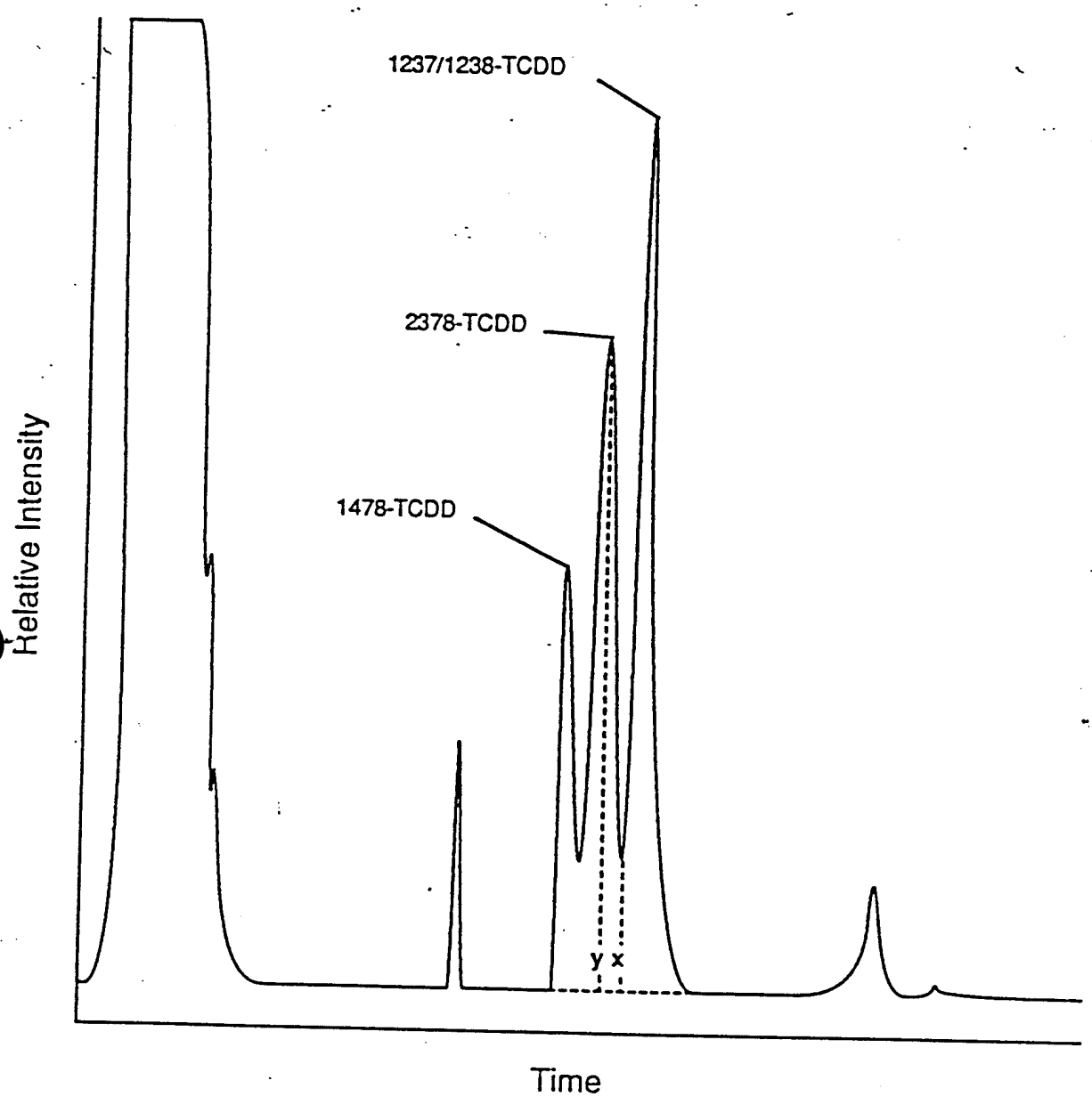


Figure 5: Valley Between 2378-TCDD and Other Closely Eluting Isomers on an SP-2331 (or Equivalent) Column

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

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OVERVIEW

Quality assurance (QA) and quality control (QC) are integral parts of the CLP.[1,2,4,5,6] The QA process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity to ensure that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.[1]

During the planning of an environmental data collection program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and that the deficiencies uncovered by the QC system are corrected. After environmental data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support enforcement or remedial decisions.[1,2,3]

This exhibit describes the overall QA/QC operations and the processes by which the CLP meets the QA/QC objective defined above. This contract requires a variety of QA/QC activities. These contract requirements are the minimum QC operations necessary to satisfy the analytical requirements associated with the determination of the different method analytes. These QC operations are designed to facilitate laboratory comparison by providing the EPA with comparable data from all Contractors. These requirements do not release the analytical Contractor from maintaining their own QC checks on method and instrument performance.

SECTION I

INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in environmental analyses requires reliance on the QC procedures and criteria incorporated into the methods. The methods in this contract have been validated on samples typical of those received by the laboratories in the CLP. However, the validation of these methods does not guarantee that the methods perform equally well for all sample matrices encountered. Inaccuracies can also result from causes other than unanticipated matrix effects, such as sampling artifacts, equipment malfunctions, and operator error. Therefore, the QC component of each method is indispensable.

The data acquired from QC procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, the QC component gives an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

The necessary components of a complete QA/QC program include internal QC criteria that demonstrate acceptable levels of performance, as determined by QA review. External review of data and procedures is accomplished by the monitoring activities of the National Program Office (NPO), Regional data users, the Sample Management Office (SMO), the National Enforcement Investigations Center (NEIC), and the Environmental Monitoring Systems Laboratory (EMSL-LV). Each external review accomplishes a different purpose. These reviews are described in specific sections of this exhibit. Performance evaluation (PE) samples and magnetic tape audits provide an external QA reference for the program. A laboratory on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the contract laboratories through direct communications with the Administrative Project Officer (APO) and Technical Project Officer (TPO).

This exhibit is not a guide to constructing QA project plans, QC systems, or a QA organization. However, the exhibit does explain the QA/QC requirements of the program, outlines some minimum standards for QA/QC programs, and includes specific items that are required in a QA Plan and QA/QC documentation detailed in this contract. Delivery of this documentation provides EPA with a complete data package which will stand alone, and limits the need for contact with the Contractor or with an analyst, at a later date, if some aspect of the analysis is questioned.

In order to assure that the product delivered by the Contractor meets the requirements of the contract, and to improve interlaboratory data comparison, EPA requires the following from the Contractor:

- A written QA Plan, the elements of which are designated in Section II.
- Written preparation of and adherence to QA/QC standard operating procedures (SOPs) as described in Section III.
- Adherence to the analytical methods and associated QC requirements specified in the contract.
- Verification of an analytical standard and documentation of the purity of neat materials and the purity and accuracy of solutions obtained from private chemical supply houses.
- Submission of all raw data and pertinent documentation for Regional review.
- Participation in the analysis of laboratory evaluation samples, including adherence to corrective action procedures.
- Submission, upon request, of GC/MS tapes and applicable documentation for tape audits.
- Participation in on-site laboratory evaluations, including adherence to corrective action procedures.
- Submission of all original documentation generated during sample analyses for EPA review.

SECTION II

QUALITY ASSURANCE PLAN

The Contractor shall establish a QA program with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

As evidence of such a program, the Contractor shall prepare a written QA Plan (QAP) which describes the procedures that are implemented to achieve the following:

- Maintain data integrity, validity, and usability.
- Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility.
- Detect problems through data assessment and establish corrective action procedures which keep the analytical process reliable.
- Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA and QC activities designed to achieve the data quality requirements in this contract. Where applicable, SOPs pertaining to each element shall be included or referenced as part of the QAP. The QAP must be available during an on-site laboratory evaluation. Additional information relevant to the preparation of a QAP can be found in EPA and ASTM publications.[2,4]

The elements of a QAP are as follows:

A. Organization and Personnel
   1. QA Policy and Objectives
   2. QA Management
      a. Organization
      b. Assignment of QC and QA Responsibilities
      c. Reporting Relationships
      d. QA Document Control Procedures
      e. QA Program Assessment Procedures
   3. Personnel
      a. Resumes
      b. Education and Experience Pertinent to this Contract
      c. Training Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives
2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy
2. Samples Tracking/Custody Procedures
3. Logbook Maintenance and Archiving Procedures
4. Case File Organization, Preparation and Review Procedures
5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs
6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency
2. Sample Preparation/Extraction Procedures
3. Sample Analysis Procedures
4. Standards Preparation Procedures
5. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures
2. Data Reduction Procedures
3. Data Validation Procedures
4. Data Reporting and Authorization Procedures

F. Quality Control

1. Solvent, Reagent and Adsorbent Check Analysis
2. Reference Material Analysis
3. Internal Quality Control Checks
4. Corrective Action and Determination of QC Limit Procedures
5. Responsibility Designation

G. Quality Assurance

1. Data Quality Assurance
2. Systems/Internal Audits
3. Performance/External Audits
4. Corrective Action Procedures
5. Quality Assurance Reporting Procedures
6. Responsibility Designation

Updating and Submission of the QAP:

Within 60 days of contract award:

During the contract solicitation process, the Contractor was required to submit their QAP to EMSL-LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a revised QAP, fully compliant with the requirements of this contract, to the TPO, EMSL-LV and NEIC. The revised QAP will become the official QAP under the contract. The revised QAP must include:

1. Changes resulting from the Contractor's internal review of their organization, personnel, facility, equipment, policy and procedures and the Contractor's implementation of the requirements of the contract; and

2. Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the preaward laboratory site evaluation.

Subsequent submissions:

During the term of contract, the Contractor shall amend the QAP when the following circumstances occur:

1. The Agency modifies the contract,

2. The Agency notifies the Contractor of deficiencies in the QAP,

3. The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4. The Contractor identifies deficiencies resulting from the internal review of the QAP,

5. The Contractor's organization, personnel, facility, equipment, policy or procedures change, or

6. The Contractor identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy or procedures.

The Contractor shall amend the QAP within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility. When the QAP is amended, all changes in the QAP must be clearly marked (i.e., indicating where the change is in the document with a bar in the margin, underlining the change, printing the change in bold, or using a different print font). The amended pages must have the date on which the changes were implemented.

The Contractor shall incorporate all amendments to the current QAP. The Contractor shall archive all amendments to the QAP for future reference by the Agency. The Contractor shall send a copy of the current QAP within 14 days of a request by the TPO or APO to the designated recipients.

Corrective action:

If the Contractor fails to adhere to these requirements, the Contractor may expect, but the Agency is not limited to, the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Contractor, GC/MS tape audit, data package audit, on-site laboratory evaluation, remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION III

STANDARD OPERATING PROCEDURES

In order to obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of SOPs. As defined by EPA, a SOP is a written document which provides directions for the step-by-step execution of an operation, analysis or action which is commonly accepted as the method for performing certain routine or repetitive tasks.[2]

SOPs prepared by the Contractor must be functional, i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs, as presented to EPA, must reflect activities as they are currently performed in the laboratory. In addition, all SOPs must meet the following criteria:

- Be consistent with current EPA regulations, guidelines, and the contract's requirements.[3,4,5,6,7]
- Be consistent with instrument manufacturers' specific instruction manuals.
- Be available to the EPA during an on-site laboratory evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During on-site evaluations, laboratory personnel may be asked to demonstrate the application of the SOPs.
- Provide for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Demonstrate the validity of data reported by the Contractor and explain the cause of missing or inconsistent results.
- Describe the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Be reviewed regularly and updated as necessary when contract, facility or Contractor procedural modifications are made.
- Be archived for future reference in usability or evidentiary situations.
- Be available at specific work stations as appropriate
- Be subject to a document control procedure which precludes the use of outdated or inappropriate SOPs.

A. SOP Format

The format for SOPs may vary depending upon the kind of activity for which they are prepared; however, at a minimum, the following sections must be included:

- o Title page.
- o Scope and application.
- o Definitions.
- o Procedures.
- o QC limits.
- o Corrective action procedures, including procedures for secondary review of information being generated.
- o Documentation description and example forms.
- o Miscellaneous notes and precautions.
- o References.

B. Required SOPs

The following SOPs are required by EPA:

1. Evidentiary SOPs (see Exhibit F).
2. Sample receipt and storage.
3. Sample preparation.
4. Calibration.
5. Standards purity/preparation.
6. Maintaining instrument records and logbooks.
7. Sample analysis and data control systems.
8. Glassware cleaning.
9. Technical and managerial review of laboratory operation and data package preparation.
10. Internal review of contractually required QA/QC data for each individual data package.
11. Chain-of-custody procedures and document control including Complete Sample Delivery Group (SDG) File preparation.
12. Laboratory data validation/laboratory self-inspection.
    a. Data flow and chain-of-command for data review.
    b. Procedures for measuring precision and accuracy.
    c. Evaluation parameters for identifying systematic errors.[9]
    d. Procedures to assure that hardcopy deliverables are complete and compliant with the requirements in Exhibit B.

e. Demonstration of internal QA inspection procedures (demonstrated by supervisory sign-off on personal notebooks, internal PE samples, etc.).

f. Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas).

g. Demonstration of problem identification-corrective actions and resumption of analytical processing and sequence resulting from internal audit (i.e., QA feedback).

h. Documentation of audit reports (internal and external), response, corrective action, etc.

13. Data management and handling.

a. Procedures for controlling and estimating data entry errors.

b. Procedures for reviewing changes to data and deliverables and ensuring traceability of updates.

c. Lifecycle management procedures for testing, modifying and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems.

d. Database security, backup and archival procedures including recovery from system failures.

e. System maintenance procedures and response time.

f. Individuals(s) responsible for system operation, maintenance, data integrity and security.

g. Specifications for staff training procedures.

C. SOP Delivery Requirements

Updating and submission of SOPs:

During the contract solicitation process, the Contractor was required to submit their SOPs to EMSL-LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a complete revised set of SOPs, fully compliant with the requirements of this contract, to the TPO, EMSL-LV and NEIC. The revised SOPs will become the official SOPs under the contract. The revised SOPs must include:

1. Changes resulting from the Contractor's internal review of their procedures and the Contractor's implementation of the requirements of the contract;

2. Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the preaward laboratory site evaluation.

Subsequent submissions:

During the term of contract, the Contractor shall amend the SOPs when the following circumstances occur:

1. The Agency modifies the contract,

2. The Agency notifies the Contractor of deficiencies in their SOPs documentation,

3. The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4. The Contractor's procedures change,

5. The Contractor identifies deficiencies resulting from the internal review of their SOPs, or

6. The Contractor identifies deficiencies resulting from the internal review of their procedures.

The SOPs must be amended or new SOPs must be written within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs must be clearly marked (i.e, indicating where the change is in the document with a bar in the margin, underlining the change, printing the change in bold, or using a different print font). The amended/new SOPs must have the date on which the changes were implemented.

When the SOPs are amended or new SOPs are written, the Contractor shall document in a letter the reasons for the changes, and submit the amended SOPs or new SOPs to the TPO, EMSL-LV (quality assurance/technical SOPs) and NEIC (evidentiary SOPs). The Contractor shall send the letter and the amended sections of the SOPs or new SOPs within 14 days of the change. An alternate delivery schedule for the submittal of the letter and amended/new SOPs may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the TPO or APO, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the TPO, APO, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The TPO/APO will not grant an extension for greater than 30 days for amending/writing new SOPs. The TPO/APO will not grant an extension for greater than 14 days for submission of the letter documenting the reasons for the changes and for submitting amended/new SOPs. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

The Contractor shall send a complete set of current SOPs within 14 days of a request by the TPO or APO to the recipients he/she designates.

Corrective action:

If the Contractor fails to adhere to these requirements, the Contractor may expect, but the Agency is not limited to, the following action: reduction of number of samples sent under this contract, suspension of sample shipment to the Contractor, GC/MS tape audit, data package audit, on-site laboratory evaluation, remedial laboratory evaluation sample, and/or contract sanction, such as a Cure Notice.

SECTION IV

QA/QC REQUIREMENTS

This section outlines the minimum QC operations necessary to satisfy the analytical requirements associated with the detection and quantitative measurement of 2378-tetrachlorinated dibenzo-*p*-dioxin and total tetra-, penta-, hexa-, hepta- and octachlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), by using the procedures outlined in Exhibit D. This section is not intended as a comprehensive QC document, but rather as a guide to the specific QC operations that must be considered for PCDD/PCDF analysis.

The QC operations that must be considered include the following:

- Mass Calibration.
- Window Defining Mix.
- Chromatographic Resolution.
- GC/MS Initial Calibration.
- GC/MS Continuing Calibration.
- Instrument Sensitivity.
- Identification Criteria.
- Method Blank Analysis.
- Spiked Sample Analysis.
- Duplicate Sample Analysis.
- Toxicity Equivalency Factor and Isomer Specificity.
- Dilutions.
- Reanalyses.

1. Mass Calibration

1.1 Mass calibration of the mass spectrometer is recommended prior to analyzing the calibration solutions, blanks, samples and QC samples. It is recommended that the instrument be tuned to greater sensitivity in the high mass range in order to achieve better response for the later eluting compounds.

1.2 Optimum results using FC-43 for mass calibration can be achieved by scanning from 222-510 amu every one second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode (see Exhibit D, Section 6).

1.3 m/z 414 and m/z 502 should be 30-50 percent of m/z 264 base peak (see Exhibit D, Section 6).

2. Window Defining Mix

2.1 The window defining mix is analyzed to verify that the switching times between the descriptors have been appropriately set.

2.2 The window defining mix is obtained from commercial sources and must contain the first and last eluting isomers in each homologue on the GC column chosen for analyses (see Exhibit D, Section 5.12 and Table 9).

2.3 The window defining mix must be analyzed before the initial calibration on each instrument and GC column used for analysis and at the frequency found in Exhibit D, Paragraph 7.1.3.

3. Chromatographic Resolution

3.1 Chromatographic resolution is evaluated using one of two standard solutions, depending on the GC column chosen for analyses.

3.2 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 standard during both the initial and continuing calibration procedures (see Exhibit D, Paragraphs 7.3.2.1 and 7.4.2).

3.3 For analyses on a SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standard by the analysis of a commercially available column performance mixture (see Exhibit D, Section 5.19) that contains the TCDD isomers that elute most closely with 2378-TCDD on this GC column (1478-TCDD and the 1237/1238-TCDD pair) (see Exhibit D, Paragraph 7.2.2).

3.4 The chromatographic resolution criteria are found in Exhibit D, Paragraphs 7.3.2.1 and 7.2.3.

4. GC/MS Initial Calibration

4.1 Prior to analysis of samples and blanks, the GC/MS system must be initially calibrated at a minimum of five concentrations to verify linearity of response.

4.2 The calibration solutions containing the labeled and unlabeled analogs must be analyzed at five concentrations as described in Exhibit D, Section 5.11 and Table 3.

4.3 The CC1, CC2, CC4 and CC5 solutions shall be used as provided by EPA (see Exhibit D, Section 7.3). The CC3 solution must be prepared as explained in Exhibit D, Paragraph 7.4.1.

4.4 The calibration standard must be analyzed using the MS/DS conditions as described in Exhibit D, Paragraph 7.3.1.

4.5 The chromatographic resolution between the $^{13}C_{12}$ 2378-TCDD and $^{13}C_{12}$ 1234-TCDD isomers must be resolved with a valley of < 25 percent, and

the chromatographic peak separation between the 123478-HxCDD and 123678-HxCDD in the CC3 solution must be resolved with a valley of ≤ 50 percent (see Exhibit D, Paragraph 7.3.2.1).

4.6 The relative ion abundance criteria for PCDDs/PCDFs must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions (see Exhibit D, Table 6).

4.7 For all calibration solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix (see Exhibit D, Section 7.1).

4.8 For all calibration solutions, the signal-to-noise ratio must meet the criteria specified in Exhibit D, Paragraph 7.3.2.4.

4.9 The relative response factors for the 17 unlabeled target analytes relative to their appropriate internal standards, and the relative response of the five labeled internal standard standards relative to the appropriate recovery standard are determined according to the procedures in Exhibit D, Paragraph 7.3.3.

4.10 Calculate the mean RRF and percent relative standard deviation (%RSD) of the five RRFs (CC1 to CC5) for each unlabeled PCDD/PCDF, and labeled internal and recovery standards, present in all five concentration calibration solutions as described in Exhibit D, Paragraph 7.3.5. As indicated in the referenced paragraph, no %RSD calculation is possible for the 2,3,7,8-substituted isomers in the CC3 supplemental calibration solution, because they are only present in the one solution.

4.11 The %RSD is calculated for the EPA-supplied unlabeled and labeled analytes only. To establish linearity, the %RSD of the five RRFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards must not exceed 15.0% (see Exhibit D, Paragraph 7.3.5).

4.12 If the initial calibration criteria for GC resolution, ion abundance ratios, retention times, instrument sensitivity and relative response factors are not met, the Contractor must take the corrective actions as explained in Exhibit D, Paragraph 7.3.7.

4.13 The response factors to be used for determining the total homologue concentrations are described in Exhibit D, Section 15.2.

5. GC/MS Continuing Calibration

5.1 Once the GC/MS system has been calibrated, the calibration must be verified for each 12-hour time period for each GC/MS system.

5.2 The continuing calibration standard is prepared by mixing the commercially supplied supplemental standard with the EPA supplied CC4 solution (see Exhibit D, Paragraph 7.4.1).

5.3 The continuing calibration consists of two parts: evaluation of the chromatographic resolution and verification of the RRF values to be used for quantitation. At the beginning of each 12-hour period, the

chromatographic resolution is verified in the same fashion as in the initial calibration, through the analysis of the CC3 solution on the DB-5 (or equivalent) column or through the analysis of the column performance solution on the SP-2331 (or equivalent) column (see Exhibit D, Section 7.4).

5.4 The continuing calibration standard must be analyzed according to the procedures given in Exhibit D, Section 7.4, and at the frequency in that section.

5.5 Calculate the relative response factors for the 17 unlabeled target analytes relative to their appropriate internal standards and the response factor for the five labeled internal standard relative to the appropriate recovery standard, according to the procedure described in Exhibit D, Paragraph 7.4.4.

5.6 The GC resolution criteria for DB-5 or SP-2331 (or equivalent) column, as specified in Exhibit D, Paragraph 7.3.2.1 or 7.4.3, must be met before the analysis of samples may begin. If the separation criteria for both DB-5 and SP-2331 (or equivalent) column analysis are met, a single column analysis may be used.

5.7 The relative ion abundance for all PCDD/PCDF peaks, including the labeled internal and recovery standards, for both beginning and ending analyses must meet the criteria listed in Exhibit D, Table 6.

5.8 The signal-to-noise ratio for the CC3 and CC1 solutions must meet the criteria specified in Exhibit D, Paragraph 7.4.6.3.

5.9 The percent difference for the RRFs must be calculated as explained in Exhibit D, Paragraph 7.4.6.4 and must meet the criteria specified in that paragraph.

5.10 If the criteria specified in Exhibit D, Paragraph 7.4.6 are not met, the Contractor must take the corrective actions outlined in Exhibit D, Paragraph 7.4.7.

6. Instrument Sensitivity

6.1 In order to demonstrate that the GC/MS/DS system has retained adequate sensitivity during the course of sample analyses, the Contractor must analyze the lowest of the calibration standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

6.2 Analyze the CC1 solution according to Exhibit D, Paragraph 7.5.1.

6.3 This analysis must meet the retention time criteria in Exhibit D, Paragraph 7.5.2.1.

6.4 This analysis must meet the ion abundance ratio criteria in Exhibit D, Table 6.

6.5 For this analysis, the signal-to-noise ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

7. Identification Criteria

7.1 For a gas chromatographic peak to be unambiguously identified as a PCDD/PCDF, the peak must meet all of the following criteria.

7.2 The identification of the PCDD/PCDF isomers is based on simultaneous detection of the two most abundant ions in the molecular ion regions and the M-COCl ion. In order to make a positive identification, the relative retention time criteria specified in Exhibit D, Section 11.1 must be met.

7.3 All of the ions specified for each PCDD/PCDF homologue and labeled standards must be present in the selected ion current profile. The ion current response for the analytes and labeled standards must meet the QC criteria (see Exhibit D, Section 11.2).

7.4 The integrated ion current for each analyte ion listed in Exhibit D, Table 5 must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10 times background noise and must not have saturated the detector (see Exhibit D, Section 11.3).

7.5 The relative ion abundance criteria for the native analytes and internal standard must be met (see Exhibit D, Table 6).

7.6 The identification of a GC peak as a PCDF cannot be made if a signal having a signal-to-noise ratio greater than 2.5 is detected in the corresponding PCDPE channel (see Exhibit D, Section 11.5).

8. Method Blank Analysis

8.1 A method blank is a volume of clean reference matrix that is carried through the entire analytical sequence.

8.2 A minimum of one blank per matrix must be analyzed with each SDG at a frequency described in Exhibit D, Section 12.1.

8.3 An acceptable method blank must not contain any chemical interferences or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions which is greater than 5 percent of the signal of the appropriate internal standard, or any peak that meets the identifications criteria as a PCDD/PCDF which is greater than 2 percent of the appropriate internal standard (see Exhibit D, Section 15.2).

8.4 If the blank is contaminated, the associated positive samples and any samples containing peaks that do not meet all the identification criteria must be rerun (see Exhibit D, Paragraph 12.2.3).

9. Spiked Sample Analysis

9.1 In order to provide data on the accuracy of the analytical method, the Contractor is required to prepare and analyze a spiked sample for each matrix being analyzed. For each SDG, the Contractor must prepare a spiked sample for all of the matrix types that occur in the SDG (see Exhibit D, Section 13).

9.2 Prepare a spiked sample according to the procedures in Exhibit D, Sections 13.1 and 13.2.

9.3 Extract and analyze the spiked sample according to the procedures in Exhibit D, Sections 9 and 10.

9.4 Calculate the recovery of the spiked analytes according to the procedures in Exhibit D, Section 13.5.

10. Duplicate Sample Analysis

10.1 In order to provide data on the precision of the analytical method, the Contractor is required to prepare and analyze a duplicate of one sample for each matrix being analyzed. For each group of samples, the laboratory must prepare a duplicate sample for all of the following matrix types that occur in the SDG (see Exhibit D, Section 14).

10.2 Prepare a duplicate sample according to the procedures in Exhibit D, Section 14.1.

10.3 Extract and analyze the spiked sample according to the procedures in Exhibit D, Sections 9 and 10.

10.4 Calculate the relative percent difference between the results of the original analysis and the duplicate analysis according to the procedures in Exhibit D, Section 14.3.

11. Toxicity Equivalency Factor and Isomer Specificity

11.1 The 2378-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample must be calculated according to procedures outlined in Exhibit D, Section 15.8.

11.2 Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60-m DB-5 column alone. Historically, problems have been associated with the separation of 2378-TCDD from 1237-TCDD and 1268-TCDD, and the separation of 2378-TCDF from 2347-TCDF. Because of the toxicologic concern associated with 2378-TCDD and 2378-TCDF, additional analyses may be required for some samples as described in Exhibit D, Section 16.

11.3 If the toxicity equivalence calculated in Section 15 is greater than 0.7 ppb (soil/sediment or fly ash), 7 ppb (chemical waste), or 7 ppt (aqueous), better isomer specificity is required than can be achieved

on the DB-5 column. The Contractor may utilize either of the two options listed in Exhibit D, Paragraphs 16.1.1 or 16.1.2 to achieve adequate isomer specificity.

12. Dilutions

If the concentration of any PCDD/PCDF in the sample exceeds the calibration range or the detector is saturated, a dilution must be performed using the procedures given in Exhibit D, Section 10.4.

13. Reanalyses

The requirements for reextraction and for reanalysis of samples are given in Exhibit D, Section 17.

SECTION V

ANALYTICAL STANDARDS REQUIREMENTS

A. Overview

EPA will not supply all the analytical reference standards required for performance of this contract. See Exhibit D, Section 5 for the standards that may be provided by EPA, subject to availability. Contractors will be required to prepare from neat materials or purchase from private chemical supply houses the standards not supplied by EPA but necessary to successfully and accurately perform the analyses required in this contract.

B. Preparation of Chemical Standards from the Neat High Purity Bulk Material

The Contractor may prepare chemical standards from neat materials. Commercial sources for neat chemical standards pertaining to compounds listed on the Target Compound List are given in Appendix C of the "Quality Assurance Materials Bank: Analytical Reference Standards," Seventh Edition, January 1988. Laboratories should obtain the highest purity possible when purchasing neat chemical standards; standards purchased at less than 97% purity must be documented as to why a higher purity could not be obtained.

1. Neat chemical standards must be kept refrigerated when not being used in the preparation of standard solutions. Proper storage of neat chemicals is essential in order to safeguard them from decomposition.

2. The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, the Contractor is responsible for having analytical documentation ascertaining that the purity of each compound is correctly stated. Purity confirmation, when performed, should use either differential scanning calorimetry, gas chromatography with flame ionization detection, high performance liquid chromatography, infrared spectrometry, or other appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

Equation 1

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity}/100)}$$

where "weight of pure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

3. Mis-identification of compounds occasionally occurs and it is possible that a mislabeled compound may be received from a chemical supply house. The Contractor is responsible for having analytical documentation ascertaining that all compounds used in the preparation of solution standards are correctly identified. Identification confirmation, when performed, should use gas chromatographic/mass spectrometry analysis on at least two different analytical columns, or other appropriate techniques.

4. Calculate the weight of material to be weighed out for a specified volume taking into account the purity of the compound and the desired concentration. A second person must verify the accuracy of the calculations. Check balances for accuracy with a set of standard weights. All weighing should be performed on an analytical balance to the nearest 0.1 mg and verified by a second person. The solvent used to dissolve the solute should be compatible with the protocol in which the standard is to be used; the solute should be soluble, stable, and nonreactive with the solvent. In the case of a multicomponent solution, the components must not react with each other.

5. Transfer the solute to a volumetric flask, and dilute to the specified solution volume with solvent after ensuring dissolution of the solute in the solvent. Sonication or warming may be performed to promote dissolution of the solute. This solution is to be called the primary standard, and all subsequent dilutions must be traceable back to the primary standard.

6. Log notebooks are to be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be recorded and verified by a second person. All solution standards are to be refrigerated when not in use. All solution standards are to be clearly labeled as to the identity of the compound(s), concentration, date prepared, solvent, and initials of the preparer.

C. Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by the Contractor provided they meet the following criteria:

1. Laboratories must maintain the following documentation to verify the integrity of the standard solutions they purchase:

   a. Mass spectral identification confirmation of the neat material.

   b. Purity confirmation of the neat material.

   c. Chromatographic and quantitative documentation that the solution standard was QC-checked according to the following section.

2. The Contractor must purchase standards for which the quality is demonstrated statistically and analytically by a method of the supplier's choice. One way quality can be demonstrated is to prepare and analyze three solutions; a high standard, a low

standard, and a standard at the target concentration (see parts a and b below). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations by using the Student's t-test in part d. If this consistency is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards by using the Student's t-test in part e. Thus, the standard is certified to be within 10 percent of the target concentration.

If the above procedure is used, the supplier must document that the following have been achieved:

a. Two solutions of identical concentration must be prepared independently from neat materials. An aliquot of the first solution must be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration 10 percent greater than the target standard. This aliquot is called the "high standard." One further aliquot is taken from the second solution and diluted to a concentration 10 percent less that the target standard. This aliquot is called the "low standard."

b. Six replicate analyses of each standard (a total of 18 analyses) must be performed in the following sequence: low standard, target standard, high standard, low standard, target standard, high standard, ...

c. The mean and variance of the six results for each solution must be calculated.

Equation 2

$$\text{MEAN} = (Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)/6$$

Equation 3

$$\text{VARIANCE} = (Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - (6*\text{MEAN})^2)/5$$

The values Y_1, Y_2, Y_3, ..., represent the results of the six analyses of each standard. The means of the low, target and high standards are designated M_1, M_2 and M_3, respectively. The variances of the low, target and high standards are designated V_1, V_2 and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

Equation 4

$$V_p = (V_1/(0.81) + V_2 + V_3/(1.21))/3$$

If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

d. The test statistic must be calculated:

Equation 5
$$\text{TEST STATISTIC} = |(M_3 /1.1) - (M_1 /0.9)|/(V_p /3)^{0.5}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate a twenty percent difference between the high and low standards. In such a case, the standards are not acceptable.

e. The test statistic must be calculated:

Equation 6
$$\text{TEST STATISTIC} = |M_2 - (M_1 /1.8) - (M_3 /2.2)|/(V_p /4)^{0.5}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

f. The 95 percent confidence intervals for the mean result of each standard must be calculated:

Equation 7
$$\text{Interval for Low Standard} = M_1 \pm (2.13)(V_p /6)^{0.5}$$

Equation 8
$$\text{Interval for Target Standard} = M_2 \pm (2.13)(V_p /6)^{0.5}$$

Equation 9
$$\text{Interval for High Standard} = M_3 \pm (2.13)(V_p /6)^{0.5}$$

These intervals must not overlap. If overlap is observed, the supplier has failed to demonstrate the ability to discriminate the 10 percent difference in concentrations. In such a case, the standards are not acceptable.

In any event, the Contractor is responsible for the quality of the standards employed for analyses under this contract.

D. Requesting Standards From the EPA Standards Repository

Solutions of analytical reference materials can be ordered from the U.S. EPA Chemical Standards Repository, depending on availability. The Contractor can place an order for standards only after demonstrating that these standards are not available from commercial vendors either in solution or as a neat material.

E. Documentation of the Verification and Preparation of Chemical Standards

Each laboratory is responsible for maintaining the necessary documentation to show that the chemical standards they have used in the performance of CLP analysis conform to the requirements previously listed. Weighing logbooks, calculations, chromatograms, mass spectra,

etc, whether produced by the laboratory or purchased from chemical supply houses, must be maintained by the laboratory and may be subject to review during on-site inspections. Documentation of standards preparation may be required to be sent to EPA for verification of contract compliance. In those cases where the documentation is supportive of the analytical results of data packages sent to EPA, such documentation is to be kept on file by the laboratory for a period of one year.

SECTION VI

CONTRACT COMPLIANCE SCREENING

Contract Compliance Screening (CCS) is one aspect of the Government's contractual right of inspection of analytical data. CCS examines the Contractor's adherence to the contract requirements based on the sample data package delivered to EPA.

CCS is performed by SMO under the direction of the EPA. To assure a uniform review, a set of standardized procedures have been developed to evaluate the sample data package submitted by a Contractor against the technical and completeness requirements of the contract.

CCS results are mailed to the Contractor and all other data recipients. The Contractor has a period of time to correct deficiencies. The Contractor must send all corrections to the Regional client, EMSL-LV and SMO.

CCS results are used in conjunction with other information to measure overall Contractor performance and to take appropriate actions to correct deficiencies in performance.

SECTION VII

REGIONAL DATA REVIEW

Contract laboratory data are generated to meet the specific needs of the Regions. In order to verify the usability of data for the intended purpose, each Region reviews data from the perspective of end-user, based upon functional aspects of data quality. General guidelines for data review have been developed jointly by the Region and the NPO. Each Region uses these guidelines as the basis for data evaluation. Individual Regions may augment the basic guideline review process with additional review based on Region-specific or site-specific concerns. Regional reviews, like the sites under investigation, vary based on the nature of the problems under investigation and the Regional response appropriate to the specific circumstances.

Regional data reviews, relating usability of the data to a specific site, are part of the collective assessment process. They complement the review done at SMO, which is designed to identify contractual discrepancies, and the review done at EMSL-LV which is designed to evaluate Contractor and method performance. These individual evaluations are integrated into a collective review that is necessary for program and laboratory administration and management and may be used to take appropriate action to correct deficiencies in the Contractor's performance.

SECTION VIII

LABORATORY EVALUATION SAMPLES

Although intralaboratory QC may demonstrate Contractor and method performance that can be tracked over time, an external performance evaluation program is an essential feature of a QA program. As a means of measuring Contractor and method performance, Contractors participate in interlaboratory comparison studies conducted by the EPA. Results from the analysis of laboratory evaluation samples will be used by the EPA to verify the Contractor's continuing ability to produce acceptable analytical data. The results are also used to assess the precision and accuracy of the analytical methods for specific analytes.

Sample sets may be provided to participating Contractors as frequently as on a SDG-by-SDG basis as a recognizable QC sample of known composition, as a recognizable QC sample of unknown composition, or not recognizable as a QC material. Laboratory evaluation samples may be sent either by the Regional client or the NPO and may be used for contract action.

Contractors are required to analyze the samples and return the data package and all raw data within the contract required turnaround time.

At a minimum, the results are evaluated for compound identification, quantification, and sample contamination. Confidence intervals for the quantification of target compounds are based on reported values using population statistics. EPA may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract.

A Contractor's results on the laboratory evaluation samples will determine the Contractor's performance as follows:

1. Acceptable, No Response Required (Score greater than or equal to 90 percent):

   Data meets most or all of the scoring criteria. No response is required.

2. Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75 percent but less than 90 percent):

   Deficiencies exist in the Contractor's performance.

   Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the APO, the TPO and EMSL-LV.

3. Unacceptable Performance, Response Explaining Deficiency(ies) Required (Score less than 75 percent):

Deficiencies exist in the Contractor's performance to the extent that the NPO has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the APO, the TPO and EMSL-LV.

The Contractor shall be notified by the APO or TPO concerning the remedy for their unacceptable performance. A Contractor may expect, but EPA is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, an on-site audit, a full data audit, analysis of remedial PE samples, and/or a contract sanction, such as a Cure Notice.

NOTE: A Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements will facilitate continuation of full sample delivery.

SECTION IX

GC/MS TAPE AUDITS

Periodically, EPA requests from Contractors the GC/MS magnetic tapes corresponding to a specific Case in order to accomplish tape audits. Generally, tape submissions and audits are requested for the following reasons:

- Program overview.
- Indication of data quality problems from EMSL-LV, SMO, or Regional data reviews.
- Support for on-site audits.
- Specific Regional requests.

Depending upon the reason for an audit, the tapes from a recent Case, a specific Case, or a laboratory evaluation sample may be requested. Tape audits provide a mechanism to assess adherence to contractual requirements and ensure the consistency of data reported on the hardcopy forms with that generated on the GC/MS tapes. This function provides external monitoring of CLP QC requirements and checks adherence of the Contractor to internal QA procedures. In addition, tape audits enable EPA to evaluate the utility, precision and accuracy of the analytical methods.

The GC/MS tape shall include raw data and quantitation reports for samples, blanks, laboratory evaluation samples, initial calibrations, and continuing calibrations associated with the SDG requested. The specific requirements for submissions of GC/MS tapes are discussed in Exhibit B.

Upon request of the APO or EMSL-LV, the required tapes and all necessary documentation shall be submitted to EPA within seven days of notification.

SECTION X

ON-SITE LABORATORY EVALUATIONS

At a frequency dictated by a Contractor's performance, the APO, TPO or their authorized representative will conduct an on-site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: a QA evaluation and an evidentiary audit.

A. Quality Assurance Evaluation

QA evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience or education requirements, and the acceptable performance of analytical and QC procedures. The Contractor should expect that items to be monitored will include, but not be limited to, the following items:

- Size and appearance of the facility.
- Quantity, age, availability, scheduled maintenance and performance of instrumentation.
- Availability, appropriateness, and utilization of SOPs.
- Staff qualifications, experience, and personnel training programs.
- Reagents, standards, and sample storage facilities.
- Standard preparation logbooks and raw data.
- Bench sheets and analytical logbook maintenance and review.
- Review of the Contractor's sample analysis/data package inspection procedures.

Prior to an on-site evaluation, various documentation pertaining to performance of the specific Contractor is integrated in a profile package for discussion during the evaluation. Items that may be included are previous on-site reports, laboratory evaluation sample scores, Regional review of data, Regional QA materials, GC/MS tape audit reports, results of CCS, and date trend reports.

B. Evidentiary Audit

Evidence auditors conduct an on-site laboratory evaluation to determine if laboratory policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit is comprised of the following three activities:

1. Procedural Audit

The procedural audit consists of review and examination of actual SOPs and accompanying documentation for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), and analytical project file organization and assembly.

2. Written SOPs Audit

The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), and analytical project file organization and assembly.

3. Analytical Project File Evidence Audit

The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- Accuracy of the document inventory.
- Completeness of the file.
- Adequacy and accuracy of the document numbering system.
- Traceability of sample activity.
- Identification of activity recorded on the documents.
- Error correction methods.

C. Discussion of the On-Site Team's Findings

The QA and evidentiary auditors discuss their findings with the APO/TPO prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel.

D. Corrective Action Reports For Follow-Through to Quality Assurance and Evidentiary Audit Reports

Following an on-site evaluation, QA and evidentiary audit reports which discuss deficiencies found during the on-site evaluation will be forwarded to the Contractor. The Contractor must discuss the corrective actions taken to resolve the deficiencies discussed during the on-site visit and discussed in the on-site reports in a letter to the APO, TPO, EMSL-LV (response to the QA report) and NEIC (response to the evidentiary report) within 14 days of receipt of the finding or within the time agreed upon between the APO/TPO and the Contractor. If SOPs are required to be written or amended, the Contractor must provide

the SOPs to the TPO, EMSL-LV (QA/technical SOPs) and NEIC (evidentiary SOPs) within 30 days of receipt of the finding or within the time agreed upon between the APO/TPO and the Contractor.

If the Contractor fails to take appropriate corrective action to resolve the deficiencies discussed in the on-site reports, a Contractor may expect, but the Government is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, a follow-up site visit, a full data audit, analysis of remedial PE samples and/or contract sanction, such as a Cure Notice.

SECTION XI

QUALITY ASSURANCE AND DATA TREND ANALYSIS

Data submitted by laboratories are subject to review from several aspects: compliance with contract-required QC, usability, and full data package evaluation. Problems resulting from any of these reviews may determine the need for a GC/MS tape audit, an on-site laboratory evaluation and/or a remedial laboratory evaluation sample. In addition, QC prescribed in the methods provides information that is continually used by EPA to assess sample data quality, Contractor data quality and CLP data quality via data trend analysis. Trend analysis is accomplished by entering data into a computerized database. Statistical reports that evaluate specific anomalies or disclose trends in many areas, including the following, are generated from this database:

- Internal standard recovery.
- Laboratory evaluation sample.
- Blanks.
- Gas chromatographic resolution of analytes.
- Initial and continuing calibration data.
- Other QC and method parameters.

Program-wide statistical results are used to rank laboratories in order to observe the relative performance of each Contractor using a given protocol against its peers. The reports are also used to identify trends within laboratories. The results of many of these trends analyses are included in overall evaluation of a Contractor's performance, and are reviewed to determine if corrective action or an on-site laboratory evaluation is indicated in order to meet the QA/QC requirements of the contract.

Contractor performance over time is monitored using these trend analysis techniques to detect departures of Contractor output from required or desired levels of QC, and to provide an early warning of Contractor QA/QC problems which may not be apparent from the results of an individual case.

As a further benefit to the CLP, the database provides the information needed to establish performance-based criteria in updated analytical protocols, where advisory criteria has been previously used. The vast empirical data set produced by contract laboratories is carefully analyzed, with the results augmenting theoretical and research-based performance criteria. The result is a continuously monitored set of QC and performance criteria specifications of what is routinely achievable and expected of environmental chemistry laboratories in mass production analysis of environmental samples. This information, in turn, assists EPA in meeting its objectives of obtaining data of known and documented quality.

SECTION XII

DATA MANAGEMENT

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage and security of computer-readable data and files. These procedures should be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability and QC.

Data manually entered from hardcopy must be quality controlled and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates must be estimated and recorded on a monthly basis by reentering a statistical sample of the data entered and calculating discrepancy rates by data element.

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted must be documented to allow traceability of updates. Documentation must include the following for each change:

- Justification or rationale for the change.
- Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Change documentation must be retained according to the schedule of the original deliverable.
- Resubmitted deliverables must be reinspected as a part of the laboratory's internal inspection process prior to resubmission. The entire deliverable, not just the changes, must be inspected.
- The Laboratory Manager must approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

Life cycle management procedures must be applied to computer software systems developed by the laboratory to be used to generate and edit contract deliverables. Such systems must be thoroughly tested and documented prior to utilization.

- A software test and acceptance plan including test requirements, test results and acceptance criteria must be developed, followed, and available in written form.
- System changes must not be made directly to production systems generating deliverables. Changes must be made first to a development system and tested prior to implementation.

- Each version of the production system will be given an identification number, a date of installation, and a date of last operation, and will be archived.
- System and operations documentation must be developed and maintained for each system. Documentation must include a user's manual and an operations and maintenance manual.

Individual(s) responsible for the following functions must be identified:

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and quality control.
- Data and system security, backup and archiving.

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10. Moore, J.M. and Pearson, J.G. "Quality Assurance Support for the Superfund Contract Laboratory Program," Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume, ASTM STP 925, C.L. Perket, ed., American Society for Testing and Materials, Philadelphia, 1986.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL,
AND STANDARD OPERATING PROCEDURES

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1. Sample Chain-of-Custody

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To accomplish this task, Contractors are required to develop and implement the following sample identification, chain-of-custody, sample receiving, and sample tracking procedures.

1.1 Sample Identification

To assure traceability of the samples while in the possession of the Contractor, the Contractor shall have a specified method for maintaining identification of samples throughout the laboratory. Each sample and sample preparation container shall be labeled with the EPA number or a unique laboratory identifier. If a unique laboratory identifier is used, it shall be cross-referenced to the EPA number.

1.2 Chain-of-Custody Procedures

Because of the nature of the data being collected, the custody of EPA samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. The Contractor shall have procedures ensuring that EPA sample custody is maintained and documented. A sample is under custody if:

- It is in your possession, or
- It is in your view after being in your possession, or
- It was in your possession and you locked it up, or
- It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel.)

1.3 Sample Receiving Procedures

1.3.1 The Contractor shall designate a sample custodian responsible for receiving all samples.

1.3.2 The Contractor shall designate a representative to receive samples in the event that the sample custodian is not available.

1.3.3 The condition of the shipping containers and sample bottles shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.4 The condition of the custody seals (intact/not intact) shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.5 The sample custodian or his/her representative shall check for the presence or absence of the following documents accompanying the sample shipment:

- o Airbills or airbill stickers
- o Custody seals
- o EPA custody records
- o Sample Traffic Reports or SAS Packing Lists
- o Sample tags

1.3.6 The sample custodian or his/her representative shall sign and date all forms (e.g., custody records, Traffic Reports or Packing Lists, and airbills) accompanying the samples at the time of sample receipt.

1.3.7 The Contractor shall contact the Sample Management Office (SMO) to resolve discrepancies and problems such as absent documents, conflicting information, broken custody seals, and unsatisfactory sample condition (e.g., leaking sample bottle).

1.3.8 The Contractor shall record the resolution of discrepancies and problems on Telephone Contact Logs.

1.3.9 The following information shall be recorded on Form DC-1 (see Exhibit B) by the sample custodian or his/her representative as samples are received and inspected:

- o Condition of the shipping container.
- o Presence or absence and condition of custody seals on shipping and/or sample containers.
- o Custody seal numbers, when present.
- o Condition of the sample bottles.
- o Presence or absence of airbills or airbill stickers.
- o Airbill or airbill sticker numbers.
- o Presence or absence of EPA custody records.
- o Presence or absence of Traffic Reports or SAS Packing Lists.
- o Presence or absence of sample tags.
- o Sample tag identification numbers cross-referenced to the EPA sample numbers.
- o Verification of agreement or non-agreement of information recorded on shipping documents and sample containers.
- o Problems or discrepancies.

1.4 Sample Tracking Procedures

The Contractor shall maintain records documenting all phases of sample handling from receipt to final analysis.

2. Document Control Procedures

The goal of the laboratory document control program is to assure that all documents for a specified Sample Delivery Group (SDG) will be accounted for when the project is completed. Accountable documents used by contract laboratories shall include; but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analysis. The following document control procedures have been established to ensure that all laboratory records are assembled and stored for delivery to EPA or are available upon request from EPA prior to the delivery schedule.

2.1 Preprinted Laboratory Forms and Logbooks

2.1.1 All documents produced by the Contractor that are directly related to the preparation and analysis of EPA samples shall become the property of EPA and shall be placed in the Complete SDG File (CSF). All observations and results recorded by the laboratory but not on preprinted laboratory forms shall be entered into permanent laboratory logbooks. When all data from a SDG are compiled, all original laboratory forms and copies of all SDG-related logbook entries shall be included in the documentation package.

2.1.2 The Contractor shall identify the activity recorded on all laboratory documents that are directly related to the preparation and analysis of EPA samples.

2.1.3 Pre-printed laboratory forms shall contain the name of the laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.4 Logbook entries shall be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.5 Logbook entries shall be in chronological order. Entries in logbooks, with the exception of inscrument run logs and extraction logs, shall include only one SDG per page.

2.1.6 Pages in both bound and unbound logbooks shall be sequentially numbered.

2.1.7 Instrument run logs shall be maintained so as to enable a reconstruction of the run sequence of individual instruments. Because the laboratory must provide copies of the instrument run logs to EPA, the laboratory may exercise the option of using only laboratory or EPA sample identification numbers in the logs for sample ID rather than government agency or commercial client names to preserve the confidentiality of commercial clients.

2.1.8 Corrections to supporting documents and raw data shall be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data shall be dated and initialed. No information shall be obliterated or rendered unreadable.

All notations shall be recorded in ink. Unused portions of documents shall be "z'd" out.

2.2 Consistency of Documentation

The Contractor shall assign a Document Control Officer (DCO) responsible for the organization and assembly of the CSF. All copies of laboratory documents shall be complete and legible.

Original documents which include information relating to more than one SDG shall be filed in the CSF of the lowest SDG number. The copy(ies) shall be placed in the other CSF(s), and the Contractor shall record the following information on the copy(ies) in red ink:

"COPY - ORIGINAL IS FILED IN CSF _____"

The Contractor shall sign and date this addition to the copy(ies).

Before releasing analytical results, the DCO shall assemble and cross-check the information on samples tags, custody records, lab bench sheets, personal and instrument logs, and other relevant deliverables to ensure that data pertaining to each particular sample or SDG are consistent throughout the CSF.

2.3 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in the CSF shall be inventoried and assigned a serialized number as described in Exhibit B.

All documents relevant to each SDG, including logbook pages, bench sheets, mass spectra, chromatograms, screening records, re-preparation records, reanalysis records, records of failed or attempted analysis, custody records, library research results, etc., shall be inventoried.

The DCO shall be responsible for ensuring that all documents generated are placed in the CSF for inventory and are delivered to the appropriate EPA Region or other receiver as designated by EPA. The DCO shall place the sample tags in plastic bags in the file.

2.4 Storage of EPA Files

The Contractor shall maintain EPA laboratory documents in a secure location.

2.5 Shipment of Deliverables

The Contractor shall document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that the containers cannot be opened without damaging or breaking the seal. The Contractor shall document what was sent, to whom, the date, and the method (carrier) used. A copy of the transmittal letter for the CSF shall be sent to the National Enforcement Investigations Center and SMO.

3. Specifications for Written Standard Operating Procedures

The Contractor shall have written standard operating procedures (SOPs) for receipt of samples, maintenance of custody, sample identification, sample storage, sample tracking, and assembly of completed data. A SOP is defined as a written narrative stepwise description of laboratory operating procedures including examples of laboratory documents. The SOPs shall accurately describe the actual procedures used in the laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this contract are acceptable for use in EPA enforcement case preparation and litigation. The Contractor's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

3.1 The Contractor shall have written SOPs describing the sample custodian's duties and responsibilities.

3.2 The Contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include, but not be limited to, documenting the following information:

3.2.1 Presence or absence of EPA chain-of-custody forms.

3.2.2 Presence or absence of airbills or airbill stickers.

3.2.3 Presence or absence of Traffic Reports or SAS Packing Lists.

3.2.4 Presence or absence of custody seals on shipping and/or sample containers and their condition.

3.2.5 Custody seal numbers, when present.

3.2.6 Airbill or airbill sticker numbers.

3.2.7 Presence or absence of sample tags.

3.2.8 Sample tag ID numbers.

3.2.9 Condition of the shipping container.

3.2.10 Condition of the sample bottles.

3.2.11 Verification of agreement or non-agreement of information on receiving documents and sample containers.

3.2.12 Resolution of problems or discrepancies with SMO.

3.2.13 An explanation of any terms used by the laboratory to describe sample condition upon receipt (e.g., good, fine, OK).

3.3 The Contractor shall have written SOPs for maintaining identification of EPA samples throughout the laboratory. If the Contractor assigns unique laboratory identifiers, written SOPs shall include a description of the method used to assign the unique laboratory identifier and shall include a description of the document used to cross-reference the unique laboratory identifier to the EPA sample number. If the Contractor uses prefixes or suffixes in addition to sample identification numbers, the written SOPs shall include their definitions.

3.4 The Contractor shall have written SOPs describing all storage areas for samples in the laboratory. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.

3.5 The Contractor shall have written SOPs describing the method by which the laboratory maintains samples under custody.

3.6 The Contractor shall have written SOPs describing the method by which the laboratory maintains the security of any areas identified as secure.

3.7 The Contractor shall have written SOPs for tracking the work performed on any particular samples. The tracking SOP shall include:

- A description of the documents used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.
- A description of the documents used to record calibration and QA/QC laboratory work.
- Examples of document formats and laboratory documents used in the sample receipt, sample storage, sample transfer, and sample analyses.
- A narrative step-wise description of how documents are used to track samples.

3.8 The Contractor shall have written SOPs for organization and assembly of all documents relating to each SDG. Documents shall be filed on a SDG-specific basis. The procedures shall ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the SDG are compiled in one location for submission to EPA. The written SOPs shall include:

- A description of the numbering and inventory method.

- o A description of the method used by the laboratory to verify consistency and completeness of the CSF.
- o Procedures for the shipment of deliverables packages using custody seals.

4. Handling of Confidential Information

A Contractor conducting work under this contract may receive confidential information from EPA. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

4.1 All confidential documents shall be under the supervision of a designated DCO.

4.2 Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other nonconfidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO will log these documents into a Confidential Inventory Log. The information will then be available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the Technical Project Officer and Administrative Project Officer. The DCO will enter all copies into the document control system described above. In addition, this information may not be disposed of except upon approval by the Technical Project Officer and Administrative Project Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record on the disposition in the Confidential Inventory Log.

EXHIBIT G

GLOSSARY

EXHIBIT G

GLOSSARY

ALIQUOT - a measured portion of a sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time of the injection of the sample, standard or blank into the GC/MS or GC system.

BLANK - see Method Blank.

CASE - a finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office. A Case consists of one or more Sample Delivery Groups.

CONCENTRATION CALIBRATION SOLUTION (Table 3) - solutions (tridecane) containing known amounts of selected analytes, five internal standards and two recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CONTINUING CALIBRATION SOLUTION - a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time windows for each homologue. The same solution is used for the mid-level concentration calibration solution, CC3.

DAY - unless otherwise specified, day shall refer to calendar day.

ESTIMATED DETECTION LIMIT (EDL) - the concentration of a analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC) - the concentration of a given analyte that would produce a signal with a given peak area. The EMPC is calculated for 2,3,7,8-substituted isomers for which the quantitation and/or the confirmation ion(s) has signal-to-noise in excess of 2.5 but does not meet identification criteria.

FIELD BLANK - a portion of chemical waste, soil or water that is not contaminated with PCDDs/PCDFs and is submitted with the samples. The field blank is used to check for contamination from the time of sample collection through the time of sample analysis.

HOMOLOGUE - a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HOMOLOGOUS SERIES - a series of organic compounds in which each successive member has one more atom or group of atoms than the preceding member. The straight chain hydrocarbons and the polychlorinated dibenzo-*p*-dioxins are examples of a homologous series.

IN-HOUSE - at the Contractor's facility.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations. The initial calibration used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS (Tables 2 and 4) - $^{13}C_{12}$-2378-TCDD, $^{13}C_{12}$-123678-HxCDD, $^{13}C_{12}$-OCDD, $^{13}C_{12}$-2378-TCDF and $^{13}C_{12}$-1234678-HpCDF (in isooctane) are added to every sample and are present at the same concentration in every blank, quality control sample, and concentration calibration solution. The internal standards are added to the sample before extraction and are used to measure the concentrations of the analytes.

ISOMER - chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1234-TCDD and 2378-TCDD are structural isomers.

LABORATORY - synonymous with the term Contractor.

LOW RESOLUTION MASS SPECTROMETRY - a mass spectrometric technique capable of achieving unit mass (i.e., 1 amu) resolution between compounds introduced into the instrument.

MATRIX - the predominant material that comprises the sample to be analyzed. For the purpose of this contract, a sample matrix may be water, soil or chemical waste (including stillbottoms, fuel oil, sludge and fly ash). Matrix is not synonymous with phase (liquid or solid).

METHOD BLANK (previously termed reagent blank) - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background contamination.

NARRATIVE (SDG Narrative) - the portion of the data package which includes laboratory, contract, Case and sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete SDG Narrative specifications are included in Exhibit B.

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at 105°C, including water. Percent moisture is determined from decanted samples and from samples that are not decanted.

PERFORMANCE EVALUATION (PE) SAMPLE - a chemical waste, soil or water sample containing known amounts of unlabeled PCDDs/PCDFs.

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) - compounds (Figure 2) that contain from one to eight chlorine atoms. The 15 2,3,7,8-substituted PCDDs (total PCDDs is 75) and PCDFs (total PCDFs is 135) are shown in Table 13. The number of isomers at different chlorination levels is shown in Table 12.

PROTOCOL - describes the exact procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Synonymous with Statement of Work (SOW).

REAGENT WATER - water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.

RECOVERY - a determination of the accuracy of the analytical procedure made by comparing measured values for a fortified (spiked) sample against the known spike values. Recovery is determined by the following equation:

$$\%\text{Recovery} = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

RECOVERY STANDARD (Table 9) - $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD are added to every blank, quality control sample, and sample extract aliquot just prior to analysis and are present in all solutions except the internal standards solutions. Recovery standards are used to measure the recovery of the internal standards. When a dilution is required (see Exhibit D, Paragraph 13.2.5), recovery standards are used to quantitate the native PCDDs/PCDFs; the TCDD recovery standard is used to quantitate the tetra- and penta- isomers and the HxCDD recovery standard is used to quantitate the hexa- through octa- isomers.

RELATIVE RESPONSE FACTOR (RRF) - the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of an internal standard as measured in the initial and continuing calibrations. The RRF is used to determine instrument performance and is used in the quantitation calculations.

RESOLUTION (also termed separation) - the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multipled by 100.

RINSATE - a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - a unit within a single Case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a Case, received over a period of up to 14 calendar days. Data from all samples in a SDG are due concurrently. A SDG is defined by one of the following, whichever occurs first:

- o Case; or
- o Each 20 samples within a Case; or
- o Each 14-day calendar period during which samples in a Case are received, beginning with receipt of the first sample in the Case or SDG.

Samples may be assigned to SDGs by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory.

SAMPLE NUMBER (EPA Sample Number) - a unique identification number designated by EPA for each sample. The EPA sample number appears on the sample Traffic Report which documents information on that sample.

SELECTED ION MONITORING - a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SIGNAL-TO-NOISE (S/N) RATIO - the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to PCDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgement of the analyst.

SOIL - synonymous with soil/sediment and sediment.

STANDARD ANALYSIS - an analytical determination made with known quantities of target compounds. The standard analysis is used to determine response factors.

SURROGATES (Surrogate Standard) - the compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard. Surrogates are used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labelled compounds not expected to be detected in environmental media.

TIME - when recording time on any deliverable item, time shall be expressed as military time, (i.e., a 24-hour clock).

TOXICITY EQUIVALENCY FACTOR (TEF) - a method of converting concentrations of PCDDs/PCDFs to an equivalent concentration of 2378-TCDD to obtain an estimation of the toxicity of the entire sample. (Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs), March 1989, (EPA 625/3-89/016).

TRAFFIC REPORT (TR) - an EPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory.

TWELVE-HOUR TIME PERIOD - the 12-hour time period begins with the injection of the CC3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12-hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be injected within 12:00 hours of the CC3 solution or the column performance solution.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report.

APPENDIX C

CONTROL CHART EXAMPLES

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METHOD	ANALYSIS	LOT	INSTALLATION	PRIME CONTRACTOR	ANALYSIS DATE
SB07	HG	JDD	TC	CR	04/25/95
		JDE	WB	EY	05/04/95

OBSERVATION

The control chart submittal date is May 16, 1995.

A spiking error was made in lot JDE. The low control sample was spike with 3-ug/L instead of 2-ug/L. The analyst was notified and the error was documented.

TREND ANALYSIS

All control charts are trend free.

OUT-OF-CONTROL ANALYSIS

The following analyte contained a point outside the LCL in the three-day x-bar:

ANALYTE	LOT	RECOVERY	LCL
HG	JDE	91.3	93.1

The following analyte contained a point outside the UCL in the three-day x-bar range charts:

ANALYTE	LOT	RECOVERY	UCL
HG	JDD	20.0	15.7

SUMMARY RECOMMENDATION

For lots JDD and JDE, all calibration standards met the QC requirements of the program. The out of control situations should have negligible affect on the quality of the data. Lots JDD and JDE should be accepted.

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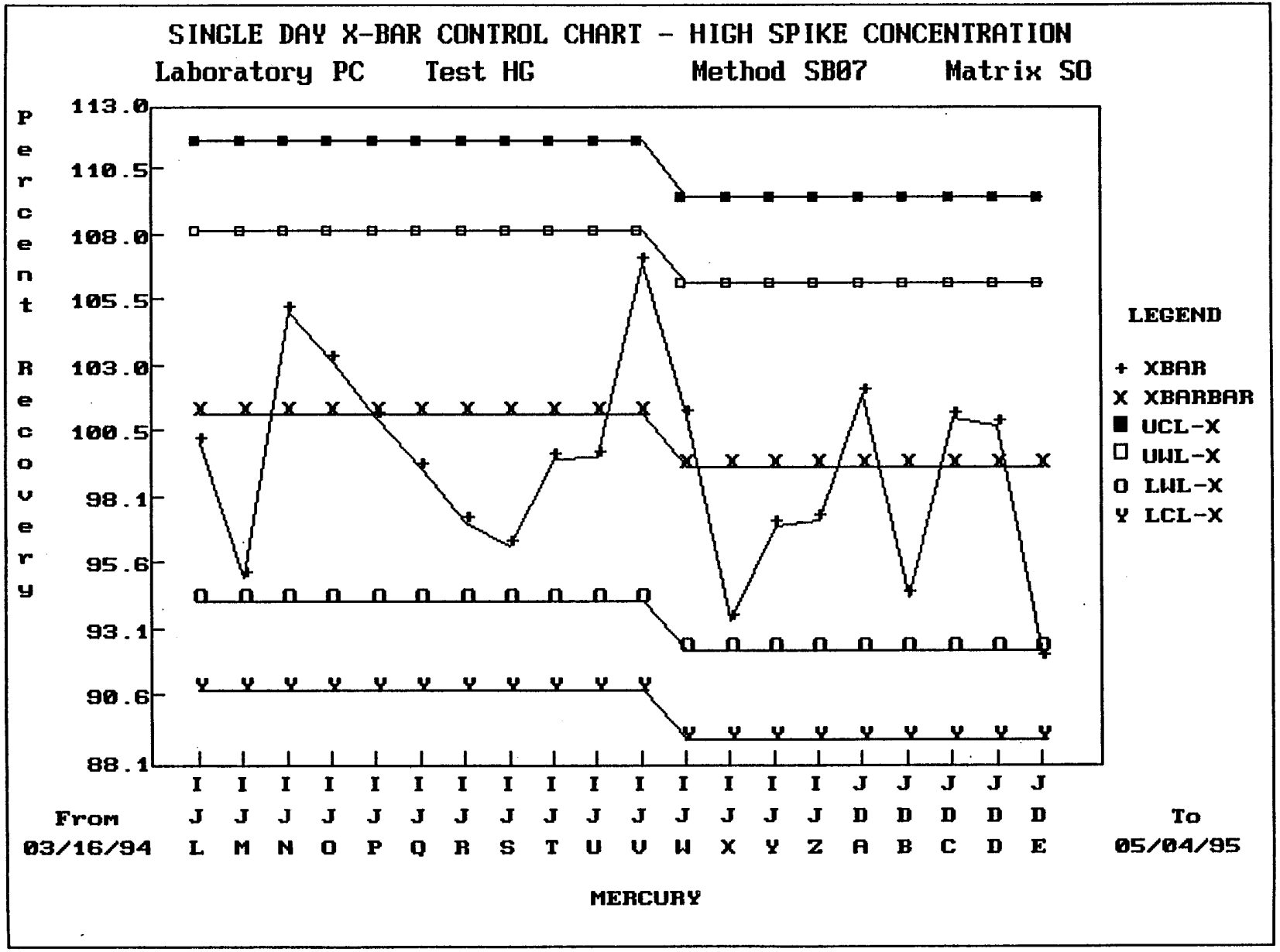
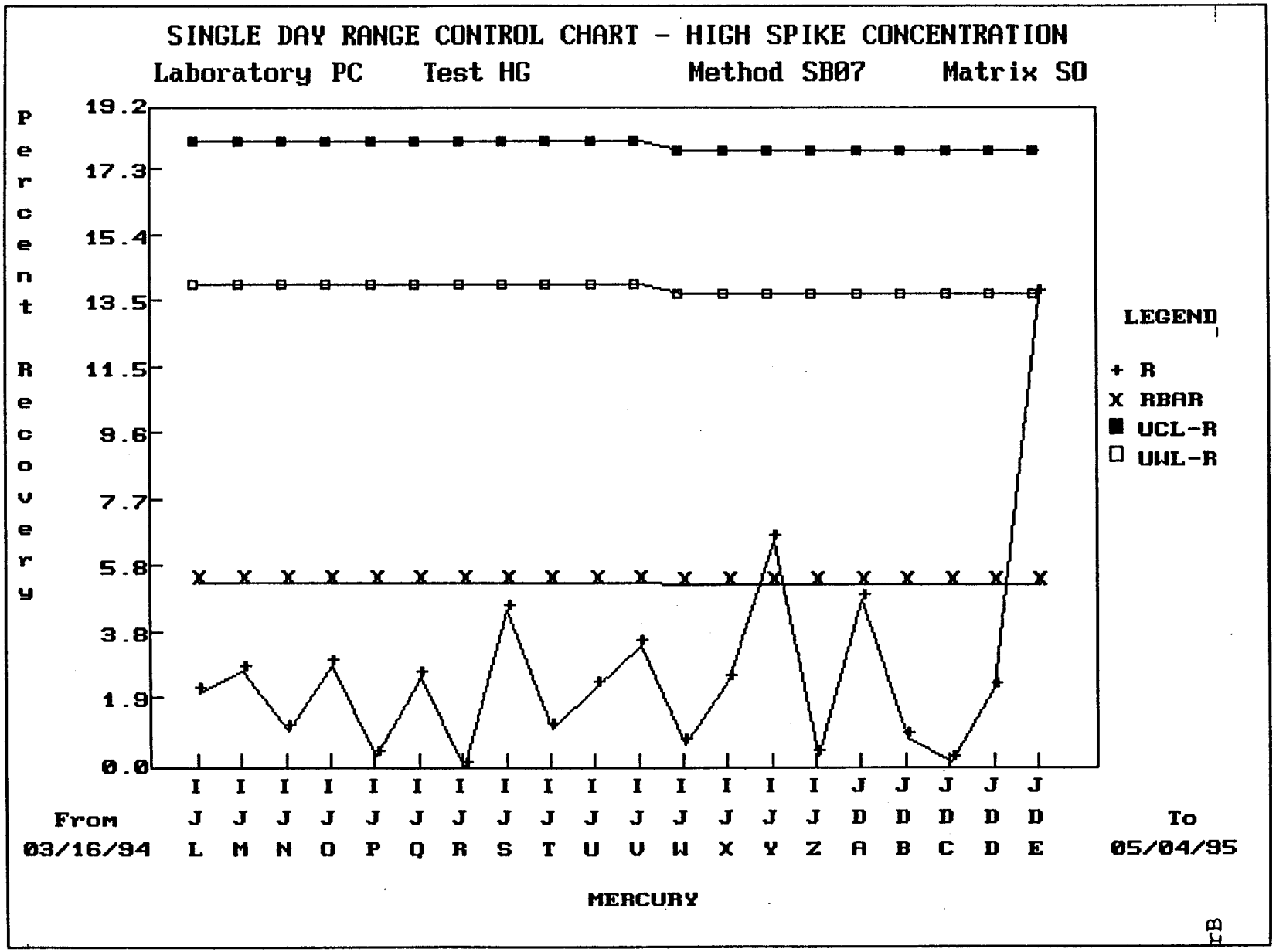

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test HG Method SB07 Matrix SO
Percent Recovery
113.0
110.5
108.0
105.5
103.0
100.5
98.1
95.6
93.1
90.6
88.1
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
03/16/94
To
05/04/95
MERCURY

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR MERCURY

Laboratory: PC	Date: 05/16/95
Method: SB07	Matrix: SO	Test Name: HG

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
012395	JDA	7.00	0	6.98	0	7.33	0	99.7	104.7	102.2	109.8	106.4	92.6	89.2	.F.
022295	JDB	7.00	0	6.66	0	6.59	0	95.1	94.1	94.6	109.8	106.4	92.6	89.2	.F.
031795	JDC	7.00	0	7.08	0	7.09	0	101.1	101.3	101.2	109.8	106.4	92.6	89.2	.F.
042595	JDD	7.00	0	6.98	0	7.14	0	99.7	102.0	100.9	109.8	106.4	92.6	89.2	.F.
050495	JDE	7.00	0	6.93	0	5.97	0	99.0	85.3	92.2	109.8	106.4	92.6	89.2	.F.

* Changes made to data


SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test HG Method SB07 Matrix SO
Percent Recovery
19.2
17.3
15.4
13.5
11.5
9.6
7.7
5.8
3.8
1.9
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
03/16/94
To
05/04/95
I J L
I J M
I J N
I J O
I J P
I J Q
I J R
I J S
I J T
I J U
I J V
I J W
I J X
I J Y
I J Z
J D A
J D B
J D C
J D D
J D E
MERCURY
HB

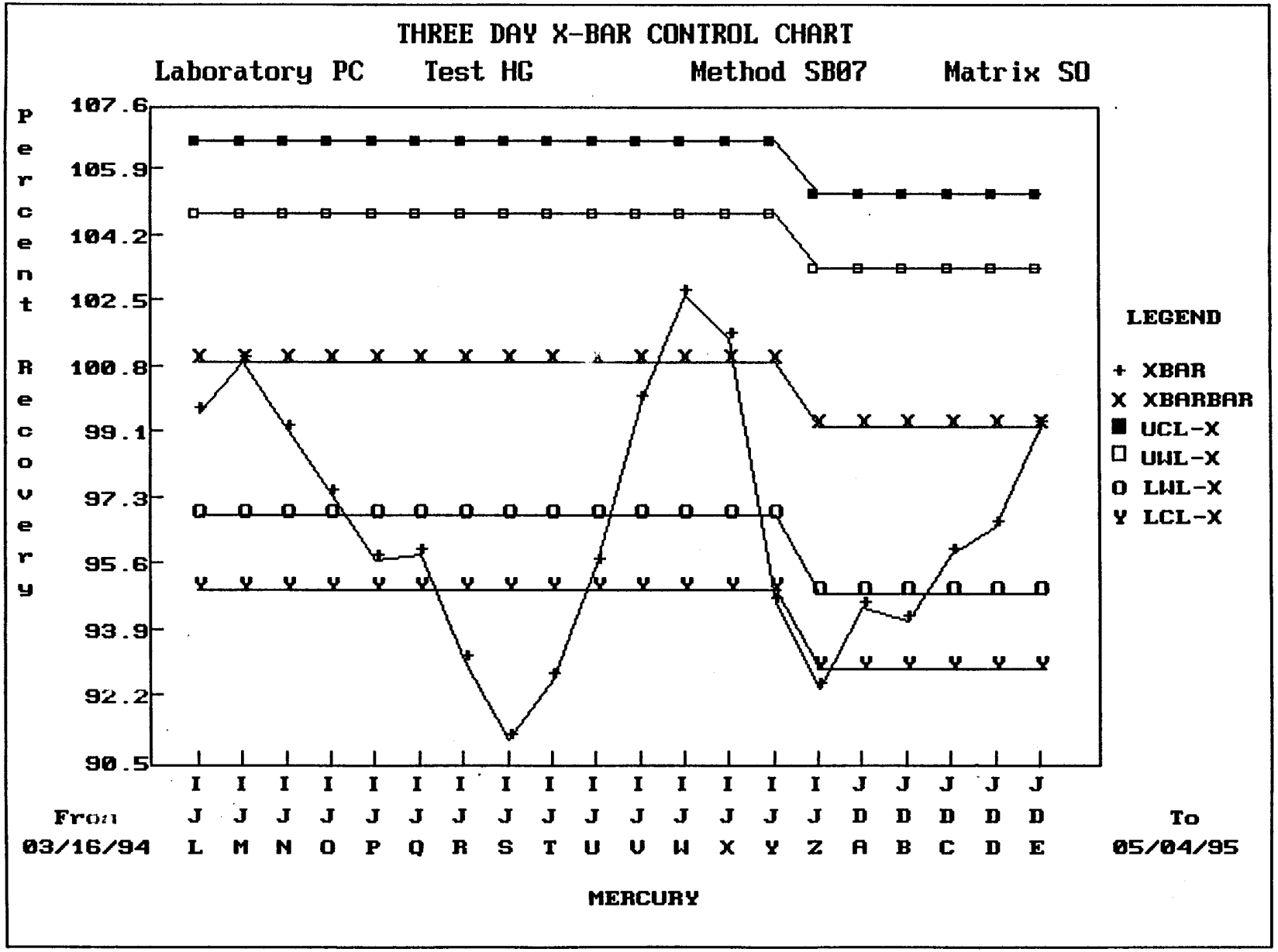
SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR MERCURY

Laboratory: PC	Date: 05/16/95

Method: SB07	Matrix: SO	Test Name: HG

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
012395	JDA	7.00	0	6.98	0	7.33	0	99.7	104.7	5.0	18.0	13.8
022295	JDB	7.00	0	6.66	0	6.59	0	95.1	94.1	1.0	18.0	13.8
031795	JDC	7.00	0	7.08	0	7.09	0	101.1	101.3	0.2	18.0	13.8
042595	JDD	7.00	0	6.98	0	7.14	0	99.7	102.0	2.3	18.0	13.8
050495	JDE	7.00	0	6.93	0	5.97	0	99.0	85.3	13.7	18.0	13.8

* Changes made to data

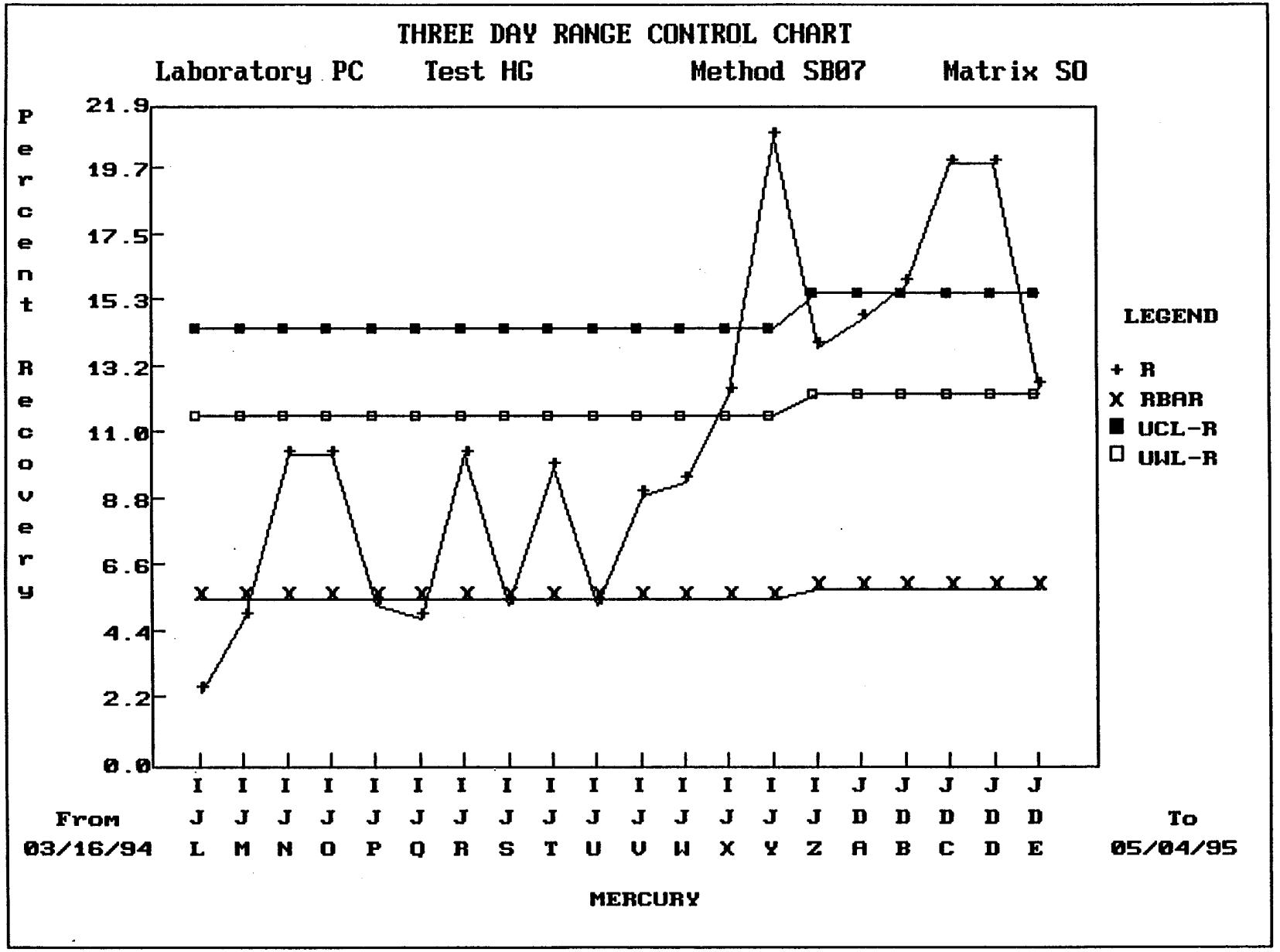

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test HG Method SB07 Matrix SO
Percent Recovery
107.6
105.9
104.2
102.5
100.8
99.1
97.3
95.6
93.9
92.2
90.5
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
O LWL-X
Y LCL-X
From
03/16/94
To
05/04/95
MERCURY

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR MERCURY

Laboratory: PC	Date: 05/16/95
Method: SB07	Matrix: SO	Test Name: HG

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
012395	JDA	2.00	0	2.00	0	100.0	94.7	105.5	103.5	95.1	93.1	.F.
022295	JDB	2.00	0	1.68	0	84.0	94.3	105.5	103.5	95.1	93.1	.F.
031795	JDC	2.00	0	2.08	0	104.0	96.0	105.5	103.5	95.1	93.1	.F.
042595	JDD	2.00	0	2.05	0	102.5	96.8	105.5	103.5	95.1	93.1	.F.
050495	JDE	3.00	0	2.74	0	91.3	99.3	105.5	103.5	95.1	93.1	.F.

* Changes made to data


THREE DAY RANGE CONTROL CHART
Laboratory PC
Test HG
Method SB07
Matrix SO
Percent Recovery
21.9
19.7
17.5
15.3
13.2
11.0
8.8
6.6
4.4
2.2
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
03/16/94
To
05/04/95
I I I I I I I I I I I I I I I J J J J J
J J J J J J J J J J J J J J J D D D D D
L M N O P Q R S T U V W X Y Z A B C D E
MERCURY

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR MERCURY

Laboratory: PC	Date: 05/16/95
Method: SB07	Matrix: SO	Test Name: HG

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
012395	JDA	2.00	0	2.00	0	100.0	15.0	15.7	12.5
022295	JDB	2.00	0	1.68	0	84.0	16.0	15.7	12.5
031795	JDC	2.00	0	2.08	0	104.0	20.0	15.7	12.5
042595	JDD	2.00	0	2.05	0	102.5	20.0	15.7	12.5
050495	JDE	3.00	0	2.74	0	91.3	12.7	15.7	12.5

* Changes made to data

METHOD	ANALYSIS	LOT	INSTALLATION	PRIME CONTRACTOR	ANALYSIS DATE
TY03	CYN	IML	WB	EY	04/28/95

OBSERVATION

The control chart submittal date is May 9, 1995.

TREND ANALYSIS

All control charts are trend free.

OUT-OF-CONTROL ANALYSIS

The following analyte contained a point outside the LCL in the three-day x-bar charts:

ANALYTE	LOT	RECOVERY	LCL
CYN	IML	90.0	91.6

SUMMARY RECOMMENDATION

For lot IML, all calibration standards met the QC requirements of the program. The out of control situations should have negligible affect on the quality of the data. Lot IML should be accepted.

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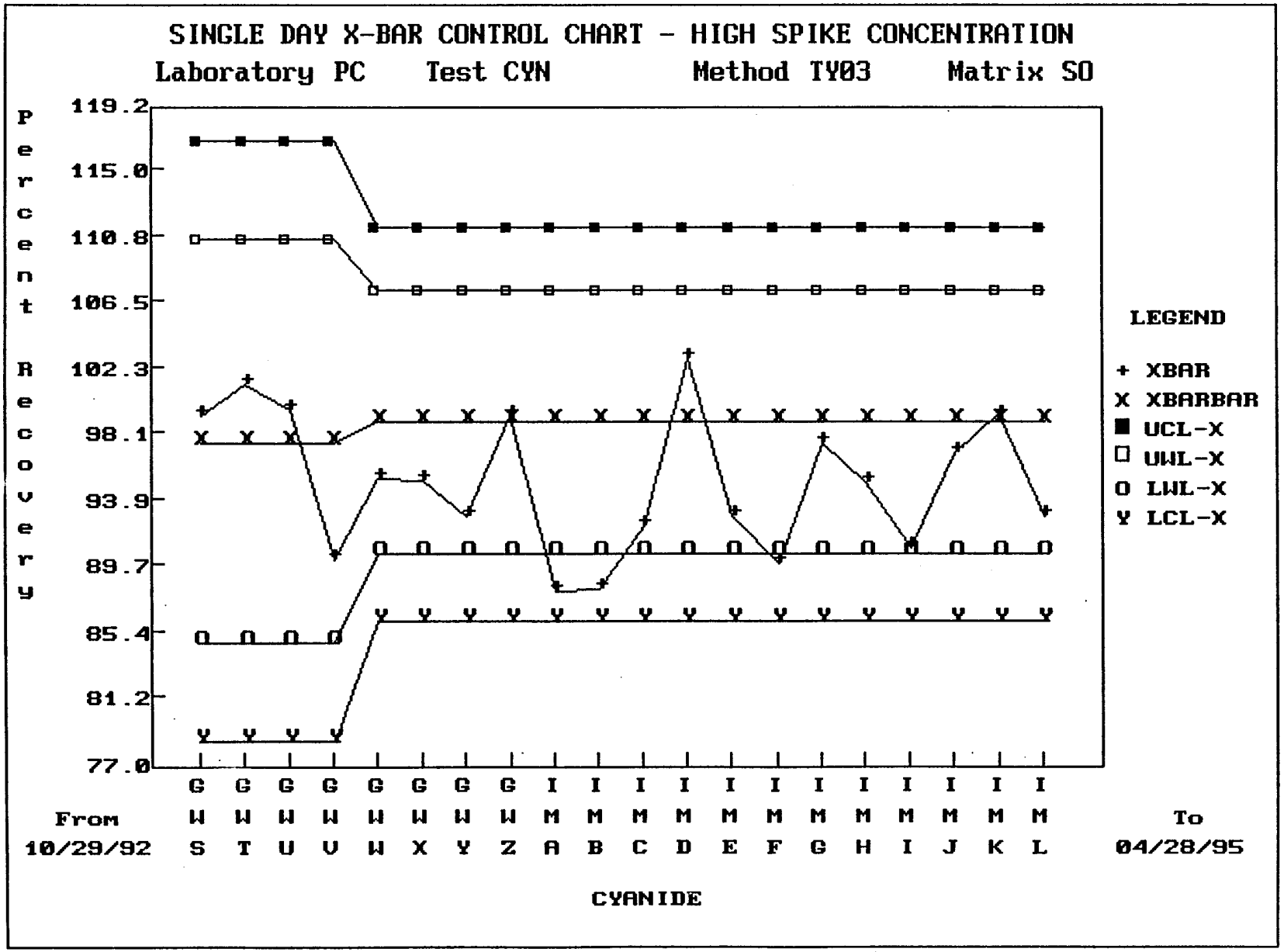
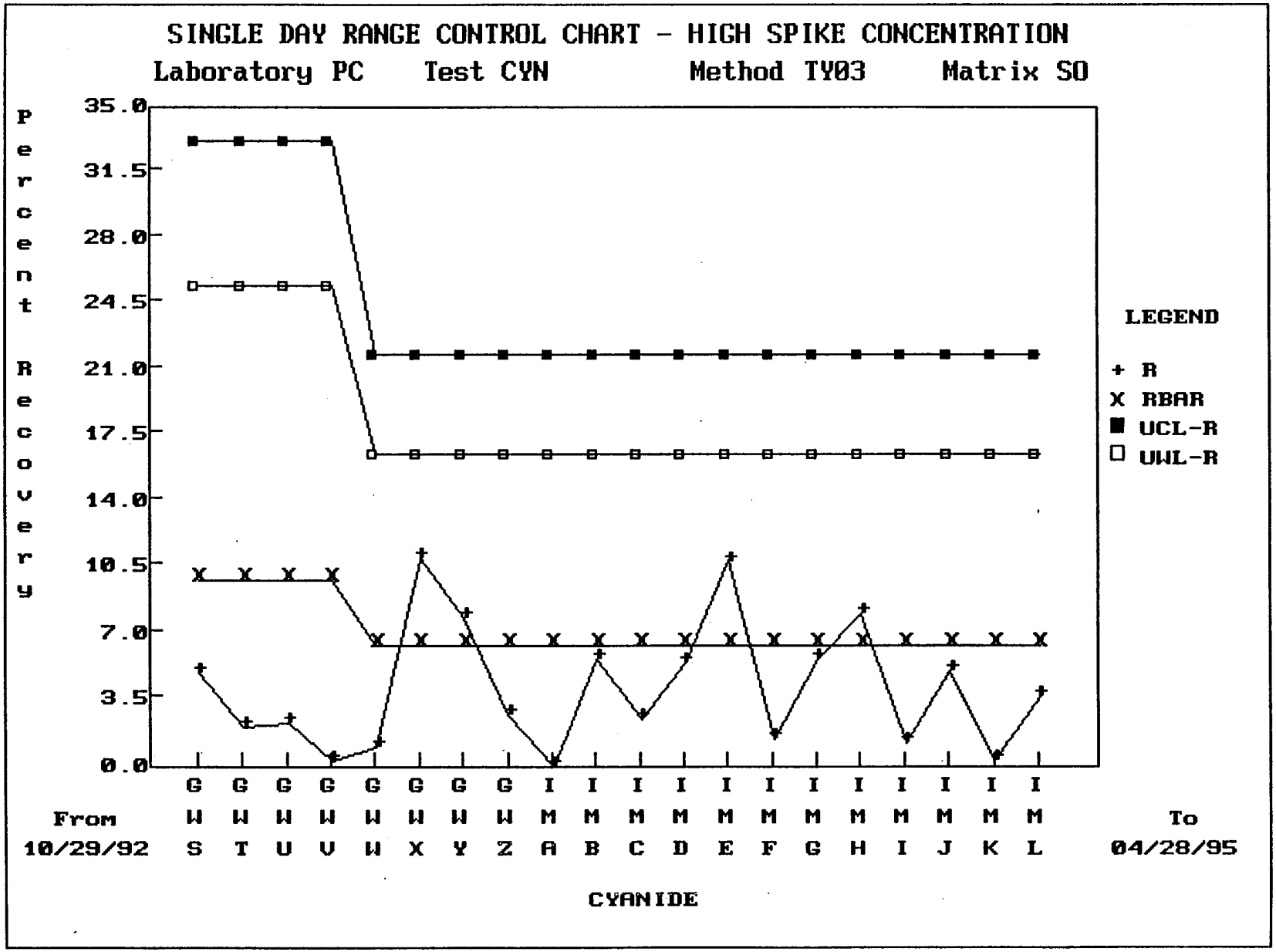

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test CYN Method TY03 Matrix SO
Percent Recovery
119.2
115.0
110.8
106.5
102.3
98.1
93.9
89.7
85.4
81.2
77.0
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/29/92
To
04/28/95
CYANIDE

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR CYANIDE

Laboratory: PC	Date: 05/03/95
Method: TY03	Matrix: SO	Test Name: CYN

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
082394	IMI	5.00	1	4.52	1	4.59	1	90.4	91.8	91.1	111.7	107.5	90.7	86.5	.F.
091694	IMJ	5.00	1	4.74	1	5.00	1	94.8	100.0	97.4	111.7	107.5	90.7	86.5	.F.
031495	IMK	5.00	1	4.99	1	4.97	1	99.8	99.4	99.6	111.7	107.5	90.7	86.5	.F.
042895	IML	5.00	1	4.76	1	4.58	1	95.2	91.6	93.4	111.7	107.5	90.7	86.5	.F.

* Changes made to data

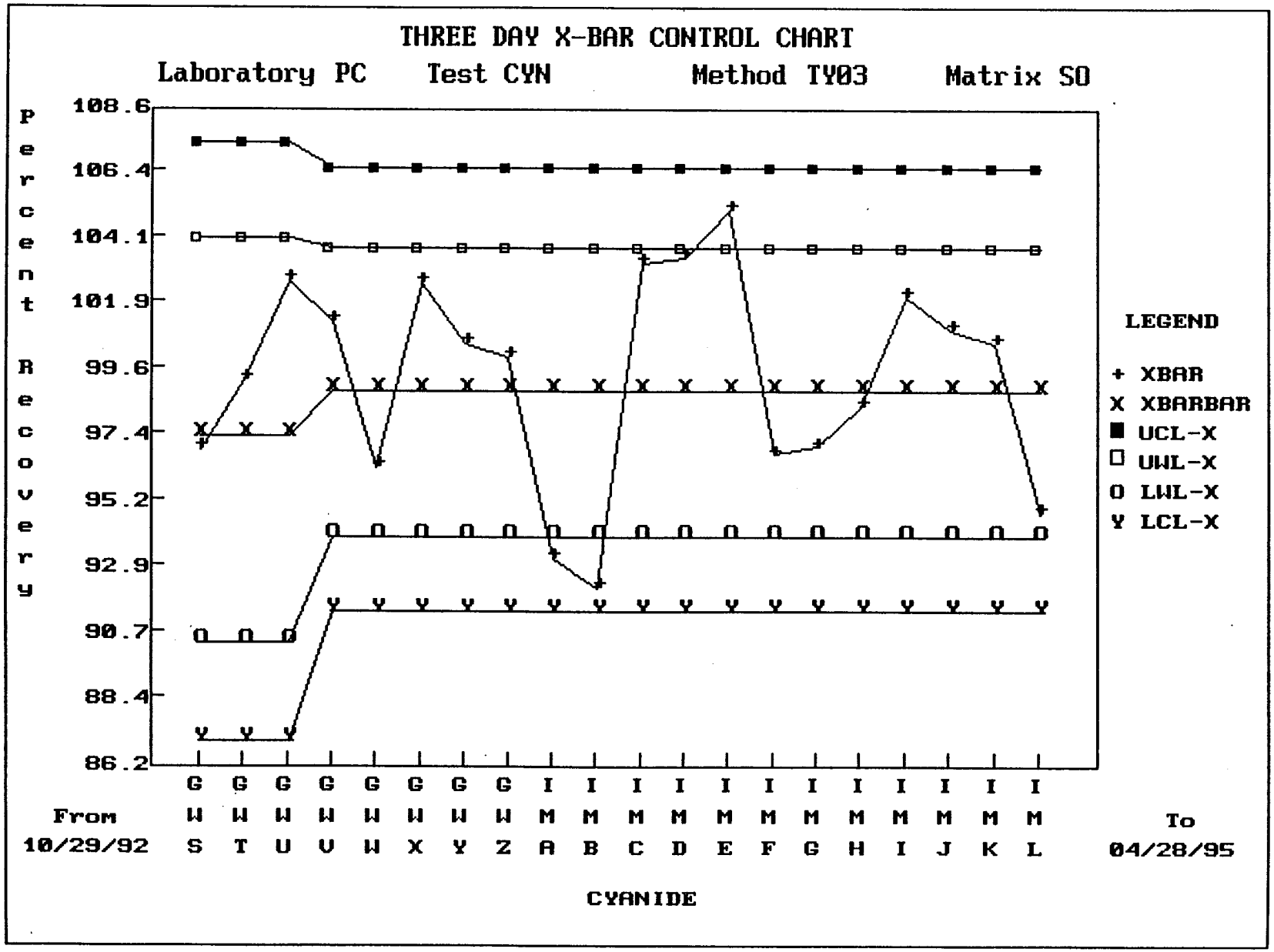

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test CYN Method TY03 Matrix SO
Percent Recovery
35.0
31.5
28.0
24.5
21.0
17.5
14.0
10.5
7.0
3.5
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/29/92
To
04/28/95
CYANIDE

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR CYANIDE

Laboratory: PC	Date: 05/03/95
Method: TY03	Matrix: SO | Test Name: CYN

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
082394	IMI	5.00	1	4.52	1	4.59	1	90.4	91.8	1.4	21.9	16.8
091694	IMJ	5.00	1	4.74	1	5.00	1	94.8	100.0	5.2	21.9	16.8
031495	IMK	5.00	1	4.99	1	4.97	1	99.8	99.4	0.4	21.9	16.8
042895	IML	5.00	1	4.76	1	4.58	1	95.2	91.6	3.6	21.9	16.8

* Changes made to data

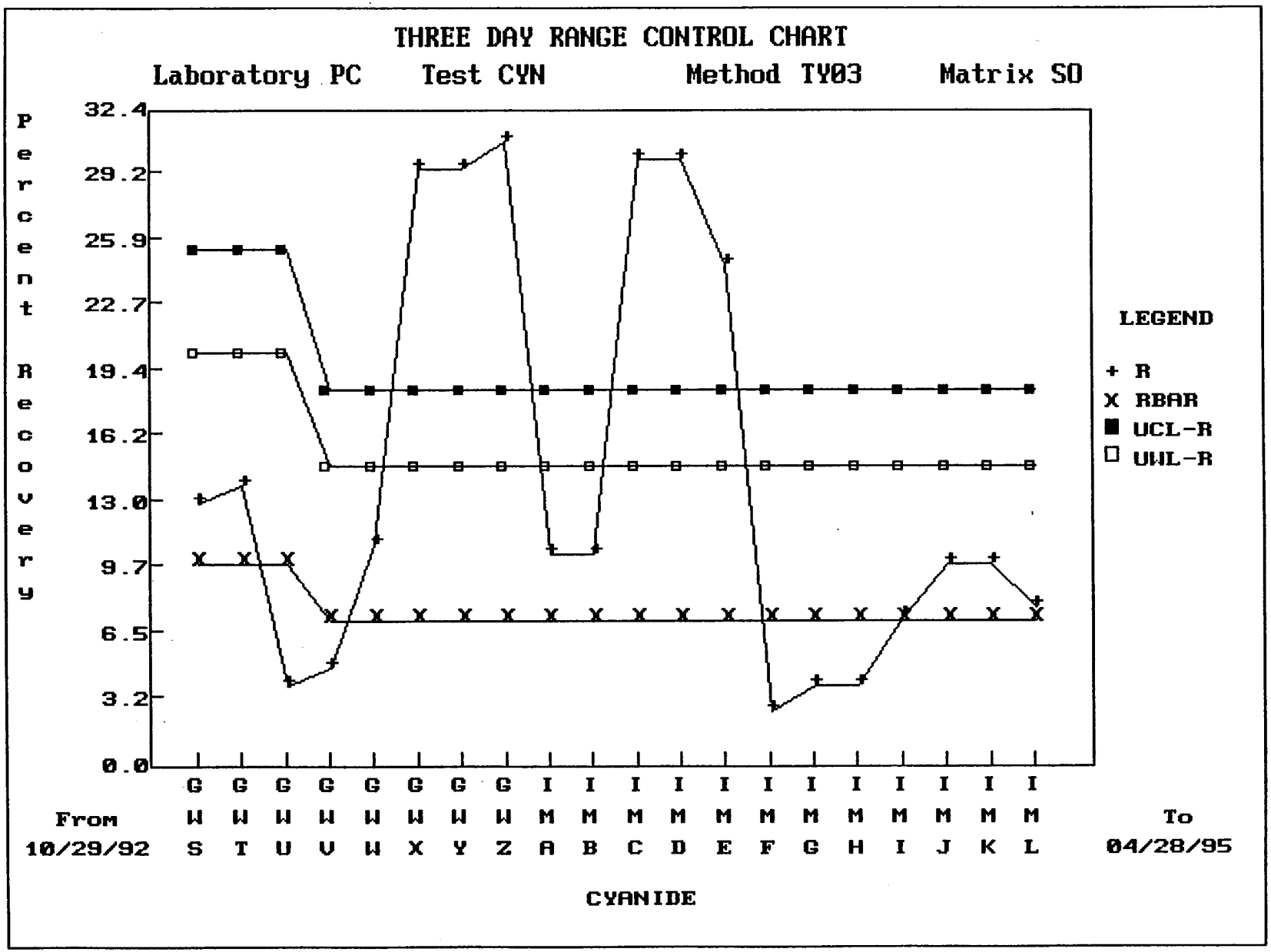

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test CYN Method TY03 Matrix SO
Percent Recovery
108.6
106.4
104.1
101.9
99.6
97.4
95.2
92.9
90.7
88.4
86.2
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From 10/29/92
To 04/28/95
CYANIDE

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR CYANIDE

Laboratory: PC	Date: 05/03/95
Method: TY03	Matrix: SO	Test Name: CYN

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
082394	IMI	2.00	1	2.14	1	107.0	102.2	106.6	104.1	94.1	91.6	.F.
091694	IMJ	2.00	1	1.94	1	97.0	101.2	106.6	104.1	94.1	91.6	.F.
031495	IMK	2.00	1	1.96	1	98.0	100.7	106.6	104.1	94.1	91.6	.F.
042895	IML	2.00	1	1.80	1	90.0	95.0	106.6	104.1	94.1	91.6	.F.

* Changes made to data


THREE DAY RANGE CONTROL CHART
Laboratory PC Test CYN Method TY03 Matrix SO
Percent Recovery
32.4
29.2
25.9
22.7
19.4
16.2
13.0
9.7
6.5
3.2
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/29/92
To 04/28/95
GWS GWT GWU GWV GWW GWX GWY GWZ IMA IMB IMC IMD IME IMF IMG IMH IMI IMJ IMK IML
CYANIDE

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR CYANIDE

Laboratory: PC	Date: 05/03/95

Method: TY03	Matrix: SO	Test Name: CYN

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
082394	IMI	2.00	1	2.14	1	107.0	7.5	18.8	15.0
091694	IMJ	2.00	1	1.94	1	97.0	10.0	18.8	15.0
031495	IMK	2.00	1	1.96	1	98.0	10.0	18.8	15.0
042895	IML	2.00	1	1.80	1	90.0	8.0	18.8	15.0

* Changes made to data

METHOD	ANALYSIS	LOT	INSTALLATION	CONTRACTOR	DATE
UM05	GC/MS VOA	INN	TC	CR	04/19/95
		INO	WB	EY	04/26/95
		INP	WB	EY	04/27/95

OBSERVATION

The control chart submittal date is May 9, 1995.

TREND ANALYSIS

All control charts are trend free.

OUT-OF-CONTROL ANALYSIS

There are no out of control situations.

SUMMARY RECOMMENDATION

For lots INN, INO, and INP all calibration standards met the QC requirements of the program. Lots INN, INO, and INP should be accepted.

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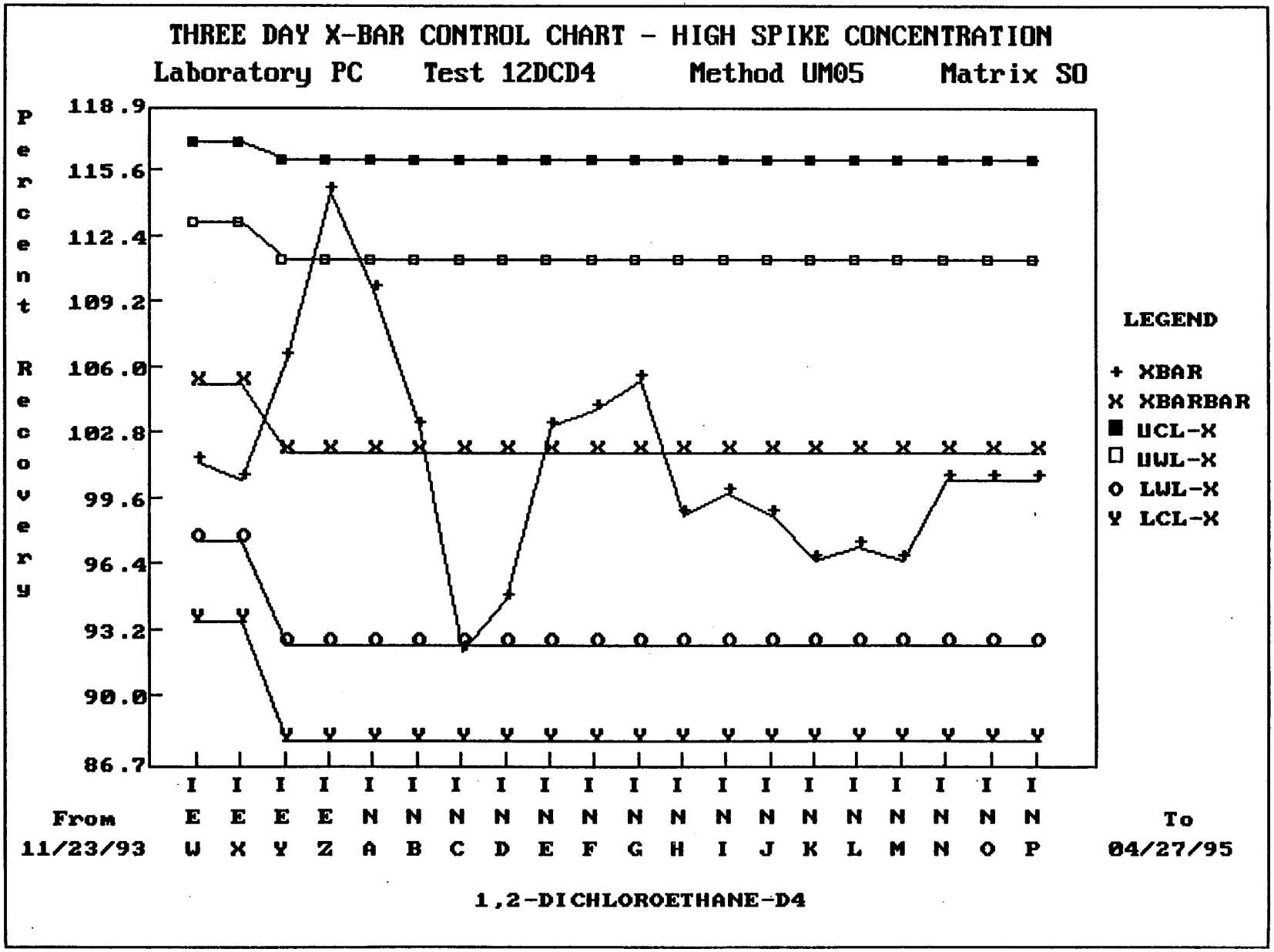

THREE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test 12DCD4 Method UM05 Matrix SO
Percent Recovery
118.9
115.6
112.4
109.2
106.0
102.8
99.6
96.4
93.2
90.0
86.7
From 11/23/93
To 04/27/95
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
1,2-DICHLOROETHANE-D4

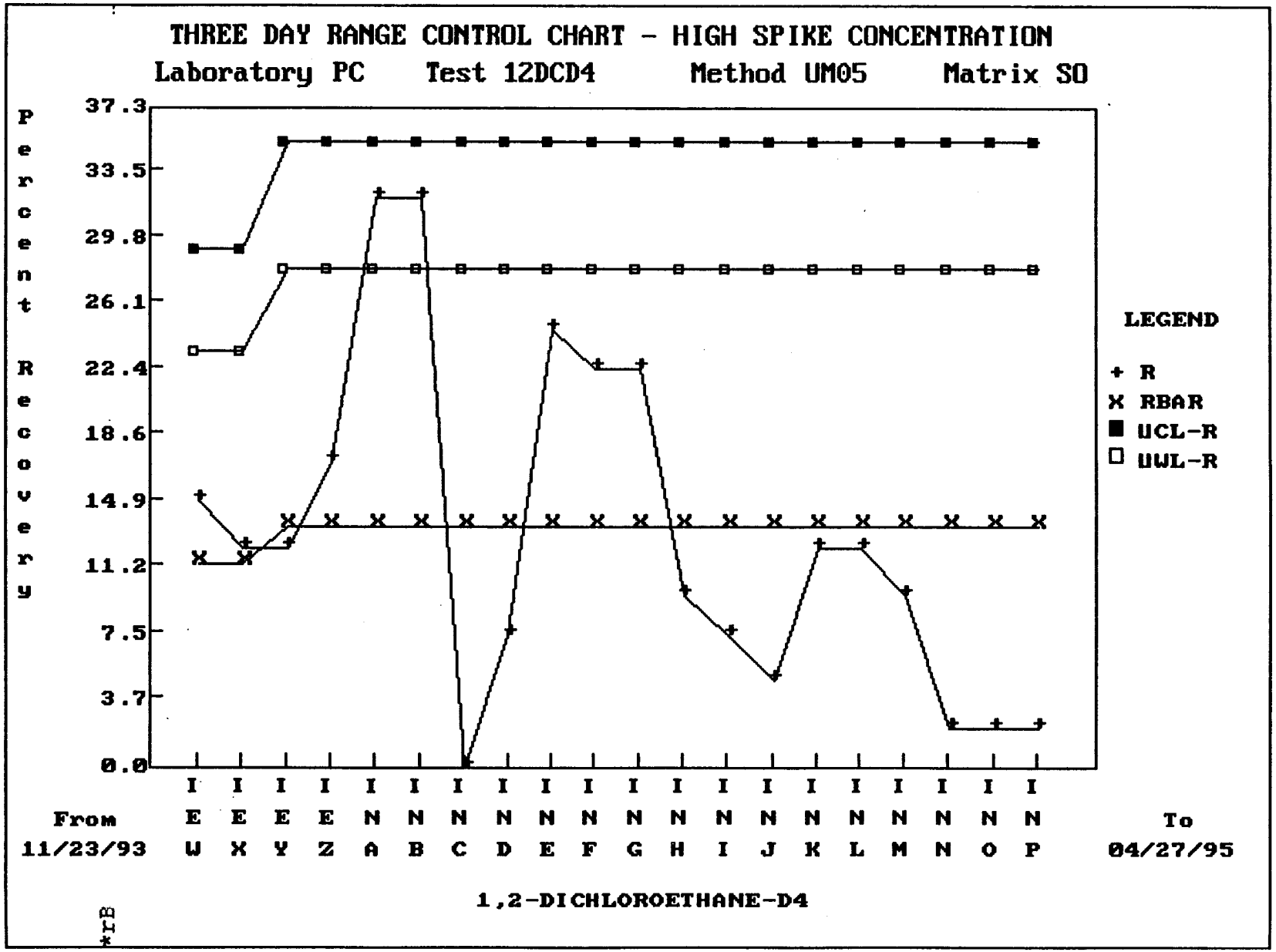
THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR 1,2-DICHLOROETHANE-D4

Laboratory: PC	Date: 04/28/95

Method: UM05	Matrix: SO	Test Name: 12DCD4

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
110494	INL	4.00	1	4.00	1	100.0	97.5	116.4	111.7	92.9	88.2	.F.
030895	INM	4.00	1	4.00	1	100.0	96.7	116.4	111.7	92.9	88.2	.F.
041995	INN	4.00	1	4.10	1	102.5	100.8	116.4	111.7	92.9	88.2	.F.
042695	INO	4.00	1	4.00	1	100.0	100.8	116.4	111.7	92.9	88.2	.F.
042795	INP	4.00	1	4.00	1	100.0	100.8	116.4	111.7	92.9	88.2	.F.

* Changes made to data

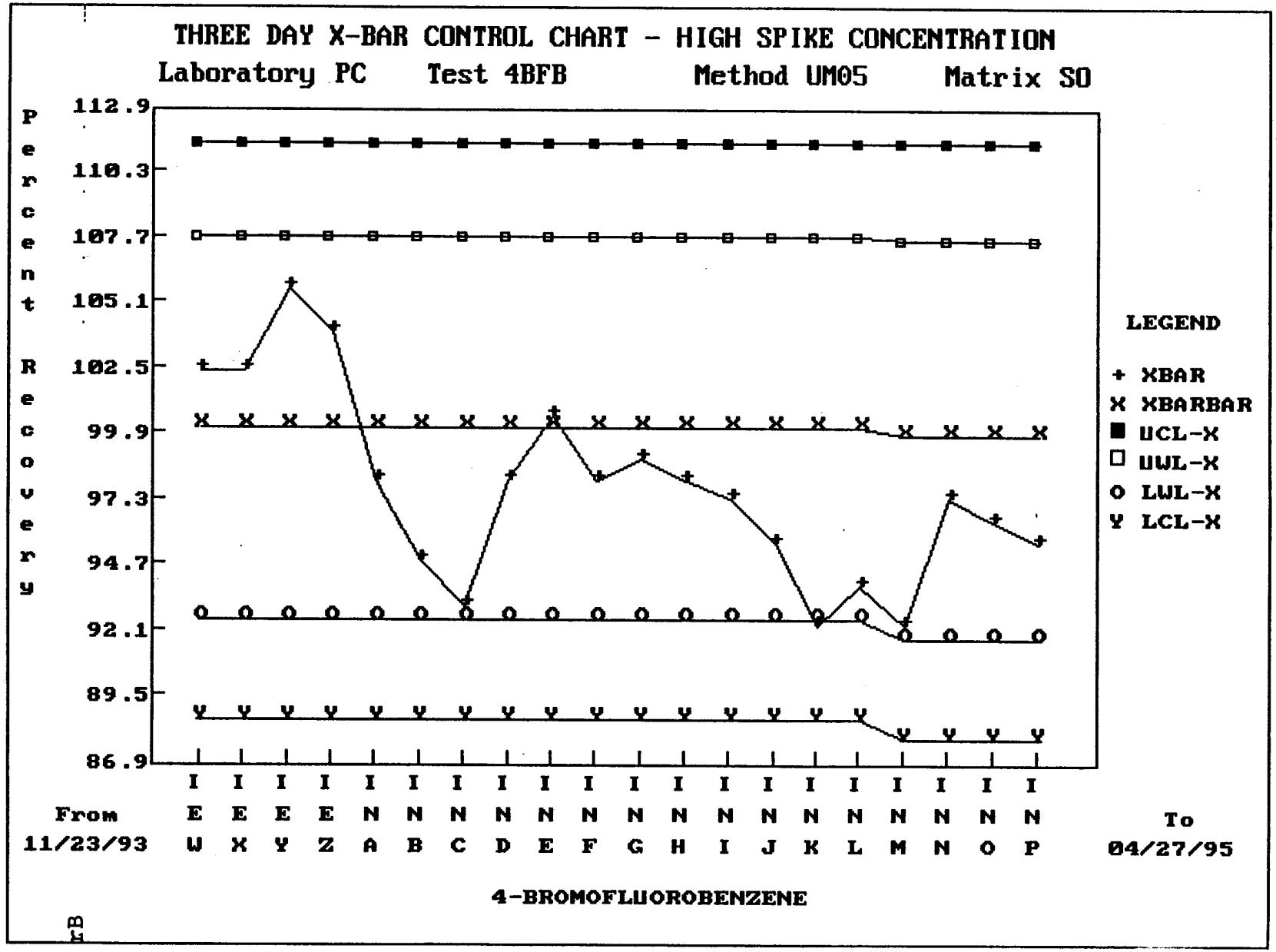

THREE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test 12DCD4 Method UM05 Matrix SO
Percent Recovery
37.3
33.5
29.8
26.1
22.4
18.6
14.9
11.2
7.5
3.7
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From 11/23/93
To 04/27/95
1,2-DICHLOROETHANE-D4

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR 1,2-DICHLOROETHANE-D4

Laboratory: PC	Date: 04/28/95
Method: UM05	Matrix: SO	Test Name: 12DCD4

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
110494	INL	4.00	1	4.00	1	100.0	12.5	35.5	28.3
030895	INM	4.00	1	4.00	1	100.0	10.0	35.5	28.3
041995	INN	4.00	1	4.10	1	102.5	2.5	35.5	28.3
042695	INO	4.00	1	4.00	1	100.0	2.5	35.5	28.3
042795	INP	4.00	1	4.00	1	100.0	2.5	35.5	28.3

* Changes made to data

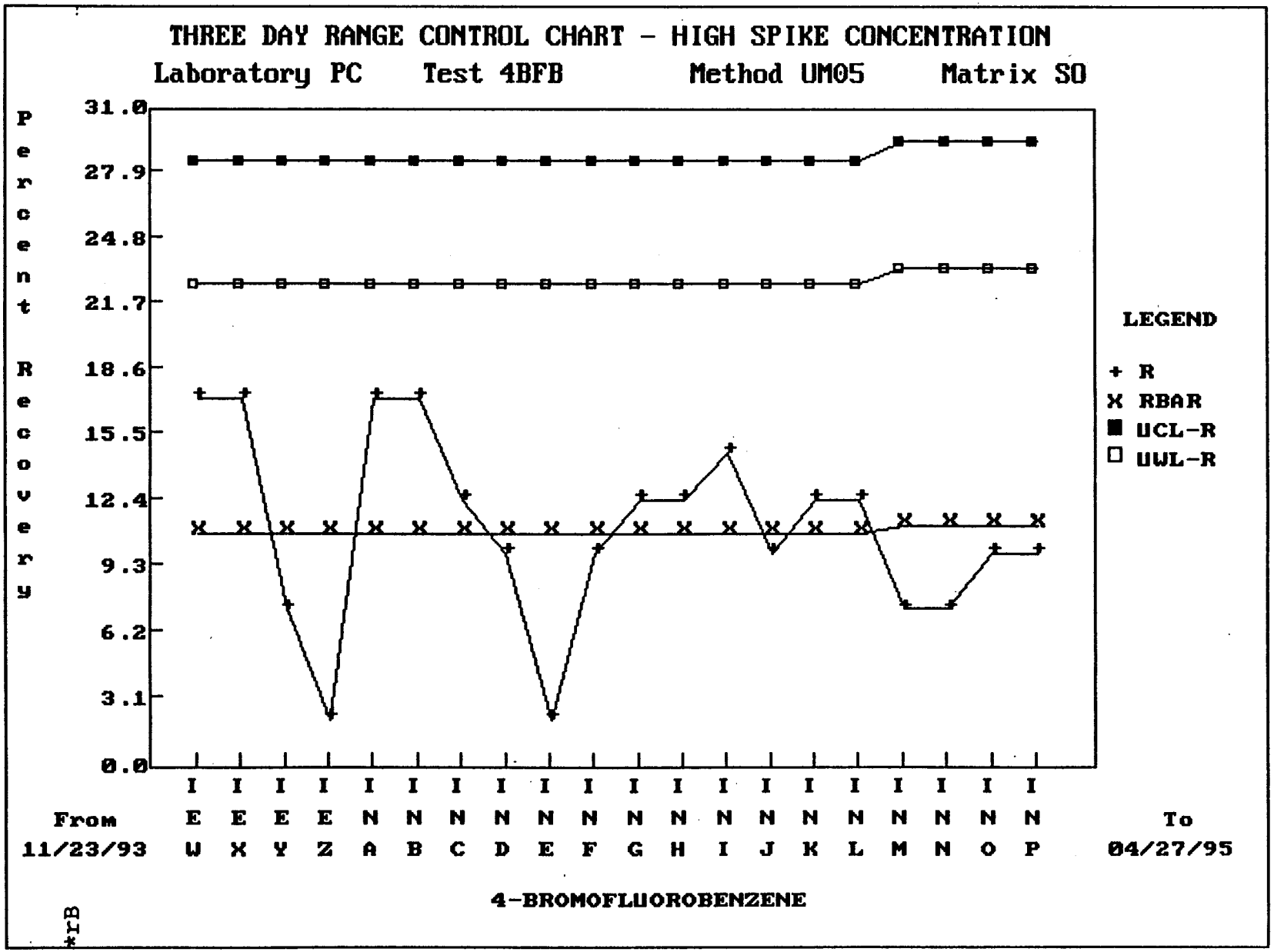

THREE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test 4BFB Method UM05 Matrix SO
Percent Recovery
112.9
110.3
107.7
105.1
102.5
99.9
97.3
94.7
92.1
89.5
86.9
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
O LWL-X
V LCL-X
From 11/23/93
To 04/27/95
IE IE IE IE IN IN IN IN IN IN IN IN IN IN IN IN IN IN IN IN
WXYZABCDEFGHIJKLMNOP
4-BROMOFLUOROBENZENE
LB

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR 4-BROMOFLUOROBENZENE

Laboratory: PC	Date: 04/28/95
Method: UM05	Matrix: SO	Test Name: 4BFB

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
110494	INL	4.00	1	3.80	1	95.0	94.2	111.7	107.9	92.7	88.9	.F.
030895	INM	4.00	1	3.80	1	95.0	92.5	111.7	107.7	92.1	88.1	.F.
041995	INN	4.00	1	4.10	1	102.5	97.5	111.7	107.7	92.1	88.1	.F.
042695	INO	4.00	1	3.70	1	92.5	96.7	111.7	107.7	92.1	88.1	.F.
042795	INP	4.00	1	3.70	1	92.5	95.8	111.7	107.7	92.1	88.1	.F.

* Changes made to data

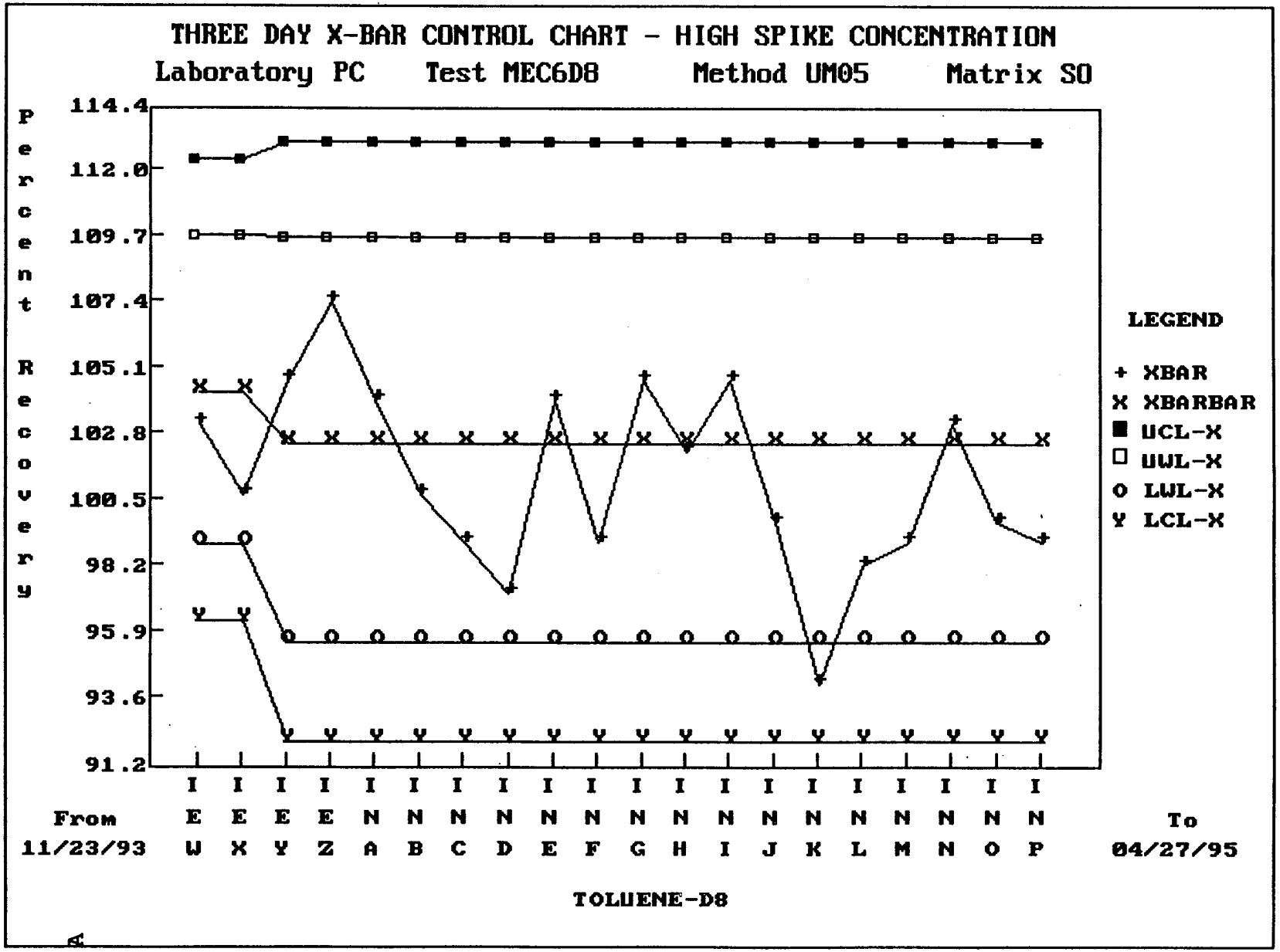

THREE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test 4BFB Method UM05 Matrix SO
Percent Recovery
31.0
27.9
24.8
21.7
18.6
15.5
12.4
9.3
6.2
3.1
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 11/23/93
To 04/27/95
4-BROMOFLUOROBENZENE
*rB

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR 4-BROMOFLUOROBENZENE

Laboratory: PC	Date: 04/28/95
Method: UM05	Matrix: SO	Test Name: 4BFB

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
110494	INL	4.00	1	3.80	1	95.0	12.5	28.6	22.8
030895	INM	4.00	1	3.80	1	95.0	7.5	29.6	23.6
041995	INN	4.00	1	4.10	1	102.5	7.5	29.6	23.6
042695	INO	4.00	1	3.70	1	92.5	10.0	29.6	23.6
042795	INP	4.00	1	3.70	1	92.5	10.0	29.6	23.6

* Changes made to data

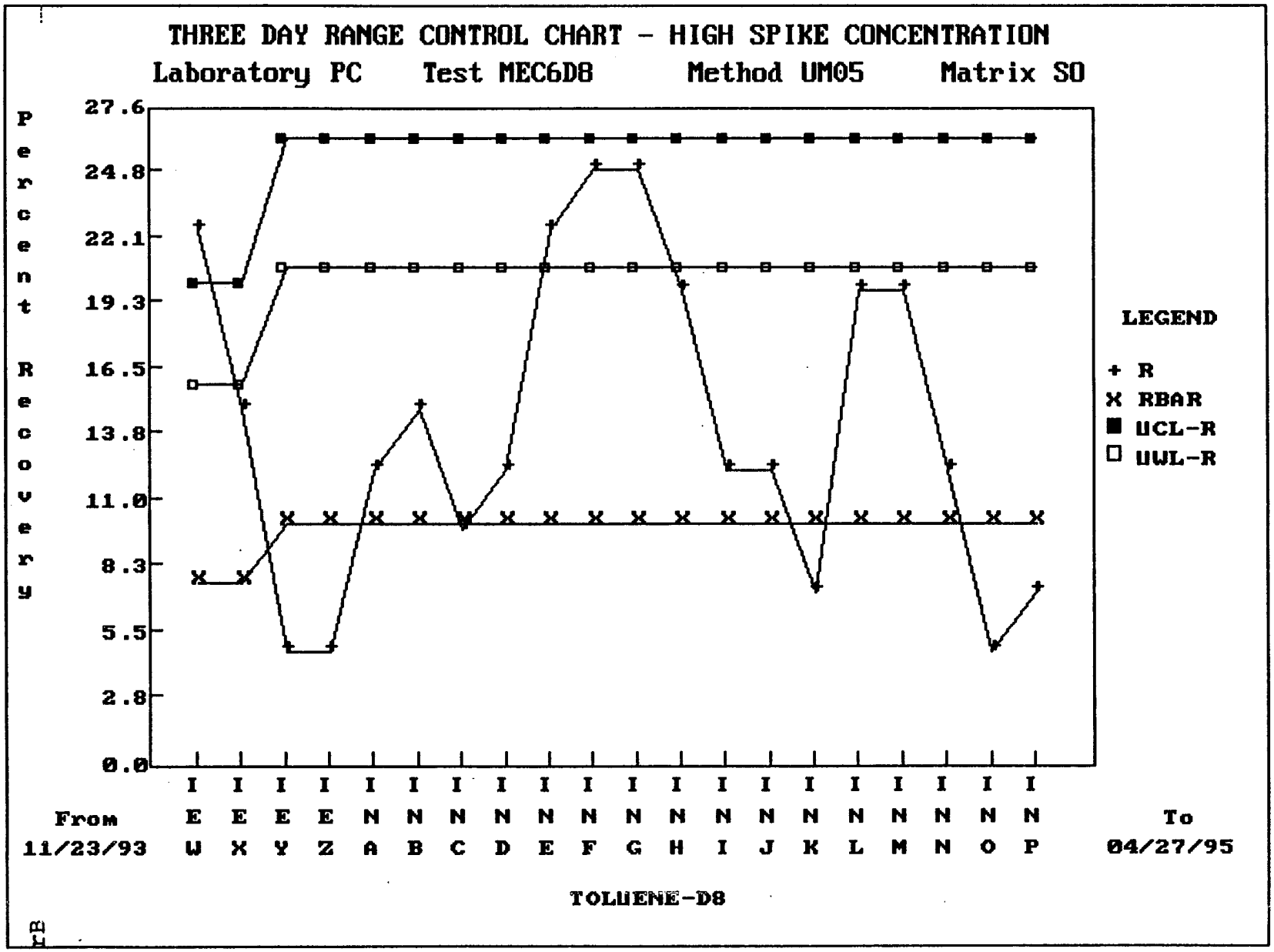

THREE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test MEC6D8 Method UM05 Matrix SO
Percent Recovery
114.4
112.0
109.7
107.4
105.1
102.8
100.5
98.2
95.9
93.6
91.2
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From 11/23/93
To 04/27/95
IEW IEX IEY IEZ INA INB INC IND INE INF ING INH INI INJ INK INL INM INN INO INP
TOLUENE-D8

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR TOLUENE-D8

Laboratory: PC	Date: 04/28/95
Method: UM05	Matrix: SO	Test Name: MEC6D8

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
110494	INL	4.00	1	4.40	1	110.0	98.3	113.3	109.8	95.8	92.3	.F.
030895	INM	4.00	1	3.90	1	97.5	99.2	113.3	109.8	95.8	92.3	.F.
041995	INN	4.00	1	4.10	1	102.5	103.3	113.3	109.8	95.8	92.3	.F.
042695	INO	4.00	1	4.00	1	100.0	100.0	113.3	109.8	95.8	92.3	.F.
042795	INP	4.00	1	3.80	1	95.0	99.2	113.3	109.8	95.8	92.3	.F.

* Changes made to data


THREE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test MEC6D8 Method UM05 Matrix SO
Percent Recovery
27.6
24.8
22.1
19.3
16.5
13.8
11.0
8.3
5.5
2.8
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From 11/23/93
To 04/27/95
TOLUENE-D8
EB

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR TOLUENE-D8

Laboratory: PC	Date: 04/28/95
Method: UM05 | Matrix: SO	Test Name: MEC6D8

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
110494	INL	4.00	1	4.40	1	110.0	20.0	26.5	21.1
030895	INM	4.00	1	3.90	1	97.5	20.0	26.5	21.1
041995	INN	4.00	1	4.10	1	102.5	12.5	26.5	21.1
042695	INO	4.00	1	4.00	1	100.0	5.0	26.5	21.1
042795	INP	4.00	1	3.80	1	95.0	7.5	26.5	21.1

* Changes made to data

METHOD	ANALYSIS	LOT	INSTALLATION	PRIME CONTRACTOR	ANALYSIS DATE
LH19	PEST/PCB	HPT	WB	EY	03/14/95

OBSERVATION

The control chart submittal date is April 28, 1995.

TREND ANALYSIS

The following analyte contained seven successive points below the central line in the single-day x-bar charts:

ANALYTE	BEGIN LOT	END LOT	NUMBER OF POINTS
AENSLF	HPE	HPT	9

OUT-OF-CONTROL ANALYSIS

The following analytes contained points outside the LCL in the three-day x-bar charts:

ANALYTE	LOT	RECOVERY	LCL
LIN	HPT	61.3	68.0
ALDRN	HPT	66.1	70.5
DLDRN	HPT	72.1	76.1
MEXCLR	HPT	80.4	81.7
BENSLF	HPT	58.8	71.3

The following analytes contained points outside the UCL in the three-day x-bar range charts:

ANALYTE	LOT	RECOVERY	UCL
ALDRN	HPT	31.4	26.5
GCLDAN	HPT	25.4	24.7
BENSLF	HPT	45.7	36.6

SUMMARY RECOMMENDATION

For lot HPT, five out of ten control analytes in the low control sample have recoveries below the LCL. An investigation into the lot by the analyst indicated the initial calibration and the external check met the requirements of the program. Both the daily continuing checks bracketing the analysis sequence also passed the QC criteria. The spiking solution was verified before use and the % recoveries range from 86.0% to 100%; all recoveries are above the required LWL. The two surrogates in all samples have recovery in the range of from 60% to 127%. There are no positive results in the environmental samples. I recommend a data qualifier be applied to test name BENSLF. Other out of control situation should have negligible affect on the quality of the data. Lot HPT should be accepted.

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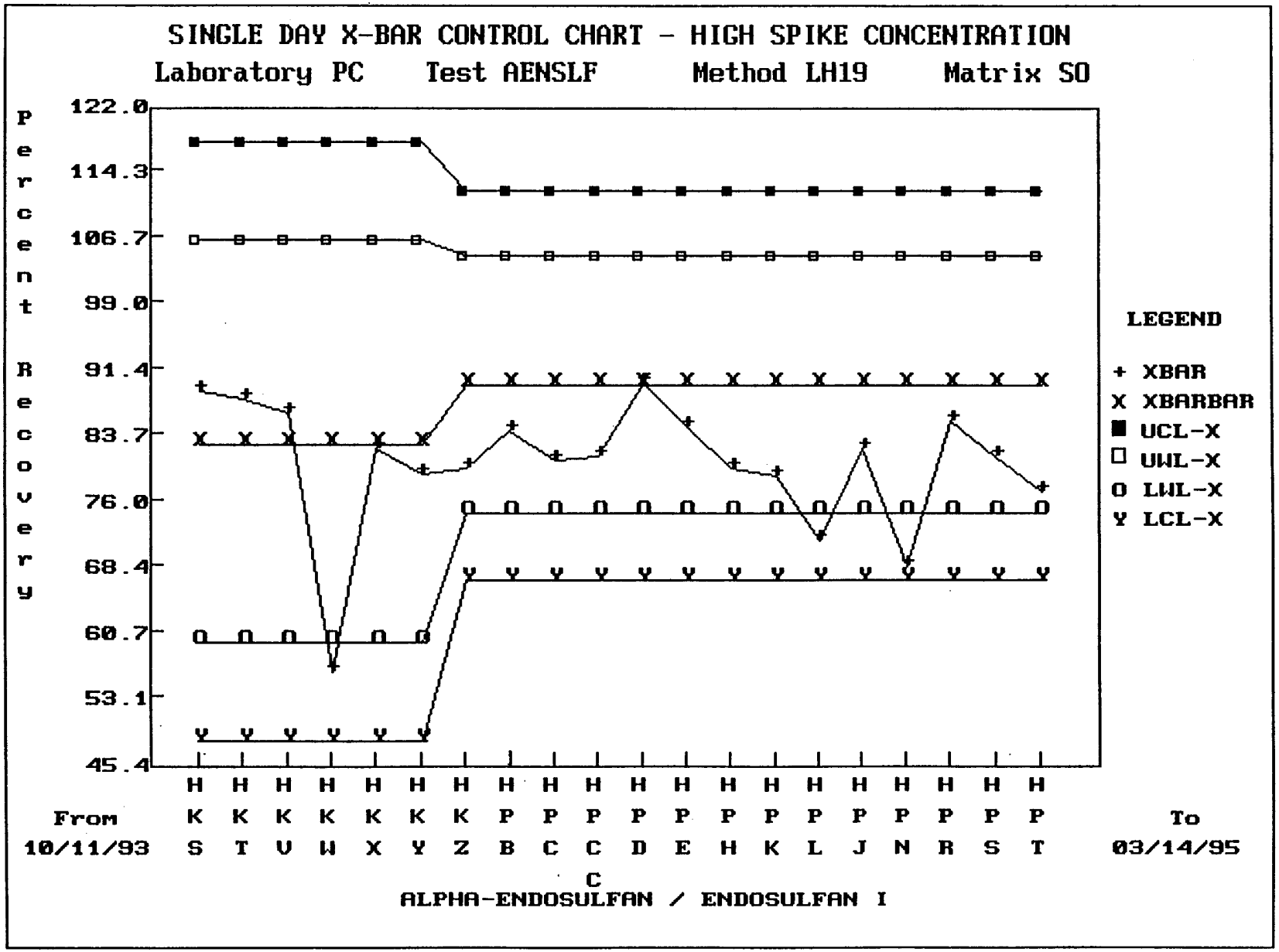
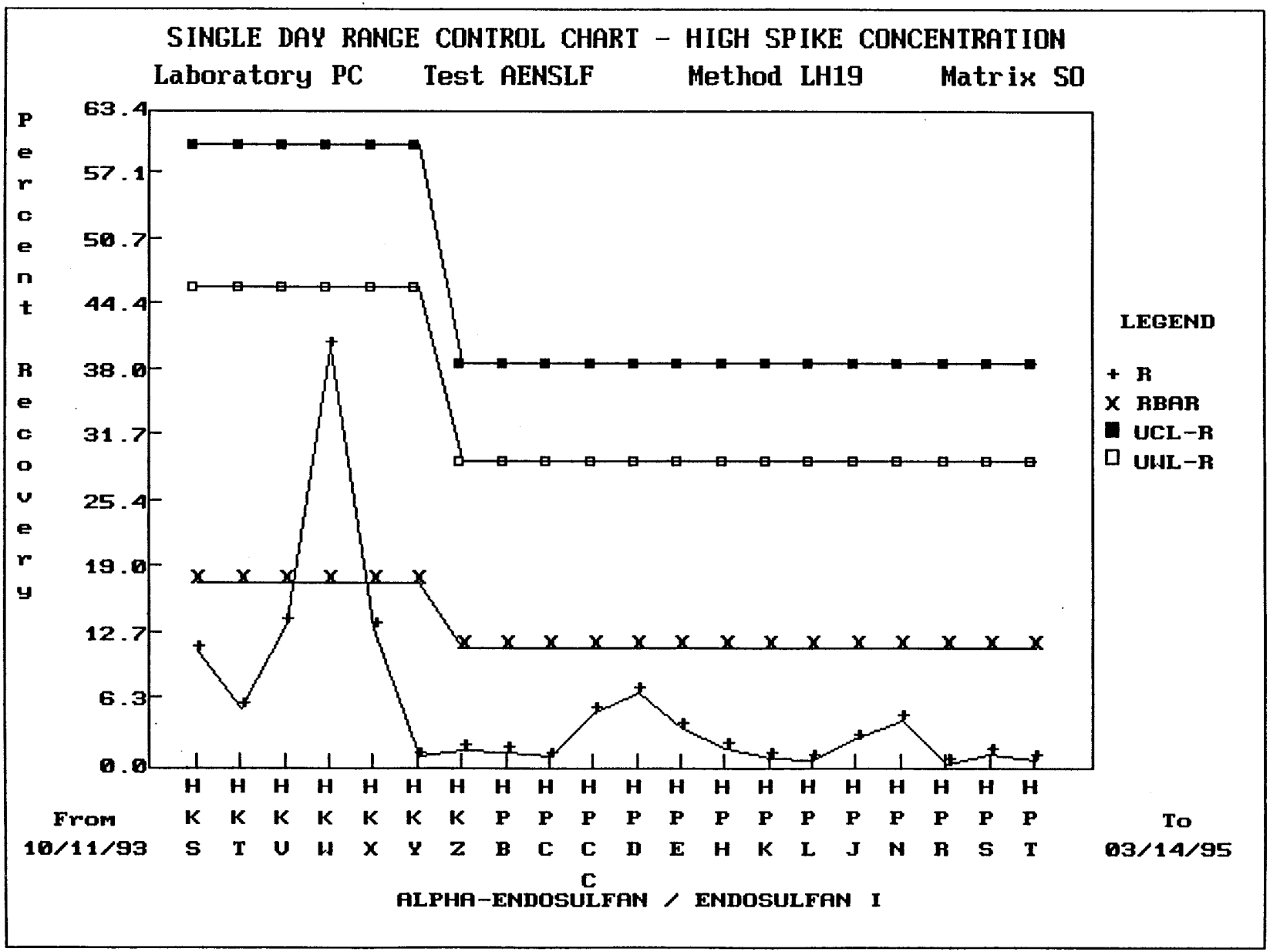

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test AENSLF Method LH19 Matrix SO
Percent Recovery
122.0
114.3
106.7
99.0
91.4
83.7
76.0
68.4
60.7
53.1
45.4
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
ALPHA-ENDOSULFAN / ENDOSULFAN I

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR ALPHA-ENDOSULFAN / ENDOSULFAN I

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: AENSLF

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.41	-2	6.29	-2	6.06	-2	84.9	81.8	83.3	113.1	105.5	75.5	67.9	.F.
*	052794	HPN	7.41	-2	4.90	-2	5.28	-2	66.1	71.2	68.7	113.1	105.5	75.5	67.9	.F.
	082494	HPR	7.41	-2	6.37	-2	6.34	-2	86.0	85.6	85.8	113.1	105.5	75.5	67.9	.F.
	092994	HPS	7.41	-2	6.14	-2	6.02	-2	82.9	81.2	82.1	113.1	105.5	75.5	67.9	.F.
	031495	HPT	7.41	-2	5.72	-2	5.78	-2	77.2	78.0	77.6	113.1	105.5	75.5	67.9	.F.

* Changes made to data

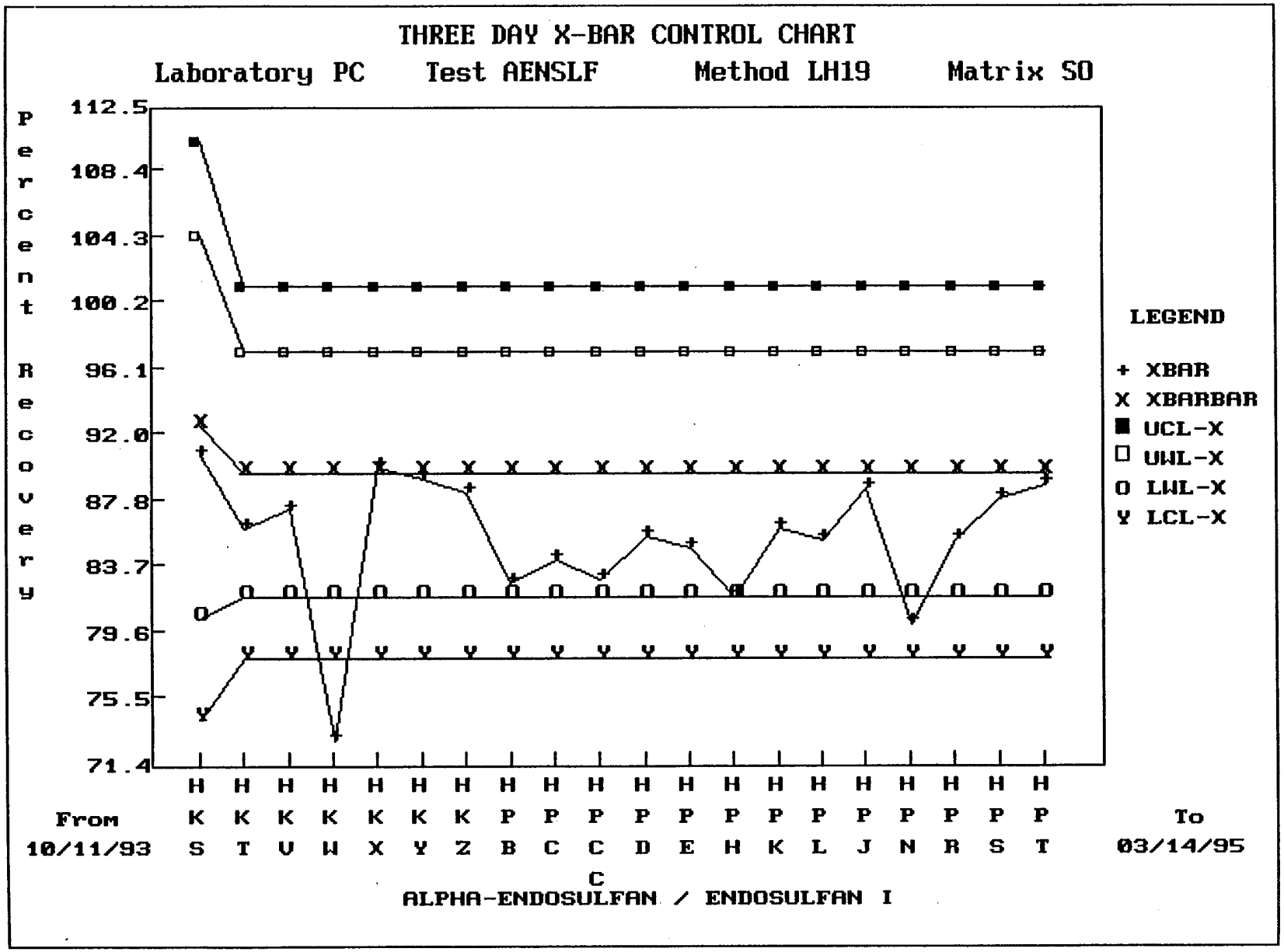

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test AENSLF Method LH19 Matrix SO
Percent Recovery
63.4
57.1
50.7
44.4
38.0
31.7
25.4
19.0
12.7
6.3
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
ALPHA-ENDOSULFAN / ENDOSULFAN I

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR ALPHA-ENDOSULFAN / ENDOSULFAN I

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: AENSLF

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.41	-2	6.29	-2	6.06	-2	84.9	81.8	3.1	39.2	30.1
*	052794	HPN	7.41	-2	4.90	-2	5.28	-2	66.1	71.2	5.1	39.2	30.1
	082494	HPR	7.41	-2	6.37	-2	6.34	-2	86.0	85.6	0.4	39.2	30.1
	092994	HPS	7.41	-2	6.14	-2	6.02	-2	82.9	81.2	1.6	39.2	30.1
	031495	HPT	7.41	-2	5.72	-2	5.78	-2	77.2	78.0	0.9	39.2	30.1

* Changes made to data

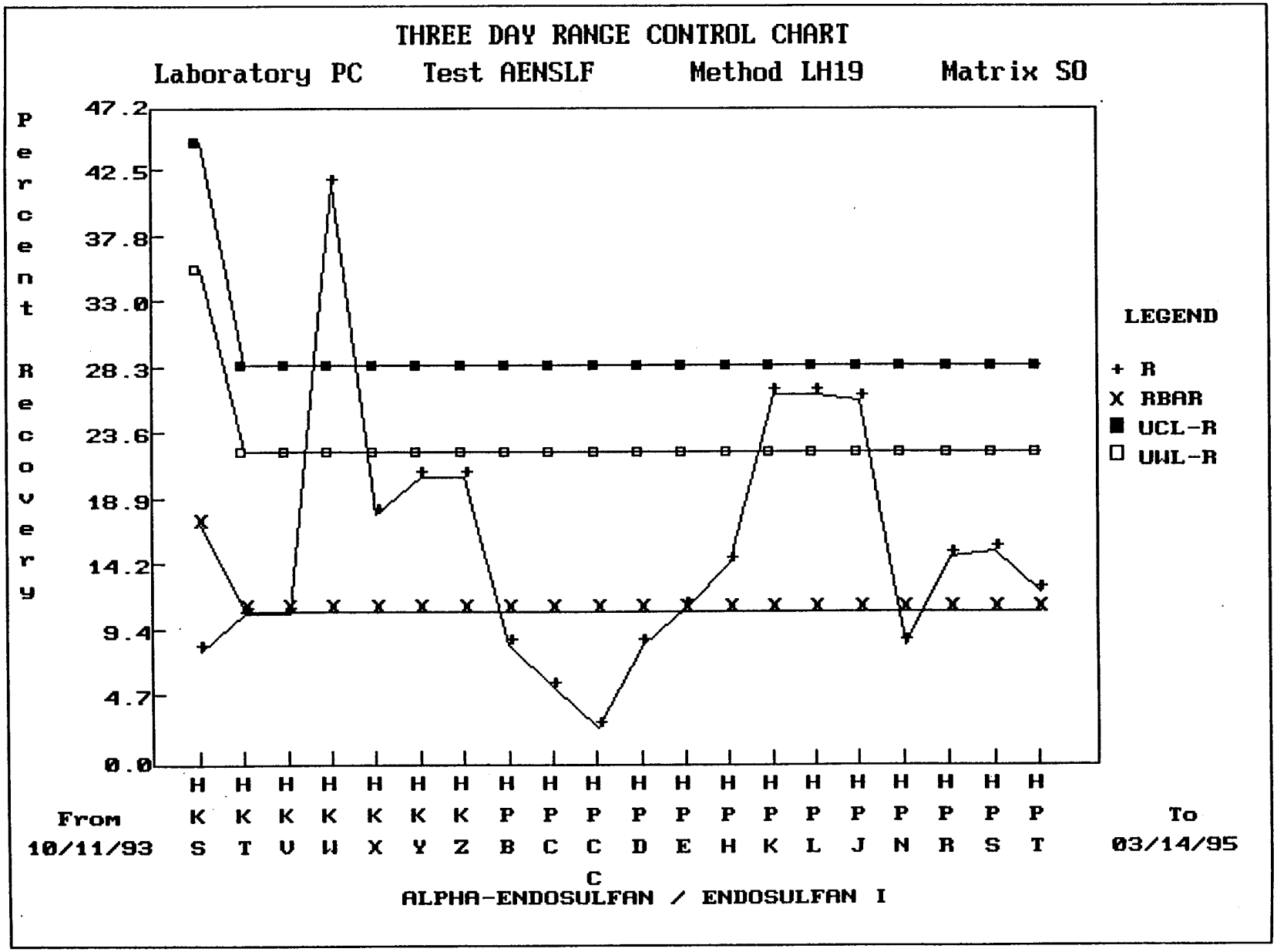

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test AENSLF Method LH19 Matrix SO
Percent Recovery
112.5
108.4
104.3
100.2
96.1
92.0
87.8
83.7
79.6
75.5
71.4
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
ALPHA-ENDOSULFAN / ENDOSULFAN I

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR ALPHA-ENDOSULFAN / ENDOSULFAN I

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: AENSLF

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.00	-2	1.72	-2	86.0	88.8	101.4	97.5	82.3	78.4	.F.
*	052794	HPN	2.00	-2	1.56	-2	78.0	80.3	101.4	97.5	82.3	78.4	.F.
	082494	HPR	2.00	-2	1.86	-2	93.0	85.7	101.4	97.5	82.3	78.4	.F.
	092994	HPS	2.00	-2	1.87	-2	93.5	88.2	101.4	97.5	82.3	78.4	.F.
	031495	HPT	2.00	-2	1.61	-2	80.8	89.1	101.4	97.5	82.3	78.4	.F.

* Changes made to data

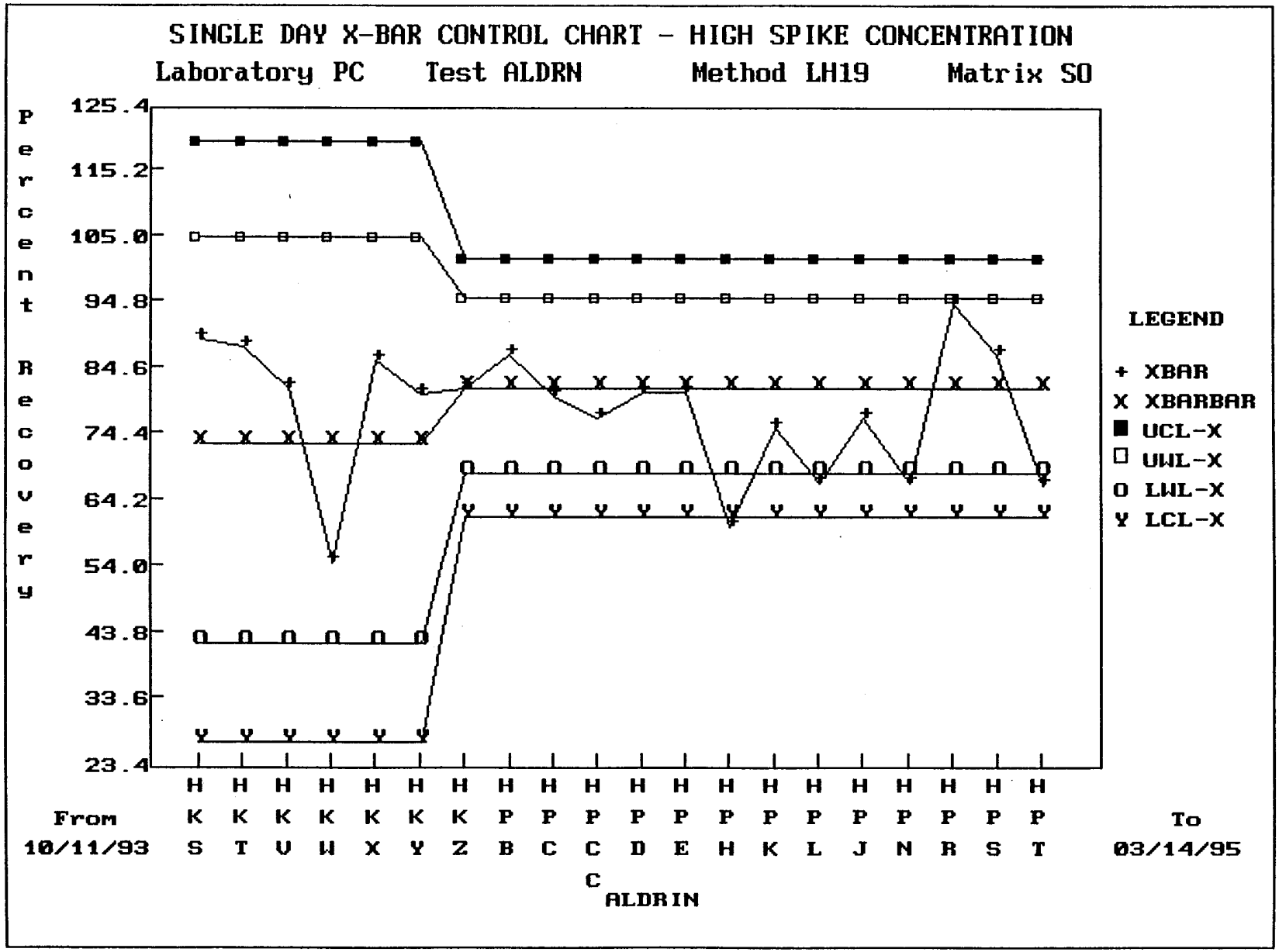

THREE DAY RANGE CONTROL CHART
Laboratory PC Test AENSLF Method LH19 Matrix SO
Percent Recovery
47.2
42.5
37.8
33.0
28.3
23.6
18.9
14.2
9.4
4.7
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
ALPHA-ENDOSULFAN / ENDOSULFAN I

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR ALPHA-ENDOSULFAN / ENDOSULFAN I

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ABNSLF

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.00	-2	1.72	-2	86.0	26.5	28.8	23.0
*	052794	HPN	2.00	-2	1.56	-2	78.0	9.0	28.8	23.0
	082494	HPR	2.00	-2	1.86	-2	93.0	15.0	28.8	23.0
	092994	HPS	2.00	-2	1.87	-2	93.5	15.5	28.8	23.0
	031495	HPT	2.00	-2	1.61	-2	80.8	12.8	28.8	23.0

* Changes made to data


SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test ALDRN Method LH19 Matrix SO
Percent Recovery
125.4
115.2
105.0
94.8
84.6
74.4
64.2
54.0
43.8
33.6
23.4
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
ALDRIN

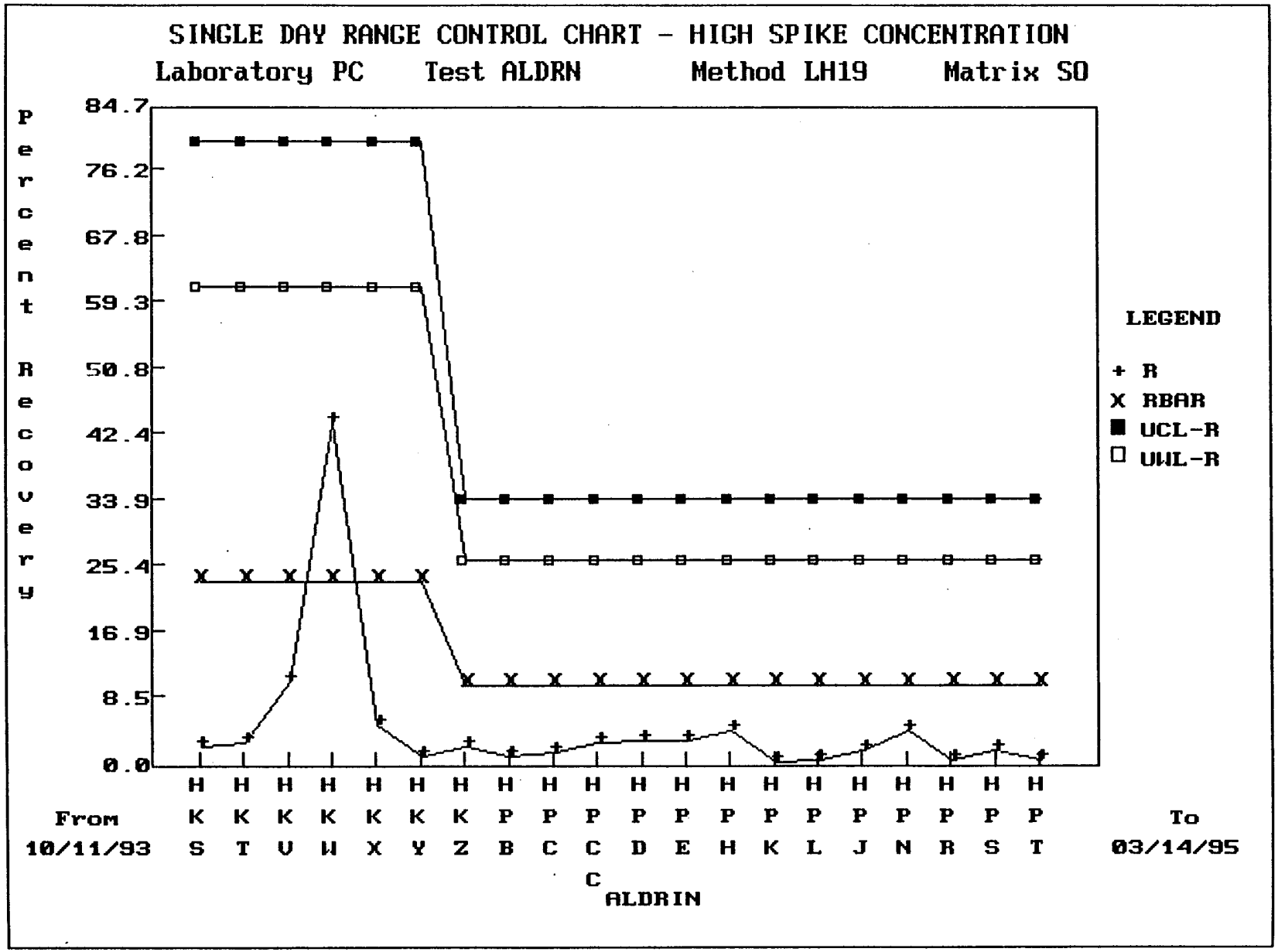
SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION

FOR ALDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ALDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.59	-2	5.80	-2	5.98	-2	76.4	78.8	77.6	102.6	95.9	69.4	62.8	.F.
*	052794	HPN	7.59	-2	4.95	-2	5.34	-2	65.2	70.4	67.8	102.6	95.9	69.4	62.8	.F.
	082494	HPR	7.59	-2	7.17	-2	7.24	-2	94.5	95.4	94.9	102.6	95.9	69.4	62.8	.F.
	092994	HPS	7.59	-2	6.71	-2	6.54	-2	88.4	86.2	87.3	102.6	95.9	69.4	62.8	.F.
	031495	HPT	7.59	-2	5.07	-2	5.13	-2	66.8	67.6	67.2	102.6	95.9	69.4	62.8	.F.

* Changes made to data


SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test ALDRN Method LH19 Matrix SO
Percent Recovery
84.7
76.2
67.8
59.3
50.8
42.4
33.9
25.4
16.9
8.5
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
ALDRIN

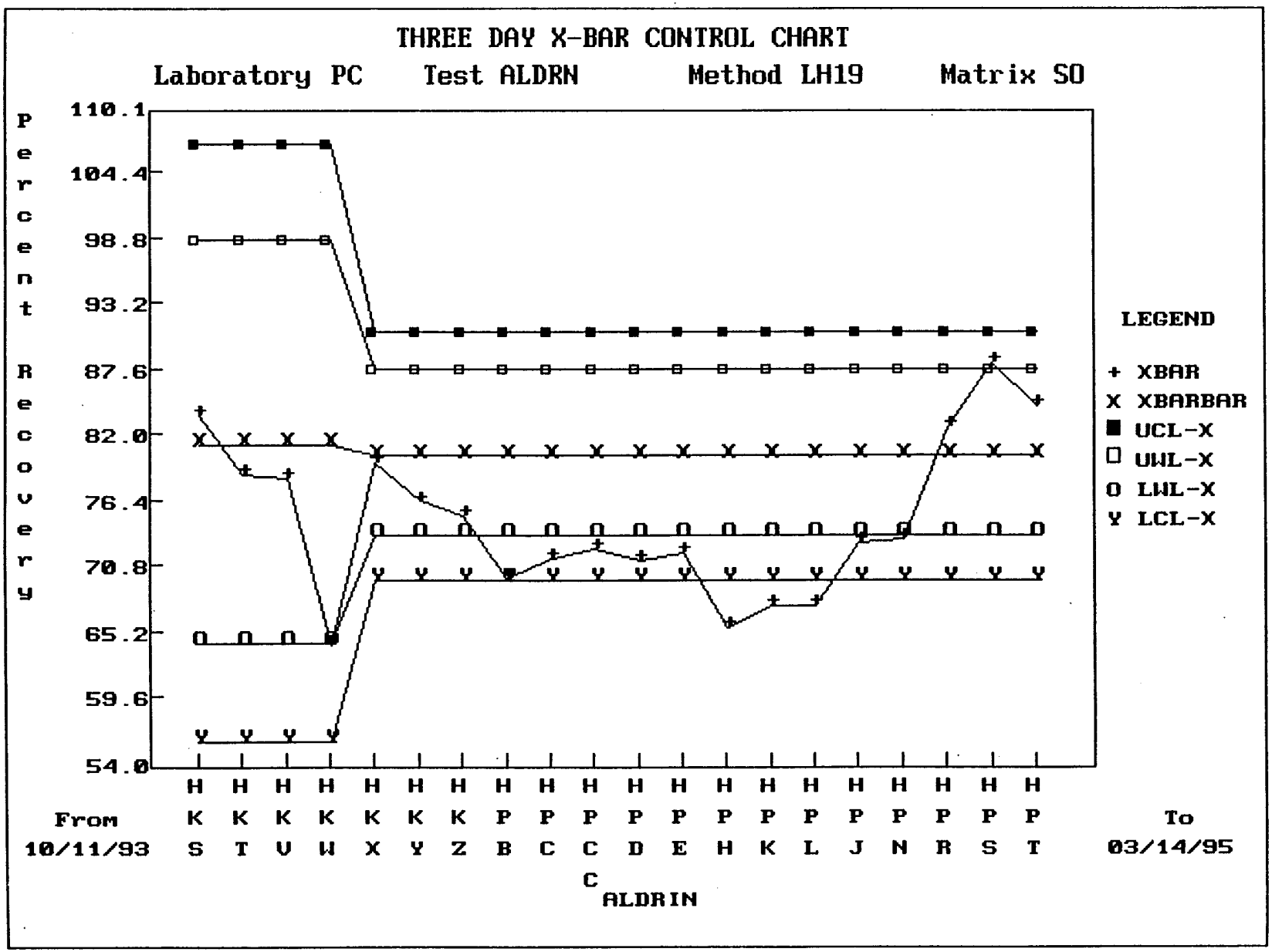
SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR ALDRIN

Laboratory: PC	Date: 04/28/95

Method: LH19	Matrix: SO	Test Name: ALDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.59	-2	5.80	-2	5.98	-2	76.4	78.8	2.4	34.6	26.6
*	052794	HPN	7.59	-2	4.95	-2	5.34	-2	65.2	70.4	5.1	34.6	26.6
	082494	HPR	7.59	-2	7.17	-2	7.24	-2	94.5	95.4	0.9	34.6	26.6
	092994	HPS	7.59	-2	6.71	-2	6.54	-2	88.4	86.2	2.2	34.6	26.6
	031495	HPT	7.59	-2	5.07	-2	5.13	-2	66.8	67.6	0.8	34.6	26.6

* Changes made to data

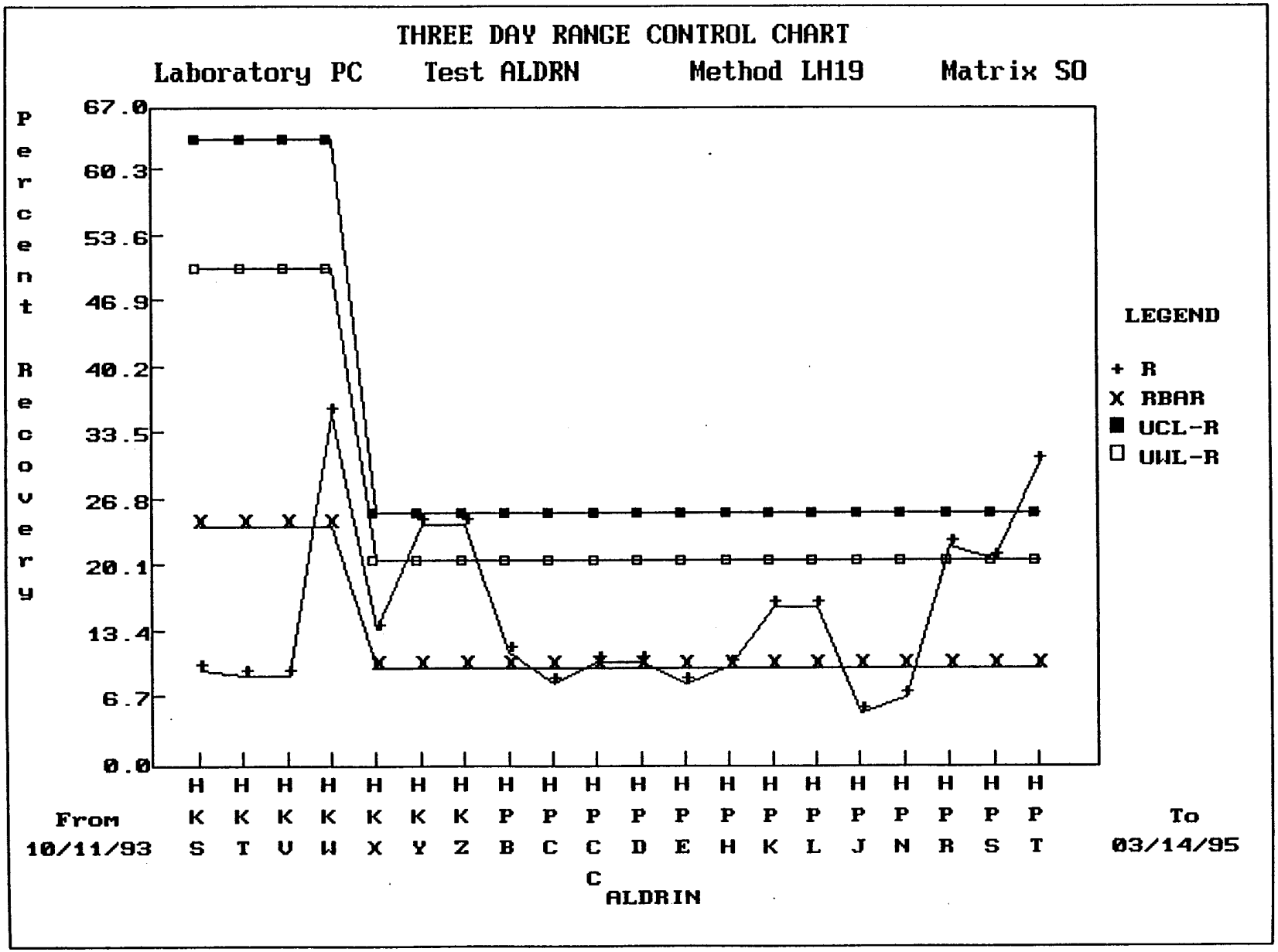

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test ALDRN Method LH19 Matrix SO
Percent Recovery
110.1
104.4
98.8
93.2
87.6
82.0
76.4
70.8
65.2
59.6
54.0
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From
10/11/93
To
03/14/95
ALDRIN

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR ALDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ALDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.00	-2	1.50	-2	75.0	73.3	91.5	88.0	74.0	70.5	.F.
*	052794	HPN	2.00	-2	1.53	-2	76.5	73.7	91.5	88.0	74.0	70.5	.F.
	082494	HPR	2.00	-2	1.95	-2	97.5	83.0	91.5	88.0	74.0	70.5	.F.
	092994	HPS	2.00	-2	1.83	-2	91.5	88.5	91.5	88.0	74.0	70.5	.F.
	031495	HPT	2.00	-2	1.32	-2	66.1	85.1	91.5	88.0	74.0	70.5	.F.

* Changes made to data

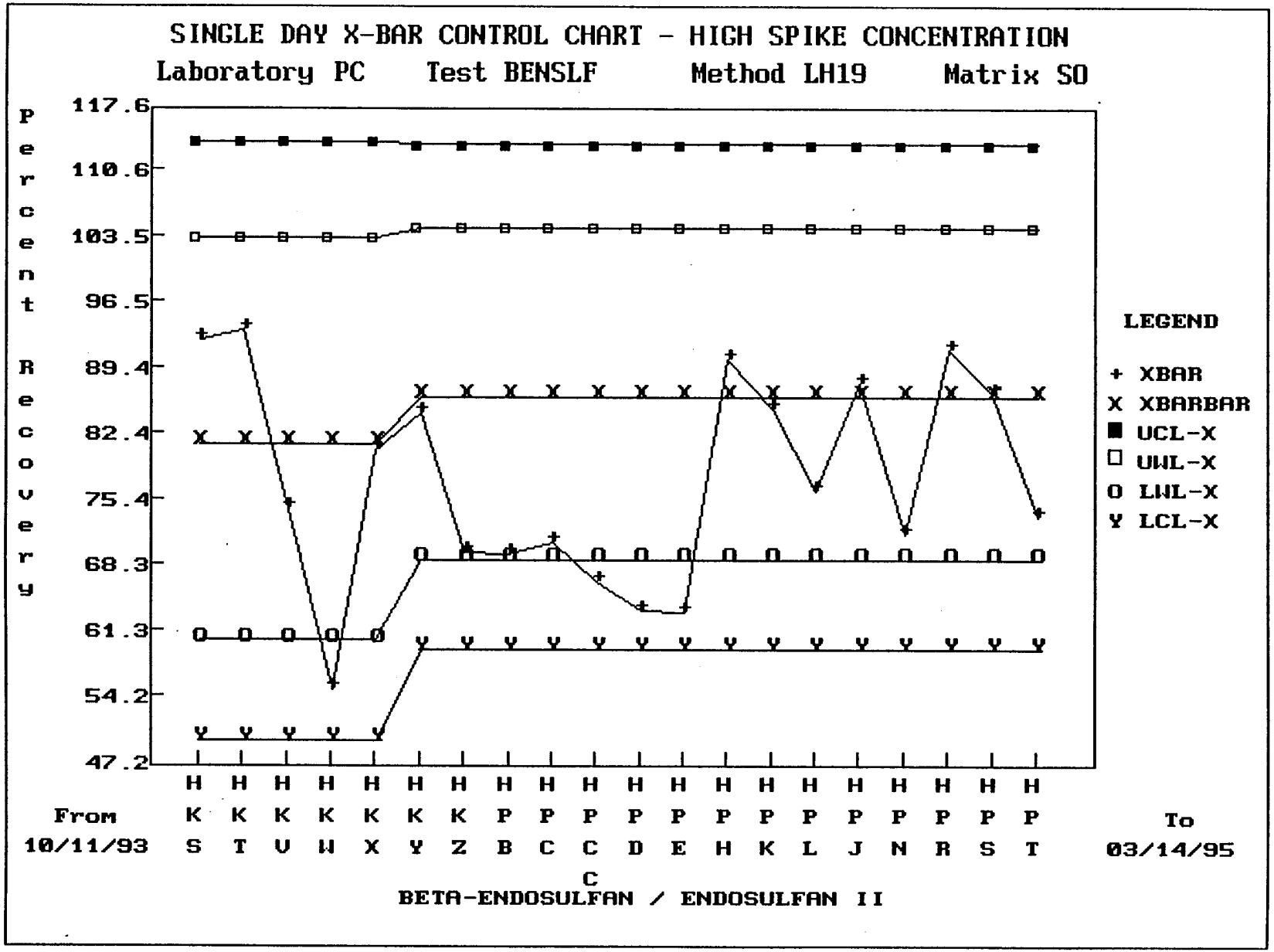

THREE DAY RANGE CONTROL CHART
Laboratory PC Test ALDRN Method LH19 Matrix SO
Percent Recovery
67.0
60.3
53.6
46.9
40.2
33.5
26.8
20.1
13.4
6.7
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C ALDRIN

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR ALDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ALDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.00	-2	1.50	-2	75.0	6.0	26.5	21.1
*	052794	HPN	2.00	-2	1.53	-2	76.5	7.0	26.5	21.1
	082494	HPR	2.00	-2	1.95	-2	97.5	22.5	26.5	21.1
	092994	HPS	2.00	-2	1.83	-2	91.5	21.0	26.5	21.1
	031495	HPT	2.00	-2	1.32	-2	66.1	31.4	26.5	21.1

* Changes made to data

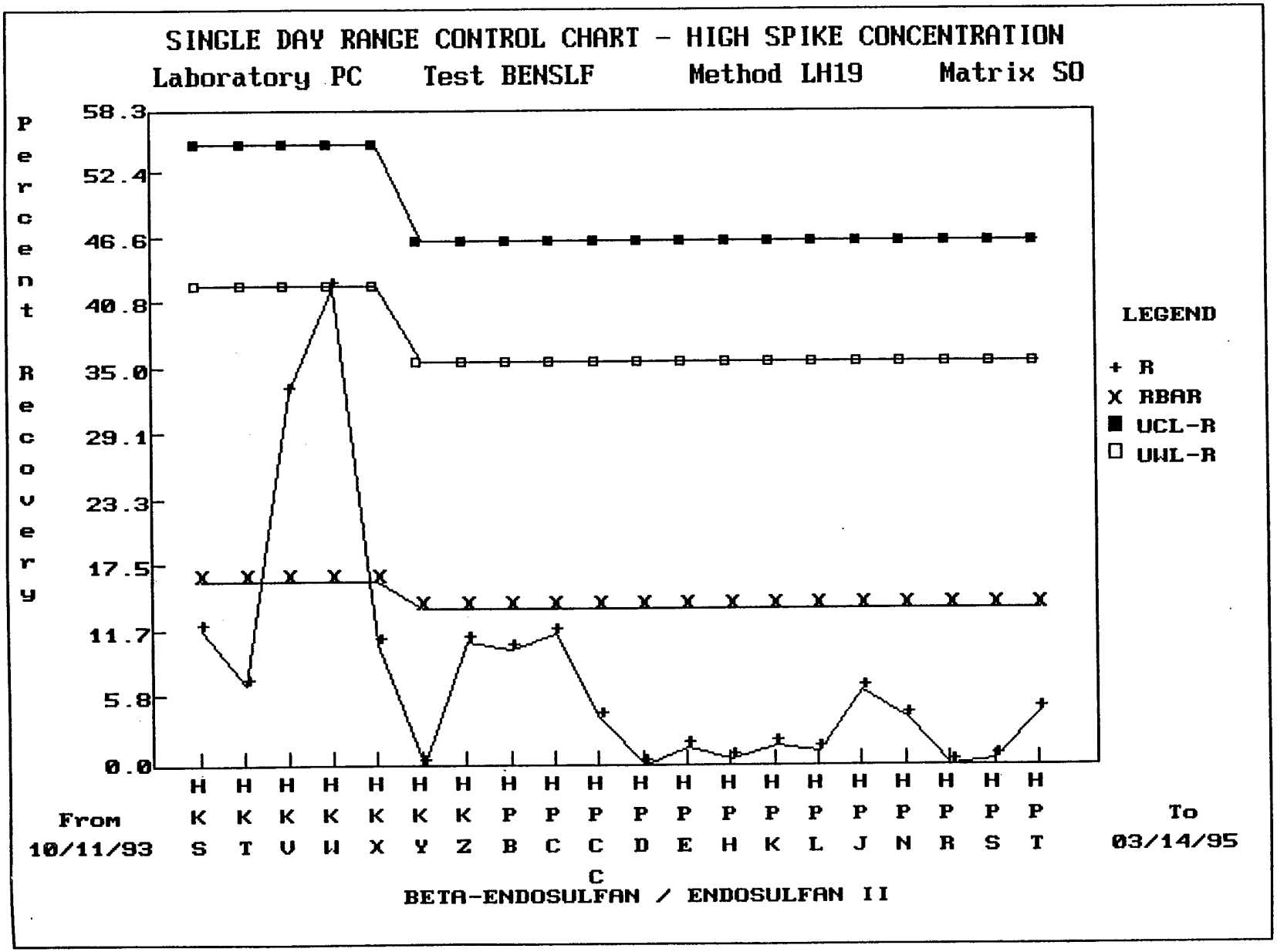

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test BENSLF Method LH19 Matrix SO
Percent Recovery
117.6
110.6
103.5
96.5
89.4
82.4
75.4
68.3
61.3
54.2
47.2
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
BETA-ENDOSULFAN / ENDOSULFAN II

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR BETA-ENDOSULFAN / ENDOSULFAN II

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: BENSLF

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	1.50	-1	1.28	-1	1.38	-1	85.3	92.0	88.7	114.0	105.0	69.2	60.2	.F.
	052794	HPN	1.50	-1	1.05	-1	1.12	-1	70.0	74.7	72.3	114.0	105.0	69.2	60.2	.F.
	082494	HPR	1.50	-1	1.38	-1	1.38	-1	92.0	92.0	92.0	114.0	105.0	69.2	60.2	.F.
	092994	HPS	1.50	-1	1.31	-1	1.32	-1	87.3	88.0	87.7	114.0	105.0	69.2	60.2	.F.
	031495	HPT	1.50	-1	1.08	-1	1.16	-1	72.0	77.1	74.5	114.0	105.0	69.2	60.2	.F.

* Changes made to data

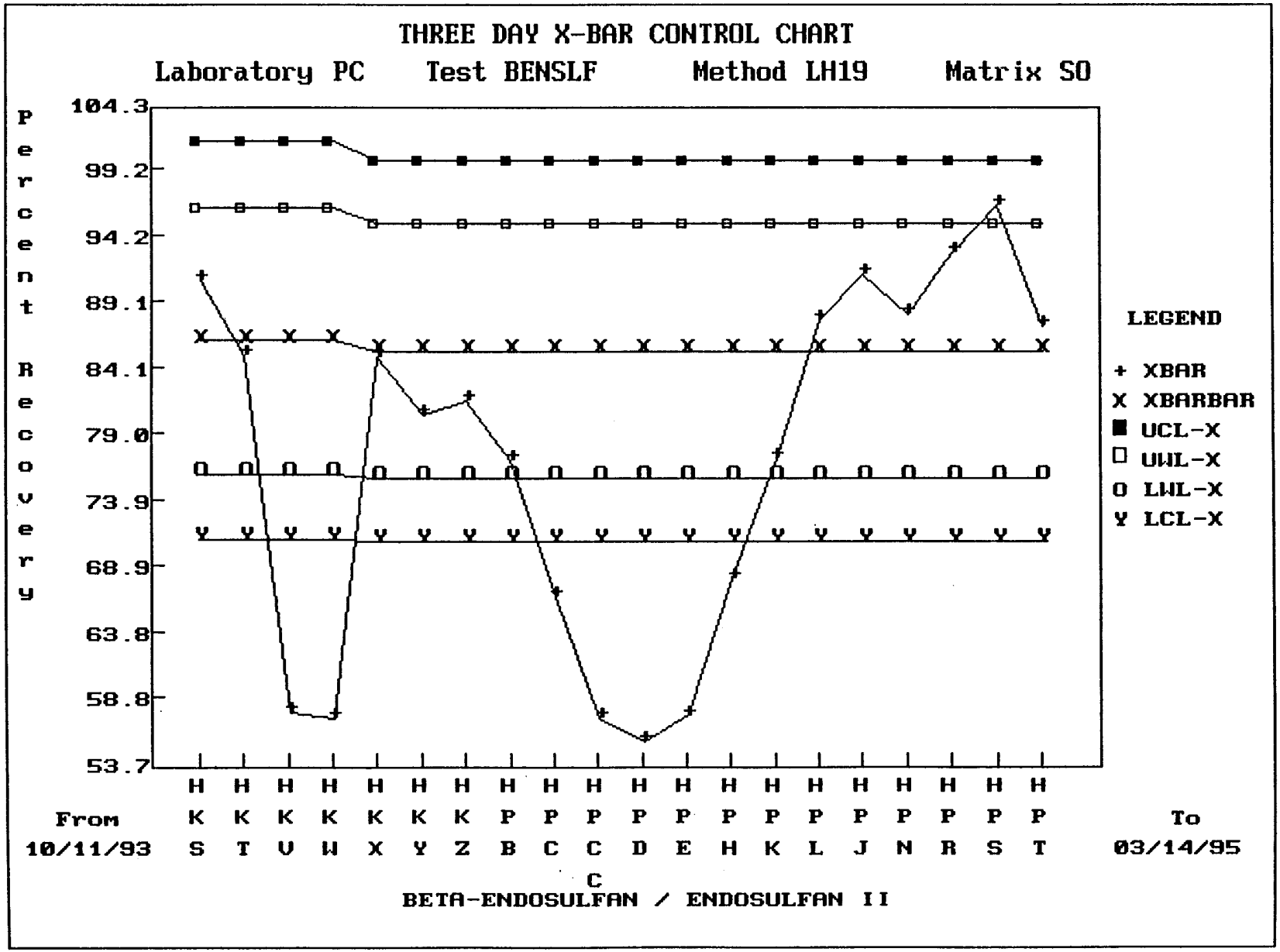

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test BENSLF Method LH19 Matrix SO
Percent Recovery
58.3
52.4
46.6
40.8
35.0
29.1
23.3
17.5
11.7
5.8
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From 10/11/93
To 03/14/95
BETA-ENDOSULFAN / ENDOSULFAN II

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR BETA-ENDOSULFAN / ENDOSULFAN II

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: BENSLF

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	1.50	-1	1.28	-1	1.38	-1	85.3	92.0	6.7	46.7	35.9
	052794	HPN	1.50	-1	1.05	-1	1.12	-1	70.0	74.7	4.7	46.7	35.9
	082494	HPR	1.50	-1	1.38	-1	1.38	-1	92.0	92.0	0.0	46.7	35.9
	092994	HPS	1.50	-1	1.31	-1	1.32	-1	87.3	88.0	0.7	46.7	35.9
	031495	HPT	1.50	-1	1.08	-1	1.16	-1	72.0	77.1	5.2	46.7	35.9

* Changes made to data

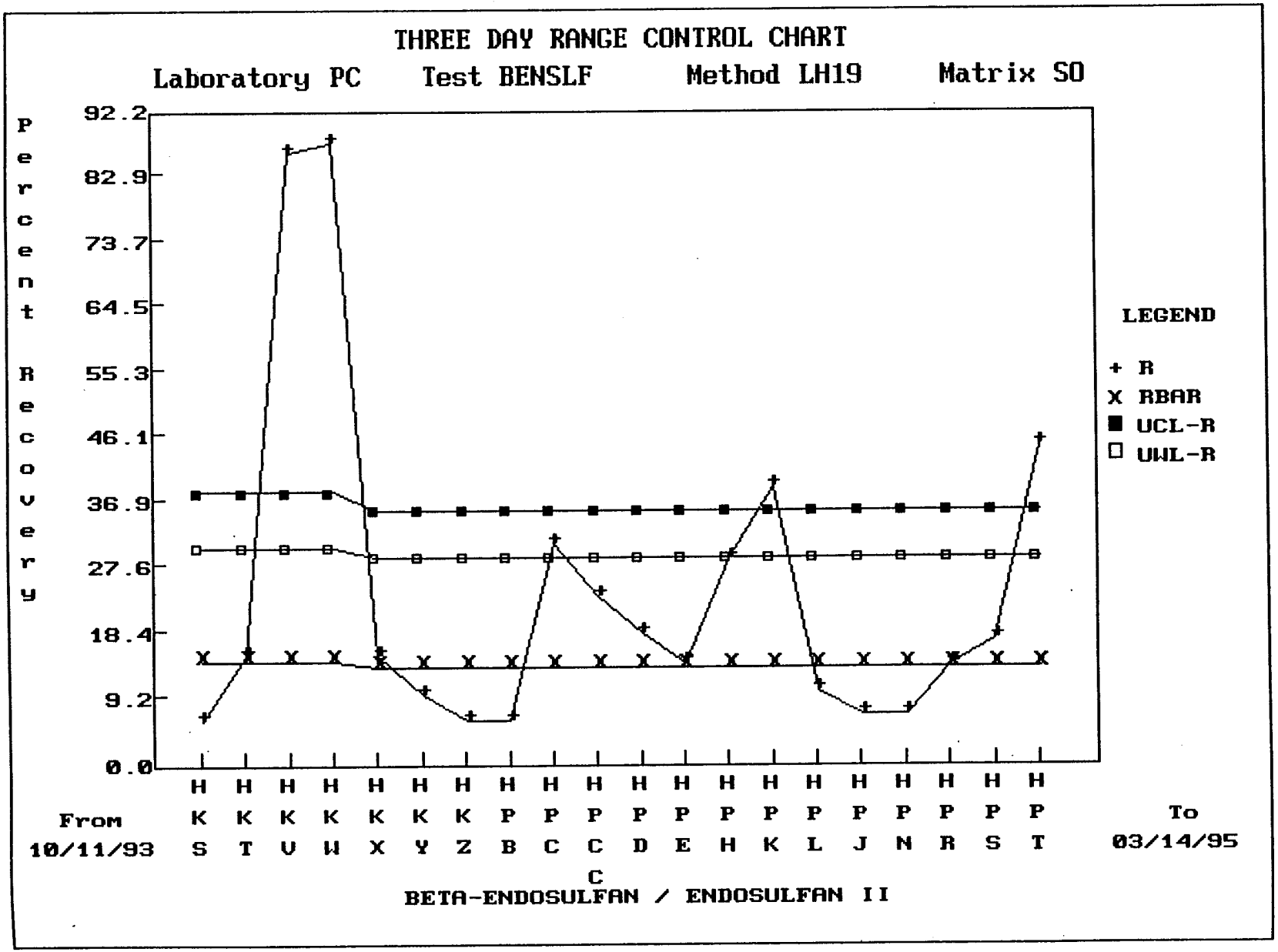

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test BENSLF Method LH19 Matrix SO
Percent Recovery
104.3
99.2
94.2
89.1
84.1
79.0
73.9
68.9
63.8
58.8
53.7
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
BETA-ENDOSULFAN / ENDOSULFAN II

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR BETA-ENDOSULFAN / ENDOSULFAN II

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: BENSLF

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.01	-2	1.89	-2	94.0	91.7	100.3	95.5	76.1	71.3	.F.
	052794	HPN	2.01	-2	1.73	-2	86.1	88.9	100.3	95.5	76.1	71.3	.F.
	082494	HPR	2.01	-2	2.02	-2	100.5	93.5	100.3	95.5	76.1	71.3	.F.
	092994	HPS	2.01	-2	2.10	-2	104.5	97.0	100.3	95.5	76.1	71.3	.F.
	031495	HPT	2.01	-2	1.18	-2	58.8	87.9	100.3	95.5	76.1	71.3	.F.

* Changes made to data

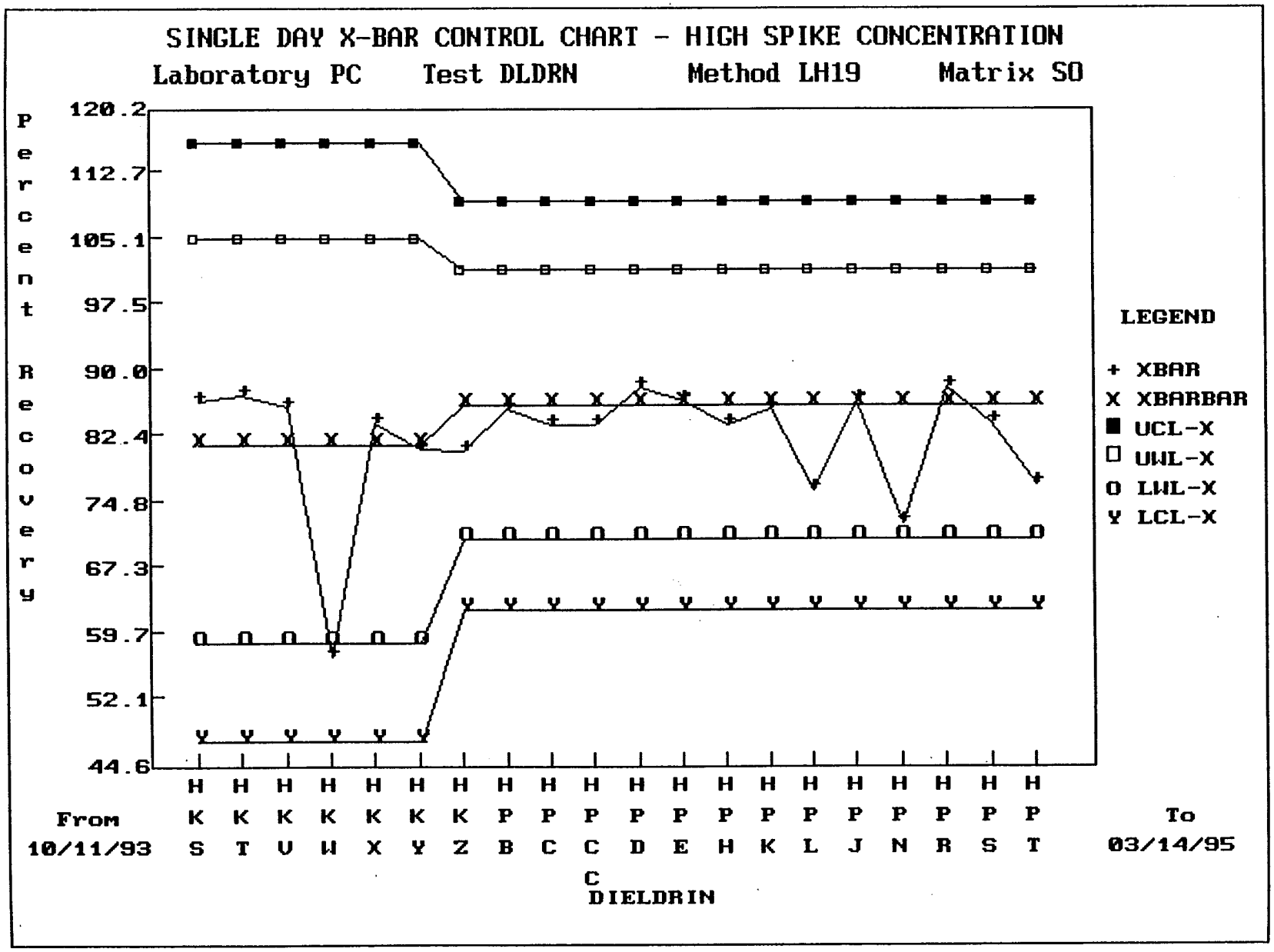

THREE DAY RANGE CONTROL CHART
Laboratory PC Test BENSLF Method LH19 Matrix SO
Percent Recovery
92.2
82.9
73.7
64.5
55.3
46.1
36.9
27.6
18.4
9.2
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
BETA-ENDOSULFAN / ENDOSULFAN II

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR BETA-ENDOSULFAN / ENDOSULFAN II

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: BENSLF

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.01	-2	1.89	-2	94.0	8.0	36.6	29.1
	052794	HPN	2.01	-2	1.73	-2	86.1	8.0	36.6	29.1
	082494	HPR	2.01	-2	2.02	-2	100.5	14.4	36.6	29.1
	092994	HPS	2.01	-2	2.10	-2	104.5	18.4	36.6	29.1
	031495	HPT	2.01	-2	1.18	-2	58.8	45.7	36.6	29.1

* Changes made to data

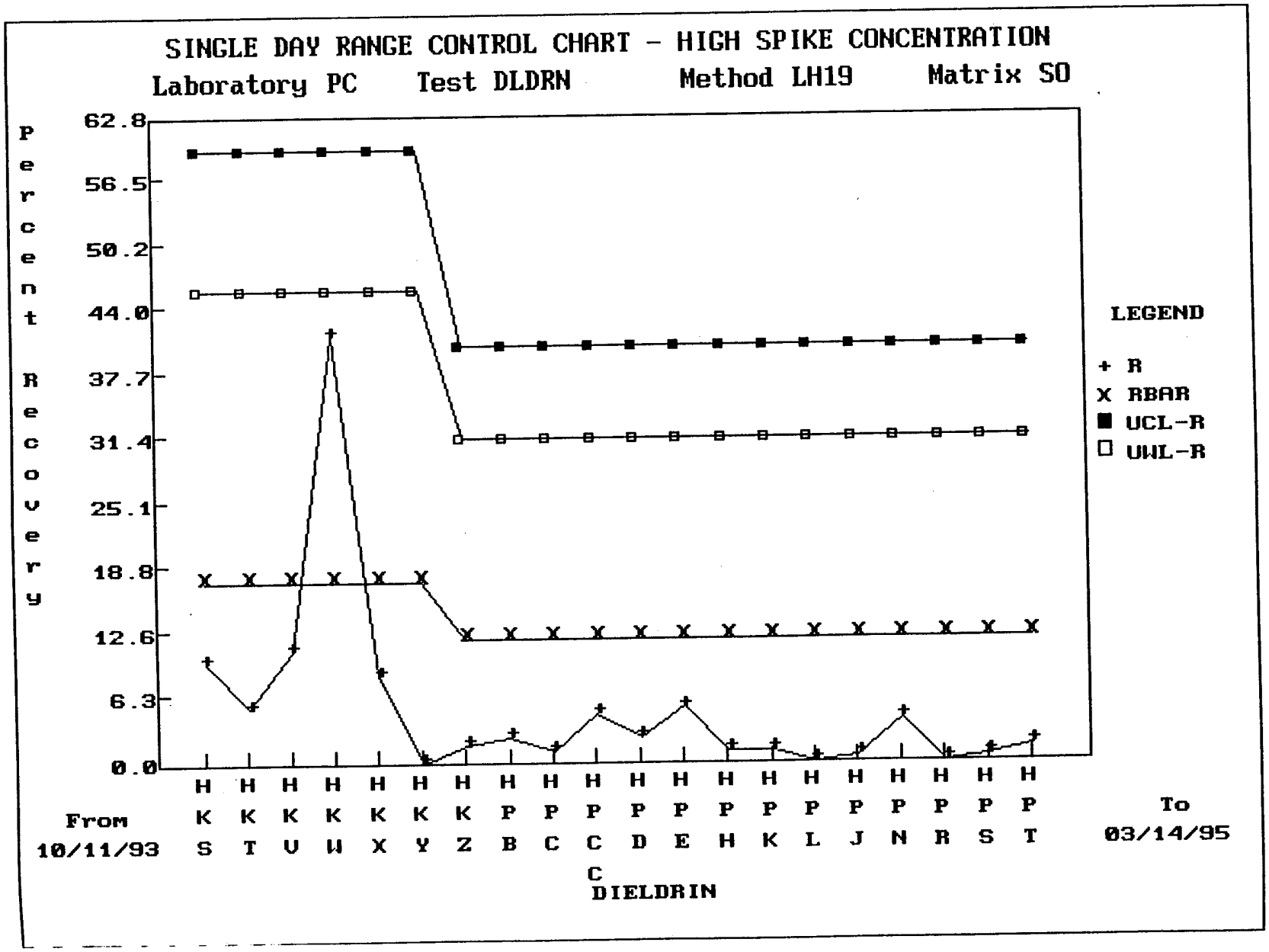

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test DLDRN Method LH19 Matrix SO
Percent Recovery
120.2
112.7
105.1
97.5
90.0
82.4
74.8
67.3
59.7
52.1
44.6
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
DIELDRIN

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR DIELDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: DLDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	1.50	-1	1.30	-1	1.31	-1	86.7	87.3	87.0	110.1	102.2	71.0	63.1	.F.
	052794	HPN	1.50	-1	1.06	-1	1.13	-1	70.7	75.3	73.0	110.1	102.2	71.0	63.1	.F.
	082494	HPR	1.50	-1	1.33	-1	1.33	-1	88.7	88.7	88.7	110.1	102.2	71.0	63.1	.F.
	092994	HPS	1.50	-1	1.27	-1	1.26	-1	84.7	84.0	84.3	110.1	102.2	71.0	63.1	.F.
	031495	HPT	1.50	-1	1.15	-1	1.17	-1	76.4	78.2	77.3	110.1	102.2	71.0	63.1	.F.

* Changes made to data

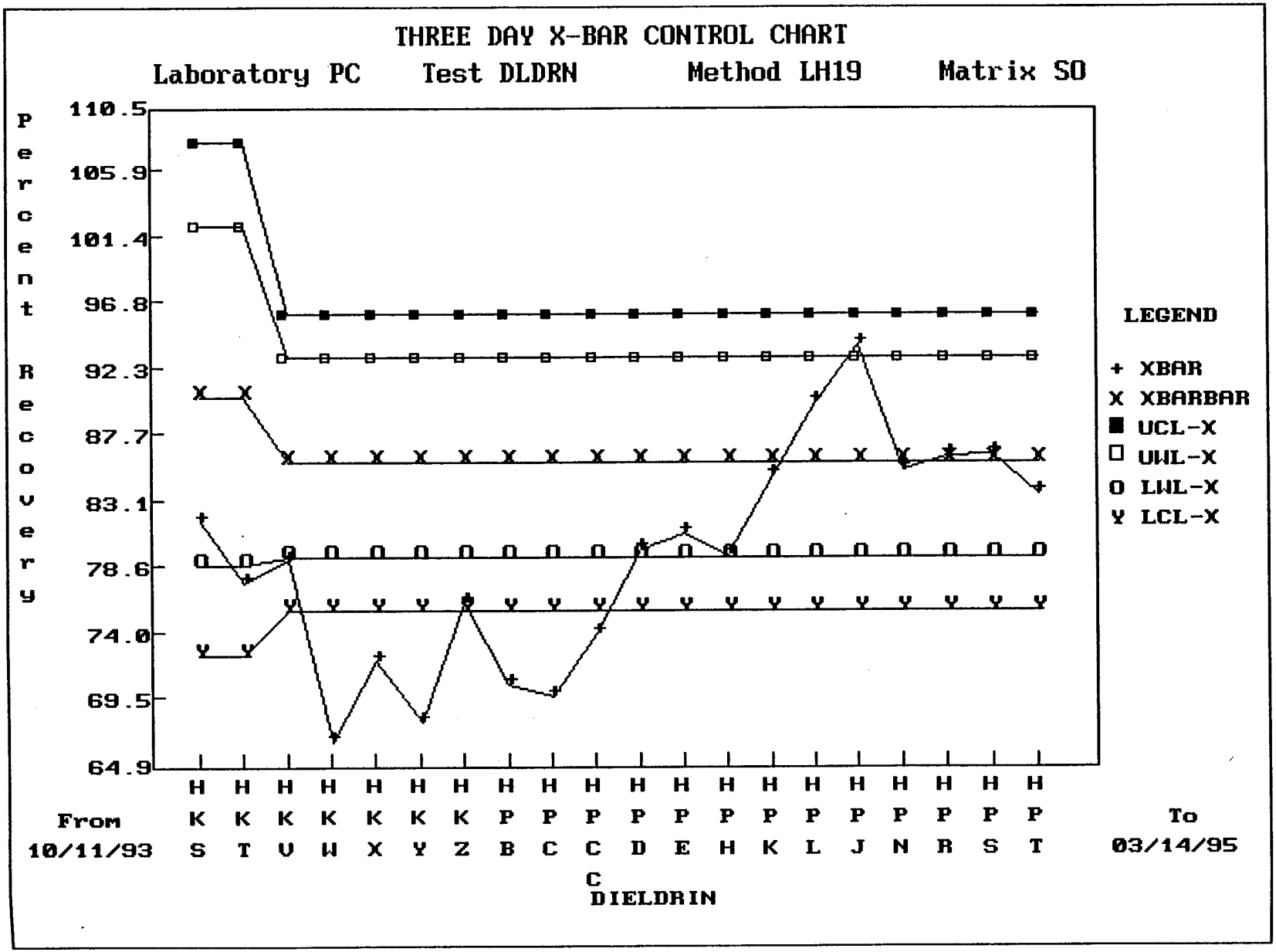

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test DLDRN Method LH19 Matrix SO
Percent Recovery
62.8
56.5
50.2
44.0
37.7
31.4
25.1
18.8
12.6
6.3
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKU HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
DIELDRIN

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR DIELDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: DLDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	1.50	-1	1.30	-1	1.31	-1	86.7	87.3	0.7	40.8	31.4
	052794	HPN	1.50	-1	1.06	-1	1.13	-1	70.7	75.3	4.7	40.8	31.4
	082494	HPR	1.50	-1	1.33	-1	1.33	-1	88.7	88.7	0.0	40.8	31.4
	092994	HPS	1.50	-1	1.27	-1	1.26	-1	84.7	84.0	0.7	40.8	31.4
	031495	HPT	1.50	-1	1.15	-1	1.17	-1	76.4	78.2	1.7	40.8	31.4

* Changes made to data

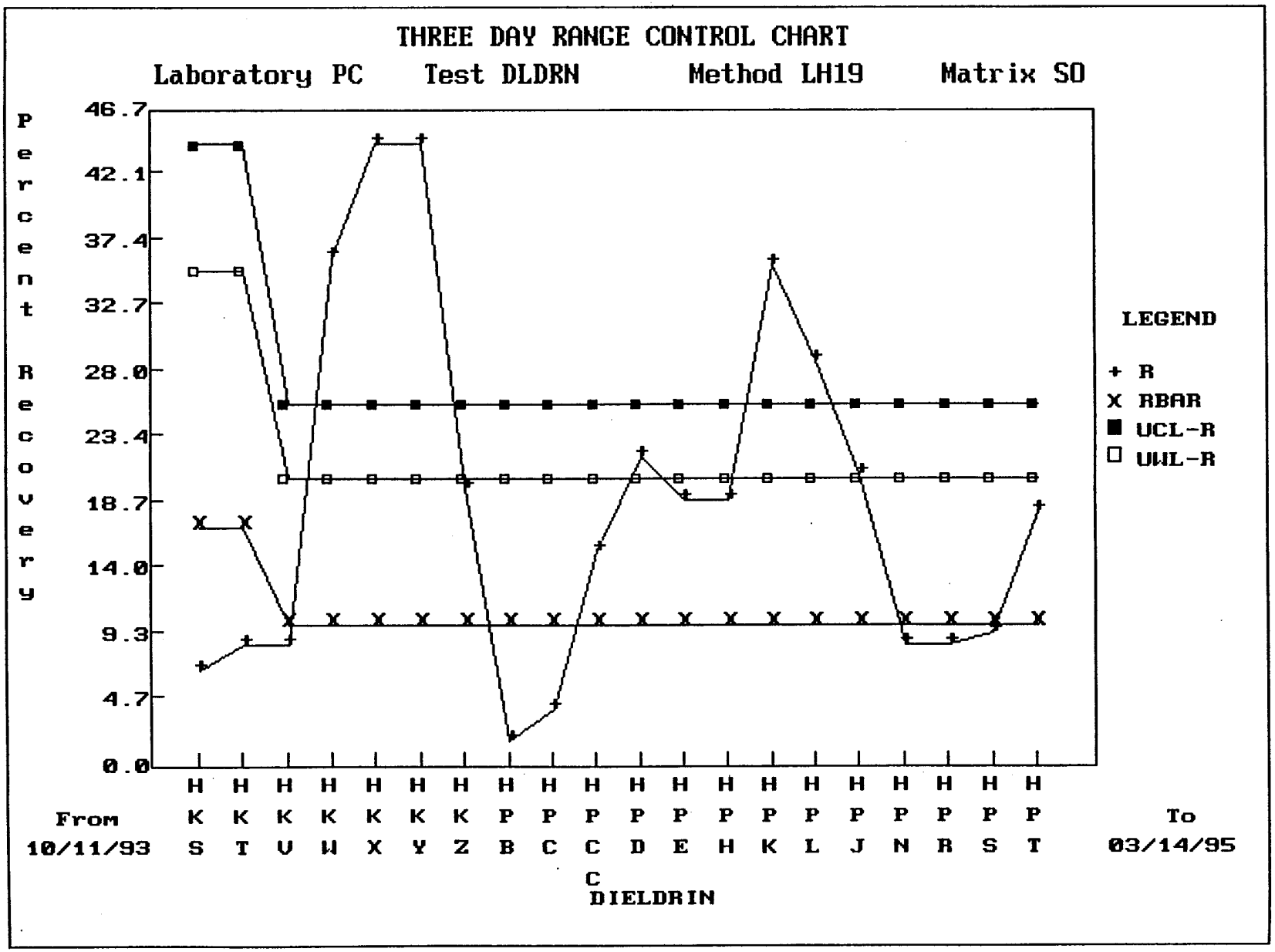

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test DLDRN Method LH19 Matrix SO
Percent Recovery
110.5
105.9
101.4
96.8
92.3
87.7
83.1
78.6
74.0
69.5
64.9
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
DIELDRIN

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR DIELDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: DLDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.00	-2	1.80	-2	90.0	94.3	96.7	93.3	79.5	76.1	.F.
	052794	HPN	2.00	-2	1.62	-2	81.0	85.7	96.7	93.3	79.5	76.1	.F.
	082494	HPR	2.00	-2	1.79	-2	89.5	86.8	96.7	93.3	79.5	76.1	.F.
	092994	HPS	2.00	-2	1.81	-2	90.5	87.0	96.7	93.3	79.5	76.1	.F.
	031495	HPT	2.00	-2	1.44	-2	72.1	84.0	96.7	93.3	79.5	76.1	.F.

* Changes made to data

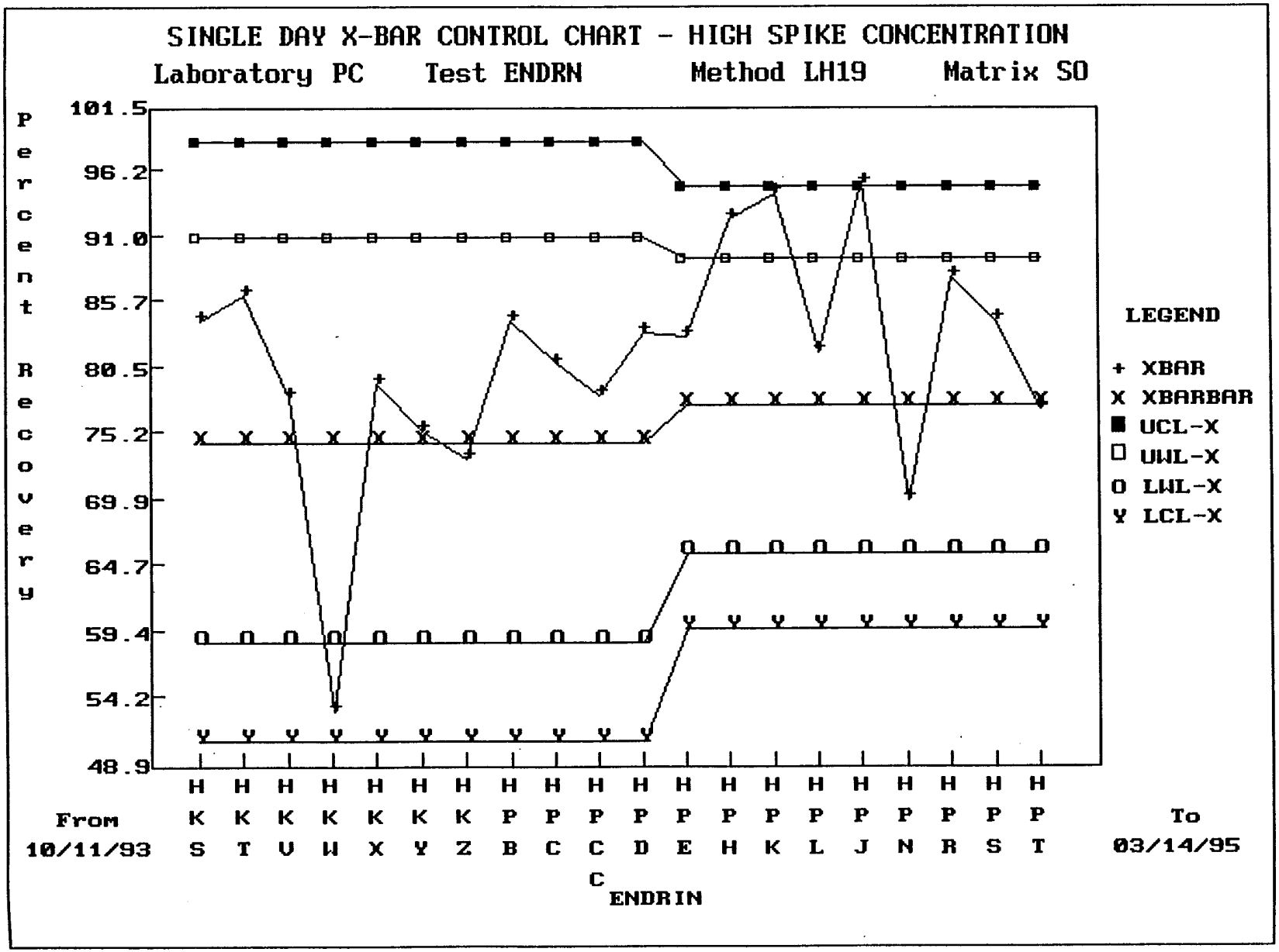

THREE DAY RANGE CONTROL CHART
Laboratory PC Test DLDRN Method LH19 Matrix SO
Percent Recovery
46.7
42.1
37.4
32.7
28.0
23.4
18.7
14.0
9.3
4.7
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
DIELDRIN

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR DIELDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: DLDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.00	-2	1.80	-2	90.0	21.0	26.0	20.7
	052794	HPN	2.00	-2	1.62	-2	81.0	9.0	26.0	20.7
	082494	HPR	2.00	-2	1.79	-2	89.5	9.0	26.0	20.7
	092994	HPS	2.00	-2	1.81	-2	90.5	9.5	26.0	20.7
	031495	HPT	2.00	-2	1.44	-2	72.1	18.5	26.0	20.7

* Changes made to data

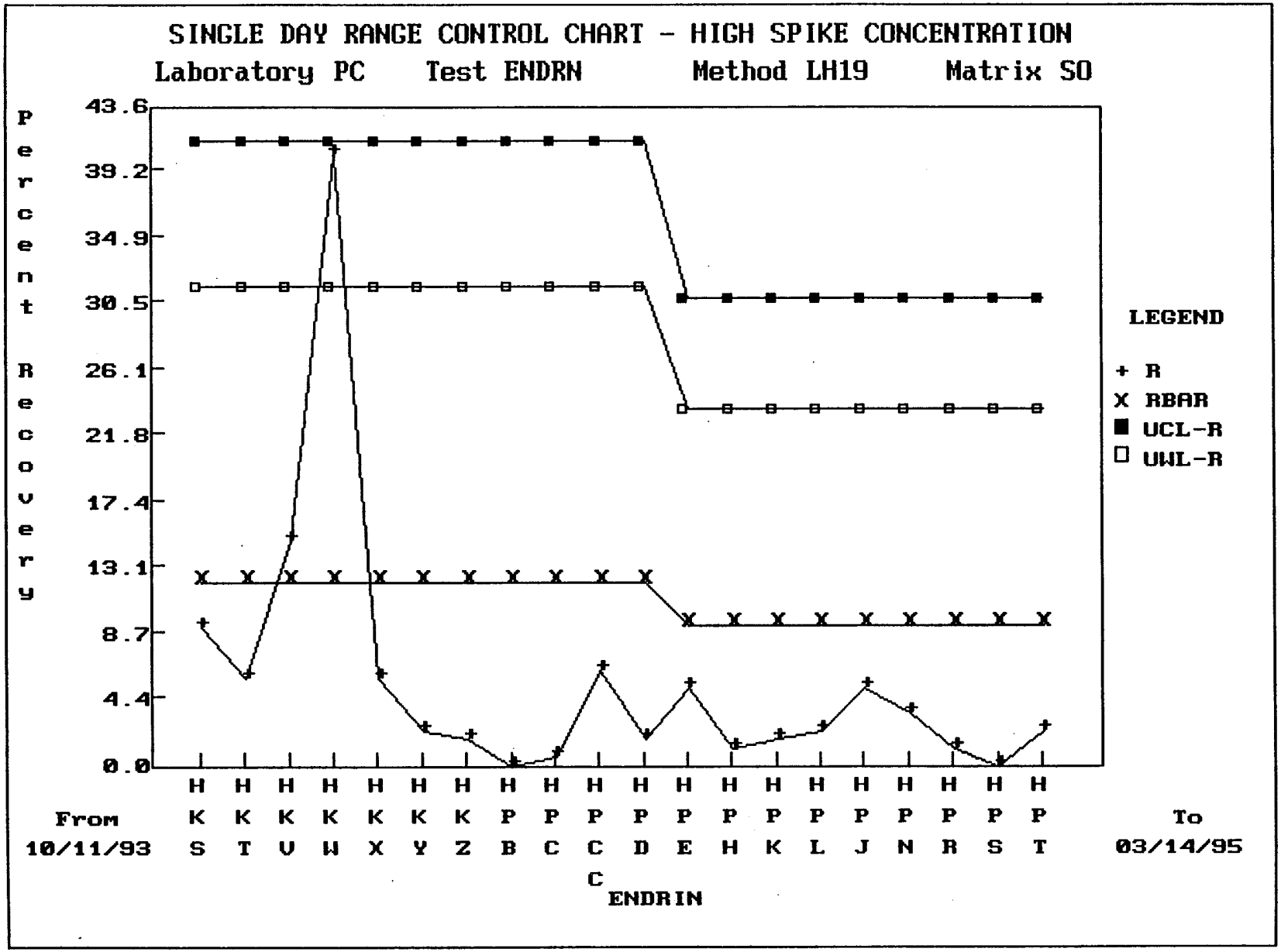

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test ENDRN Method LH19 Matrix SO
Percent Recovery
101.5
96.2
91.0
85.7
80.5
75.2
69.9
64.7
59.4
54.2
48.9
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
LWL-X
LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
ENDRIN

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR ENDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ENDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	1.51	-1	1.41	-1	1.49	-1	93.4	98.7	96.0	95.8	89.8	66.0	60.0	.F.
	052794	HPN	1.51	-1	1.03	-1	1.09	-1	68.2	72.2	70.2	95.8	89.8	66.0	60.0	.F.
	082494	HPR	1.51	-1	1.34	-1	1.32	-1	88.7	87.4	88.1	95.8	89.8	66.0	60.0	.F.
	092994	HPS	1.51	-1	1.28	-1	1.28	-1	84.8	84.8	84.8	95.8	89.8	66.0	60.0	.F.
	031495	HPT	1.51	-1	1.15	-1	1.19	-1	76.2	78.8	77.5	95.8	89.8	66.0	60.0	.F.

* Changes made to data

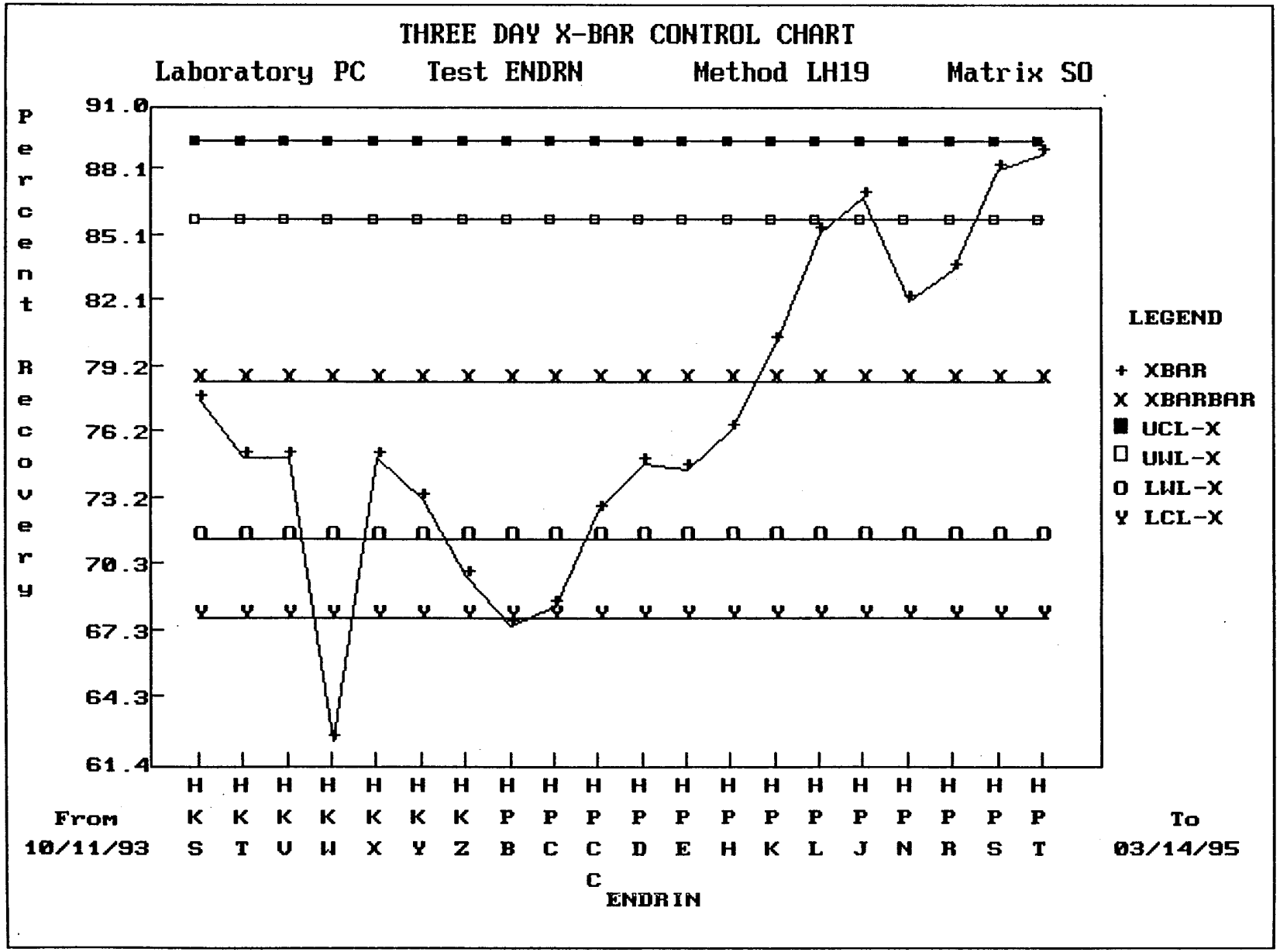

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test ENDRN Method LH19 Matrix SO
Percent Recovery
43.6
39.2
34.9
30.5
26.1
21.8
17.4
13.1
8.7
4.4
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
ENDRIN

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR ENDRIN

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: ENDRN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	1.51	-1	1.41	-1	1.49	-1	93.4	98.7	5.3	31.0	23.9
	052794	HPN	1.51	-1	1.03	-1	1.09	-1	68.2	72.2	4.0	31.0	23.9
	082494	HPR	1.51	-1	1.34	-1	1.32	-1	88.7	87.4	1.3	31.0	23.9
	092994	HPS	1.51	-1	1.28	-1	1.28	-1	84.8	84.8	0.0	31.0	23.9
	031495	HPT	1.51	-1	1.15	-1	1.19	-1	76.2	78.8	2.6	31.0	23.9

* Changes made to data


THREE DAY X-BAR CONTROL CHART
Laboratory PC Test ENDRN Method LH19 Matrix SO
Percent Recovery
91.0
88.1
85.1
82.1
79.2
76.2
73.2
70.3
67.3
64.3
61.4
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
ENDRIN

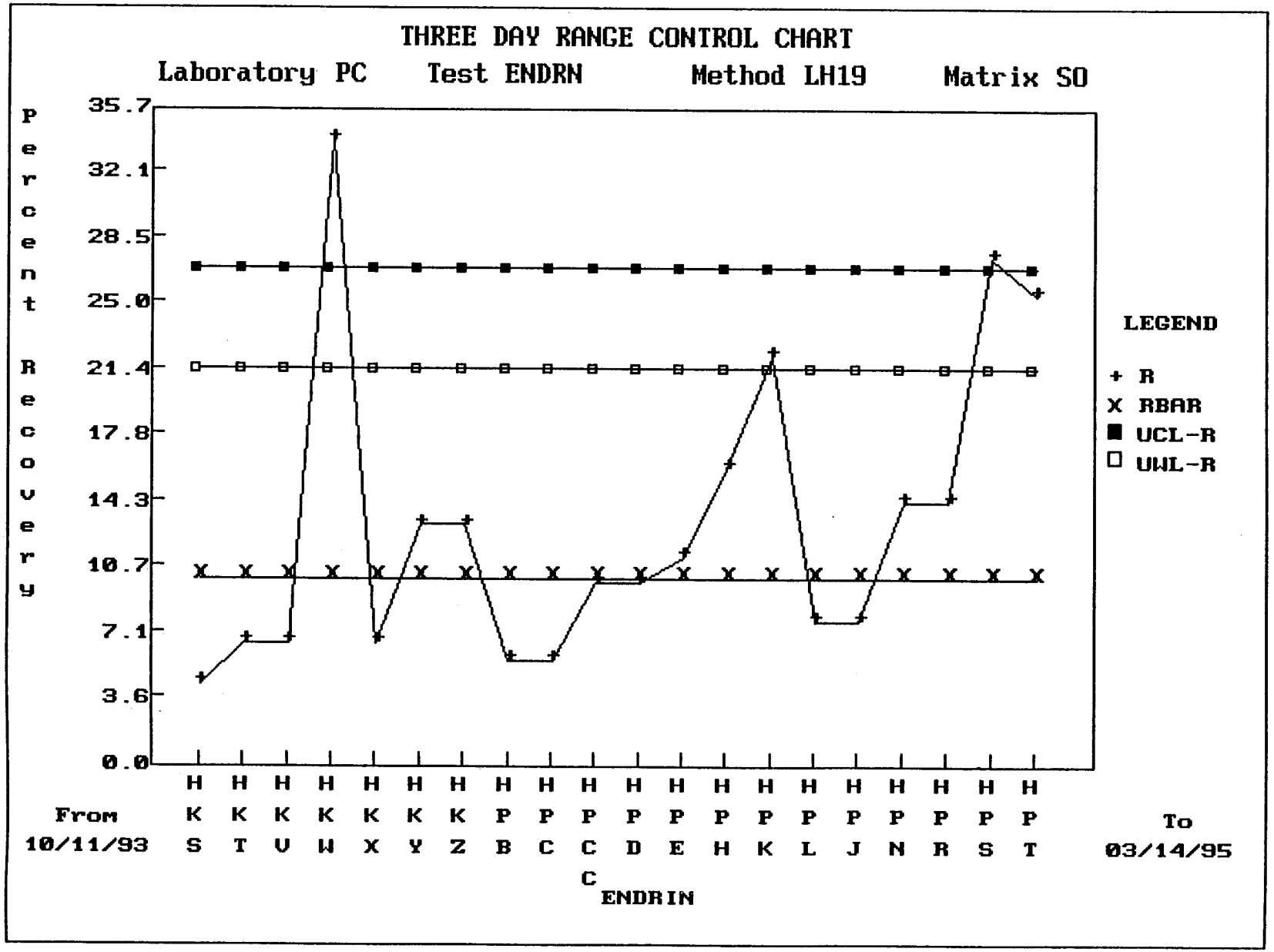
THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR ENDRIN

Laboratory: PC	Date: 04/28/95

Method: LH19	Matrix: SO	Test Name: ENDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.01	-2	1.80	-2	89.6	87.2	89.7	86.1	71.7	68.1	.F.
	052794	HPN	2.01	-2	1.51	-2	75.1	82.3	89.7	86.1	71.7	68.1	.F.
	082494	HPR	2.01	-2	1.74	-2	86.6	83.8	89.7	86.1	71.7	68.1	.F.
	092994	HPS	2.01	-2	2.07	-2	103.0	88.2	89.7	86.1	71.7	68.1	.F.
	031495	HPT	2.01	-2	1.56	-2	77.4	89.0	89.7	86.1	71.7	68.1	.F.

* Changes made to data


THREE DAY RANGE CONTROL CHART
Laboratory PC Test ENDRN Method LH19 Matrix SO
Percent Recovery
35.7
32.1
28.5
25.0
21.4
17.8
14.3
10.7
7.1
3.6
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
ENDRIN

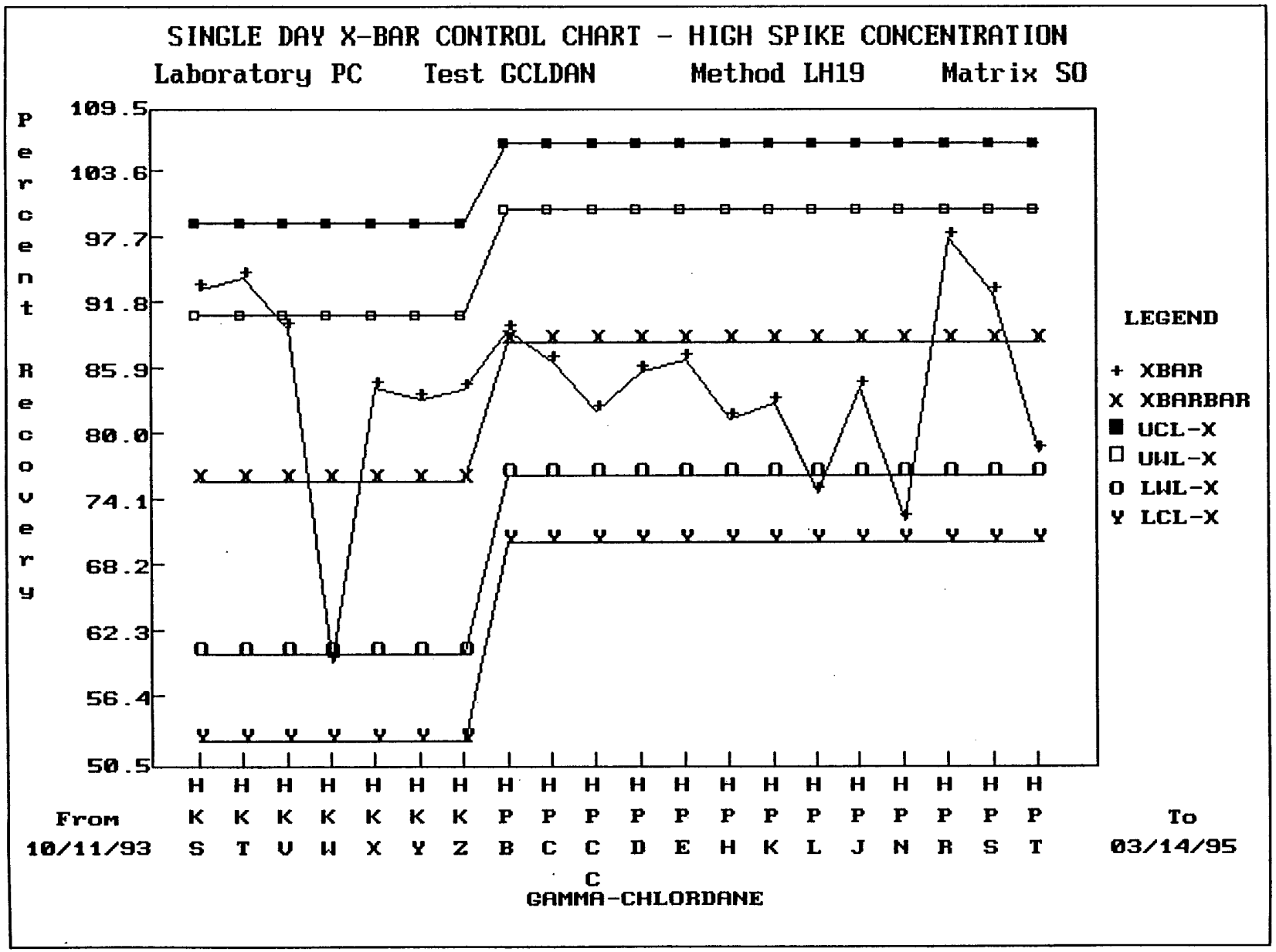
THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR ENDRIN

Laboratory: PC	Date: 04/28/95

Method: LH19	Matrix: SO	Test Name: ENDRN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.01	-2	1.80	-2	89.6	8.0	27.3	21.7
	052794	HPN	2.01	-2	1.51	-2	75.1	14.4	27.3	21.7
	082494	HPR	2.01	-2	1.74	-2	86.6	14.4	27.3	21.7
	092994	HPS	2.01	-2	2.07	-2	103.0	27.9	27.3	21.7
	031495	HPT	2.01	-2	1.56	-2	77.4	25.6	27.3	21.7

* Changes made to data

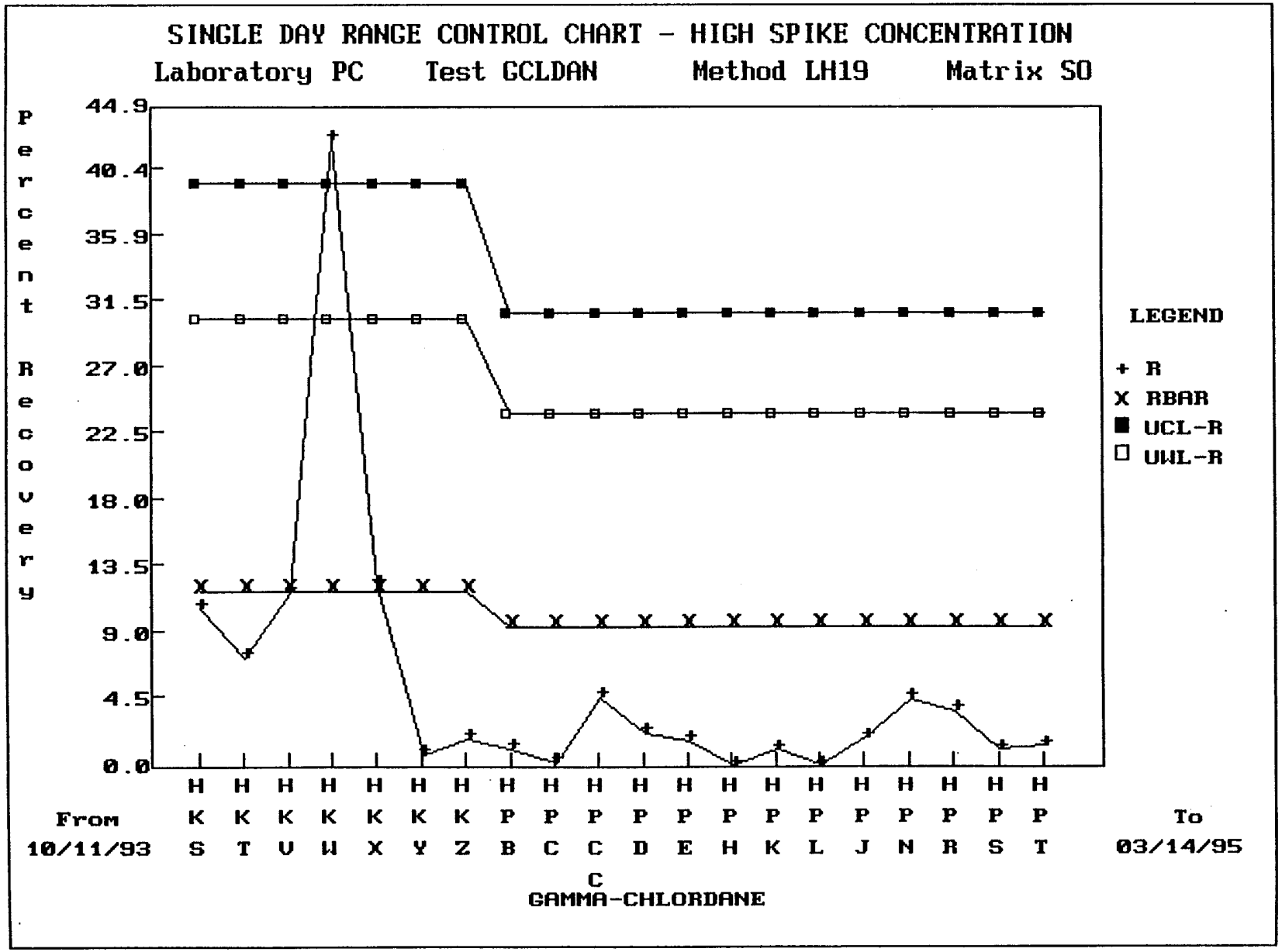

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test GCLDAN Method LH19 Matrix SO
Percent Recovery
109.5
103.6
97.7
91.8
85.9
80.0
74.1
68.2
62.3
56.4
50.5
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
GAMMA-CHLORDANE

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR GAMMA-CHLORDANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: GCLDAN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.61	-2	6.38	-2	6.55	-2	83.8	86.1	85.0	106.8	100.8	76.8	70.8	.F.
	052794	HPN	7.61	-2	5.38	-2	5.72	-2	70.7	75.2	72.9	106.8	100.8	76.8	70.8	.F.
	082494	HPR	7.61	-2	7.29	-2	7.61	-2	95.8	100.0	97.9	106.8	100.8	76.8	70.8	.F.
	092994	HPS	7.61	-2	7.13	-2	7.03	-2	93.7	92.4	93.0	106.8	100.8	76.8	70.8	.F.
	031495	HPT	7.61	-2	5.96	-2	6.09	-2	78.4	80.0	79.2	106.8	100.8	76.8	70.8	.F.

* Changes made to data

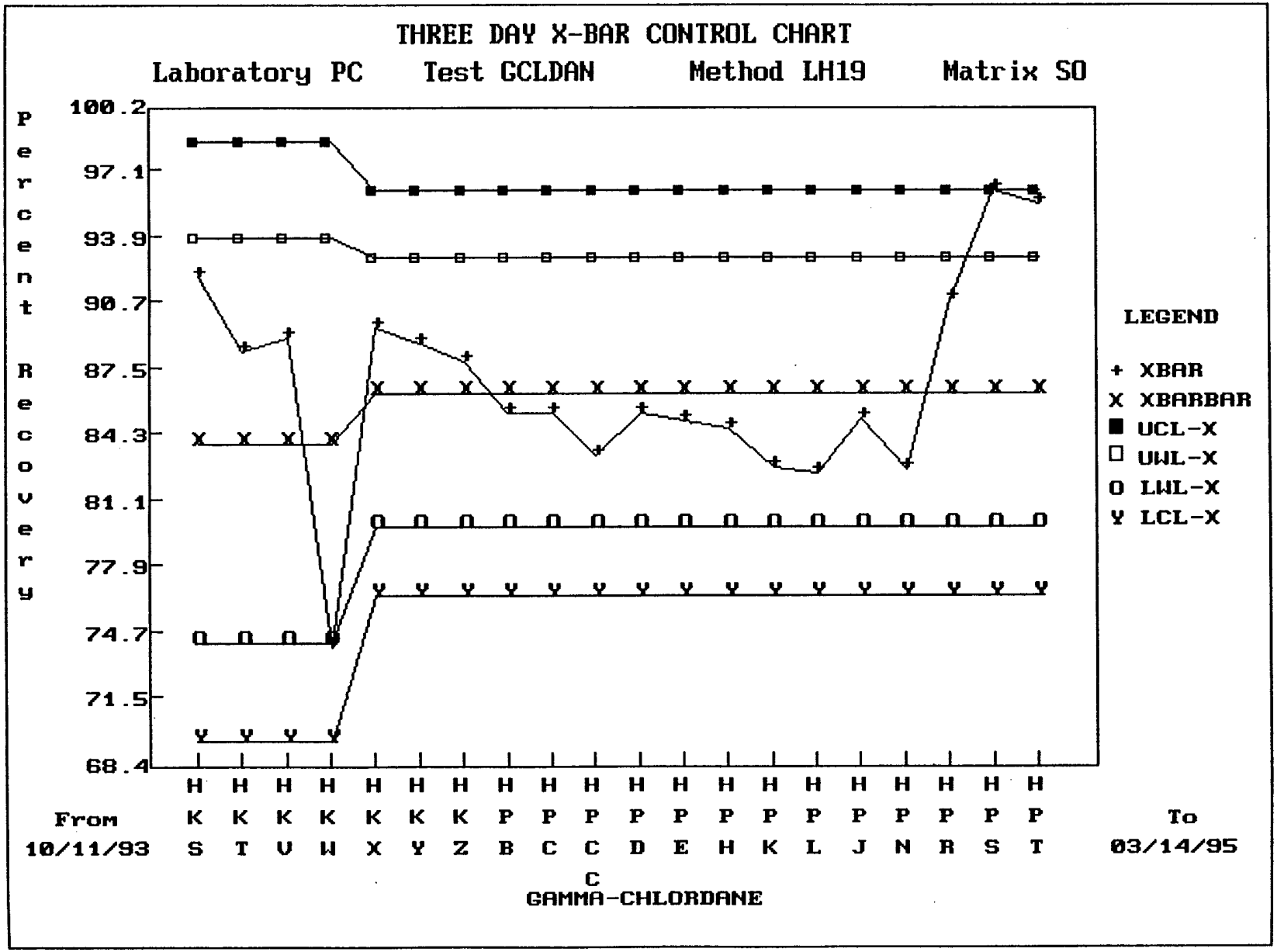

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test GCLDAN Method LH19 Matrix SO
Percent Recovery
44.9
40.4
35.9
31.5
27.0
22.5
18.0
13.5
9.0
4.5
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
GAMMA-CHLORDANE

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR GAMMA-CHLORDANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: GCLDAN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.61	-2	6.38	-2	6.55	-2	83.8	86.1	2.2	31.4	24.1
	052794	HPN	7.61	-2	5.38	-2	5.72	-2	70.7	75.2	4.5	31.4	24.1
	082494	HPR	7.61	-2	7.29	-2	7.61	-2	95.8	100.0	4.2	31.4	24.1
	092994	HPS	7.61	-2	7.13	-2	7.03	-2	93.7	92.4	1.3	31.4	24.1
	031495	HPT	7.61	-2	5.96	-2	6.09	-2	78.4	80.0	1.6	31.4	24.1

* Changes made to data


THREE DAY X-BAR CONTROL CHART
Laboratory PC Test GCLDAN Method LH19 Matrix SO
Percent Recovery
100.2
97.1
93.9
90.7
87.5
84.3
81.1
77.9
74.7
71.5
68.4
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
GAMMA-CHLORDANE

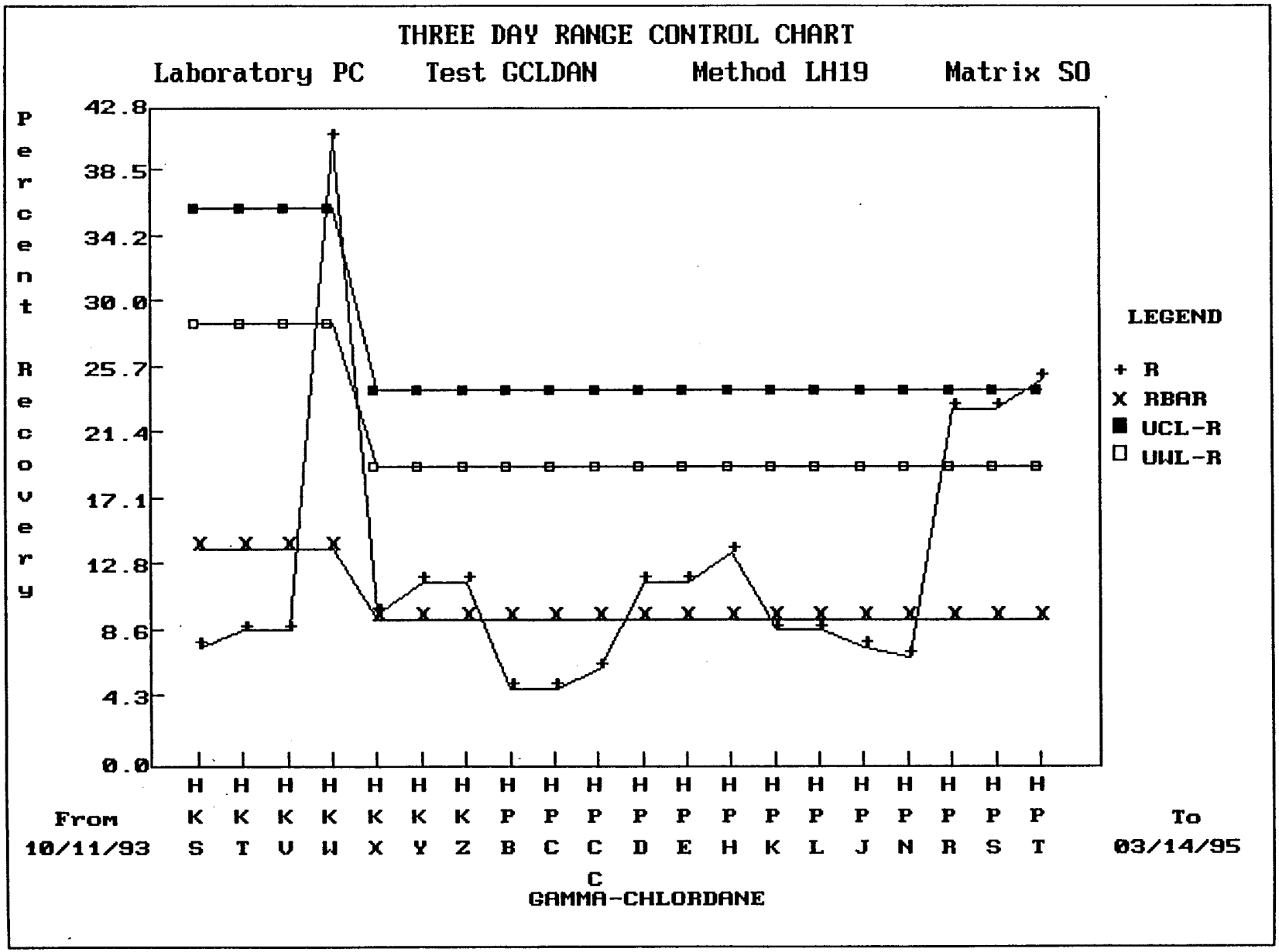
THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR GAMMA-CHLORDANE

Laboratory: PC	Date: 04/28/95

Method: LH19	Matrix: SO	Test Name: GCLDAN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	4.00	-2	3.50	-2	87.5	85.3	96.5	93.2	80.2	76.9	.F.
	052794	HPN	4.00	-2	3.24	-2	81.0	82.9	96.5	93.2	80.2	76.9	.F.
	082494	HPR	4.00	-2	4.17	-2	104.3	90.9	96.5	93.2	80.2	76.9	.F.
	092994	HPS	4.00	-2	4.17	-2	104.3	96.5	96.5	93.2	80.2	76.9	.F.
	031495	HPT	4.00	-2	3.16	-2	78.9	95.8	96.5	93.2	80.2	76.9	.F.

* Changes made to data

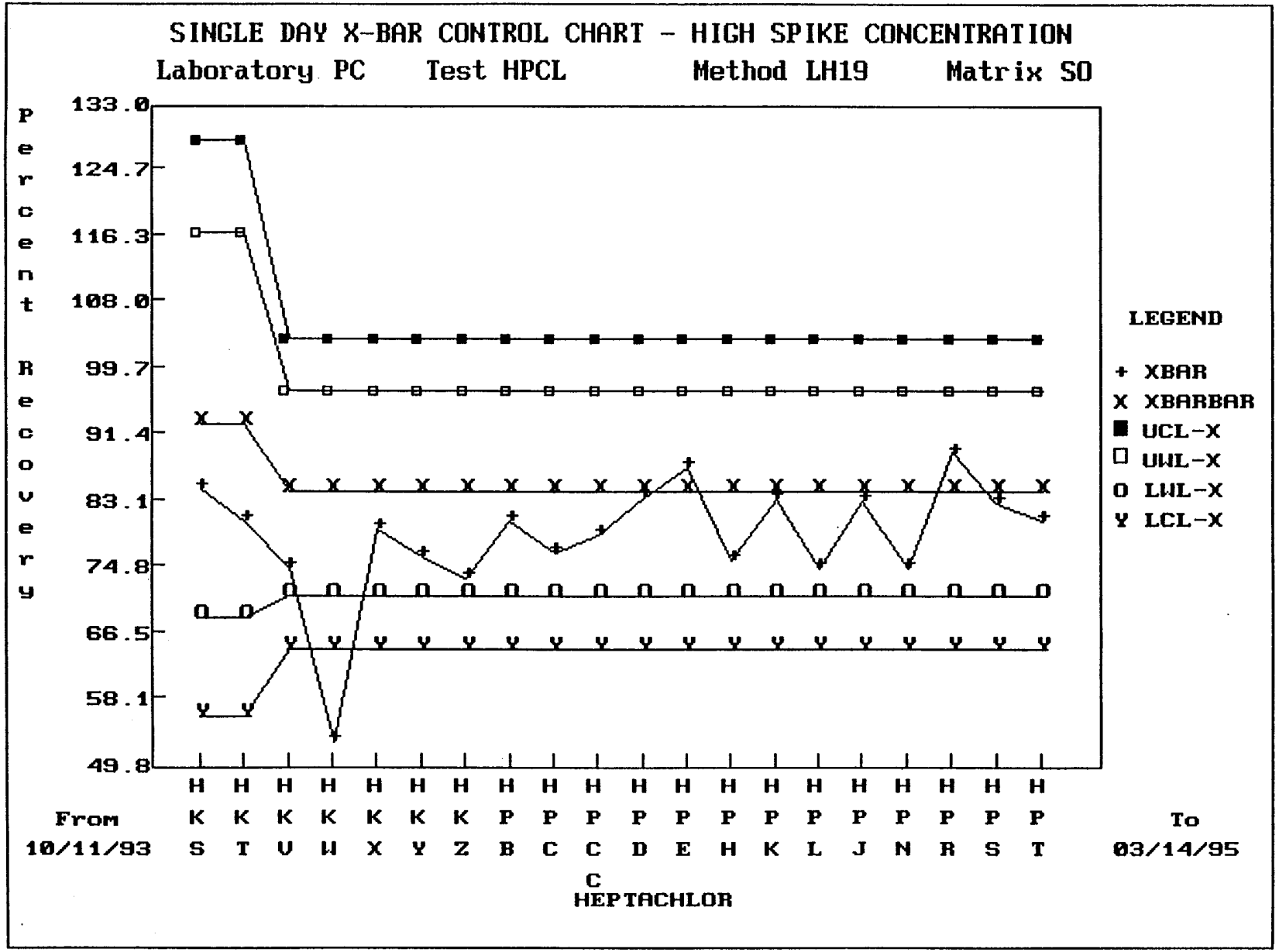

THREE DAY RANGE CONTROL CHART
Laboratory PC Test GCLDAN Method LH19 Matrix SO
Percent Recovery
42.8
38.5
34.2
30.0
25.7
21.4
17.1
12.8
8.6
4.3
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
GAMMA-CHLORDANE

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR GAMMA-CHLORDANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: GCLDAN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	4.00	-2	3.50	-2	87.5	8.0	24.7	19.7
	052794	HPN	4.00	-2	3.24	-2	81.0	7.3	24.7	19.7
	082494	HPR	4.00	-2	4.17	-2	104.3	23.3	24.7	19.7
	092994	HPS	4.00	-2	4.17	-2	104.3	23.3	24.7	19.7
	031495	HPT	4.00	-2	3.16	-2	78.9	25.4	24.7	19.7

* Changes made to data

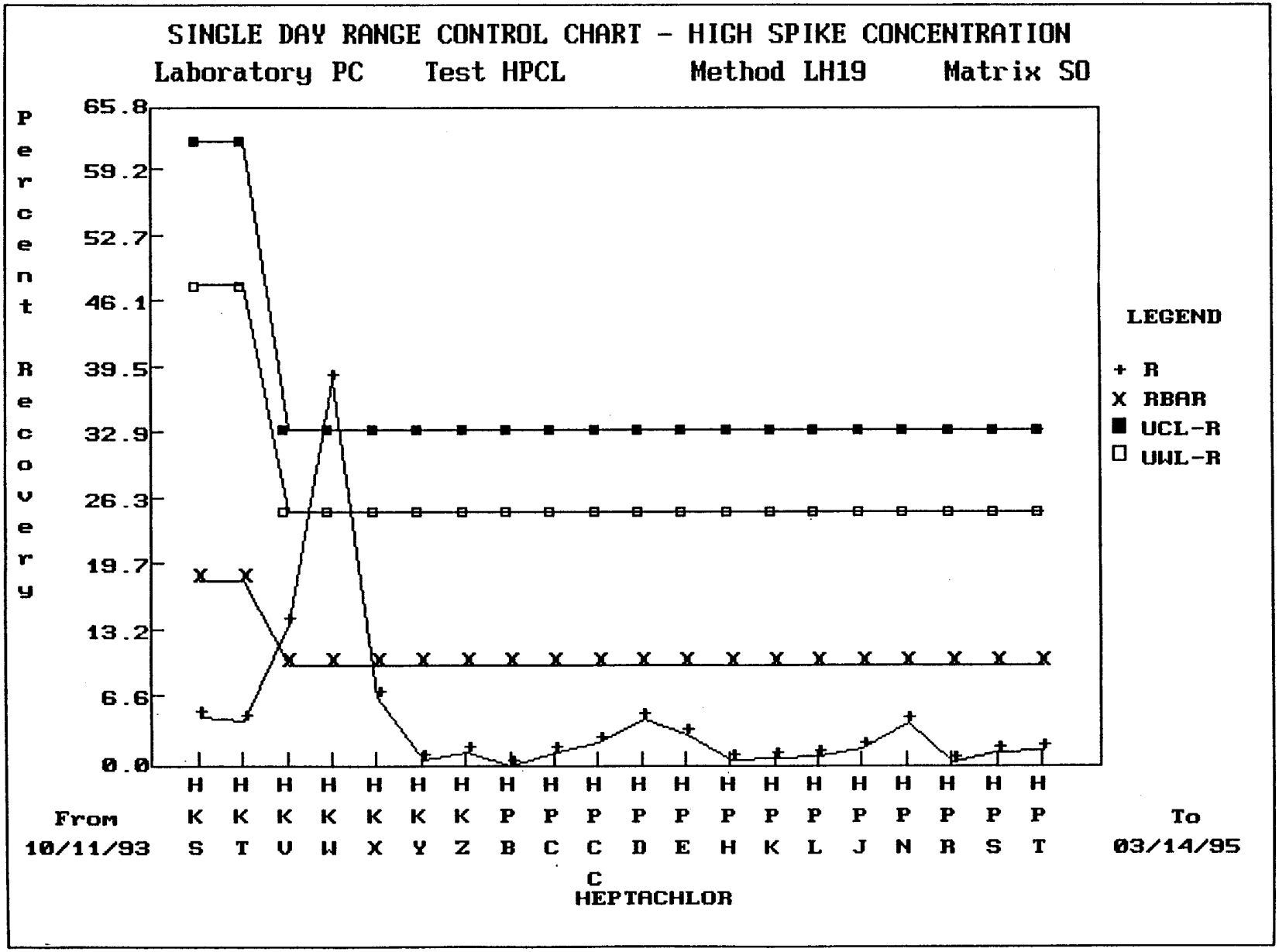

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test HPCL Method LH19 Matrix SO
Percent Recovery
133.0
124.7
116.3
108.0
99.7
91.4
83.1
74.8
66.5
58.1
49.8
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
C
HEPTACHLOR

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR HEPTACHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: HPCL

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.41	-2	6.10	-2	6.25	-2	82.3	84.3	83.3	104.3	97.8	72.0	65.5	.F.
	052794	HPN	7.41	-2	5.36	-2	5.72	-2	72.3	77.2	74.8	104.3	97.8	72.0	65.5	.F.
	082494	HPR	7.41	-2	6.70	-2	6.67	-2	90.4	90.0	90.2	104.3	97.8	72.0	65.5	.F.
	092994	HPS	7.41	-2	6.21	-2	6.10	-2	83.8	82.3	83.1	104.3	97.8	72.0	65.5	.F.
	031495	HPT	7.41	-2	5.97	-2	6.11	-2	80.6	82.5	81.5	104.3	97.8	72.0	65.5	.F.

* Changes made to data

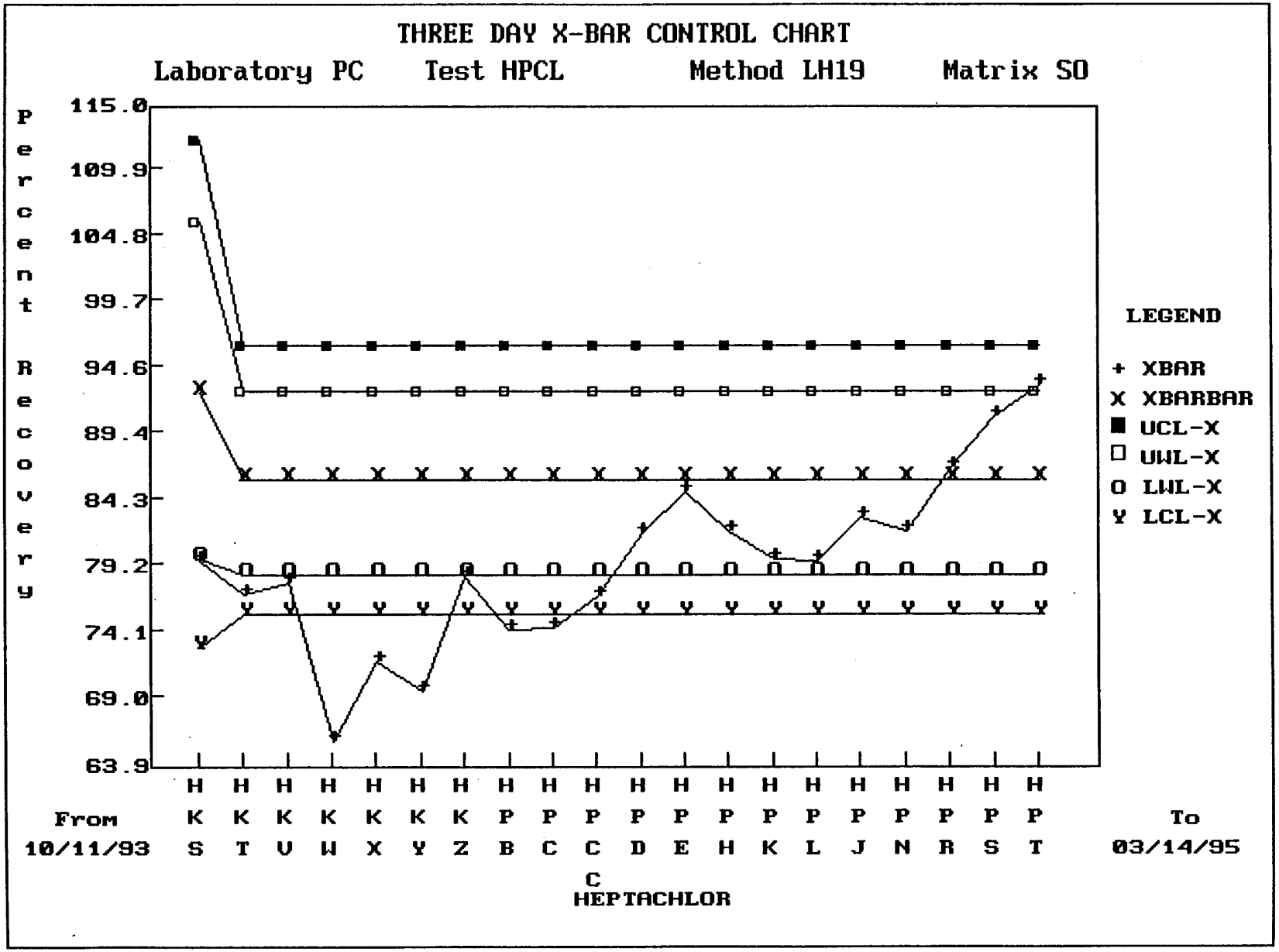

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test HPCL Method LH19 Matrix SO
Percent Recovery
65.8
59.2
52.7
46.1
39.5
32.9
26.3
19.7
13.2
6.6
0.0
LEGEND
+ R
X RBAR
■ UCL-R
□ UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C HEPTACHLOR

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR HEPTACHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: HPCL

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.41	-2	6.10	-2	6.25	-2	82.3	84.3	2.0	33.7	25.9
	052794	HPN	7.41	-2	5.36	-2	5.72	-2	72.3	77.2	4.8	33.7	25.9
	082494	HPR	7.41	-2	6.70	-2	6.67	-2	90.4	90.0	0.4	33.7	25.9
	092994	HPS	7.41	-2	6.21	-2	6.10	-2	83.8	82.3	1.5	33.7	25.9
	031495	HPT	7.41	-2	5.97	-2	6.11	-2	80.6	82.5	1.8	33.7	25.9

* Changes made to data

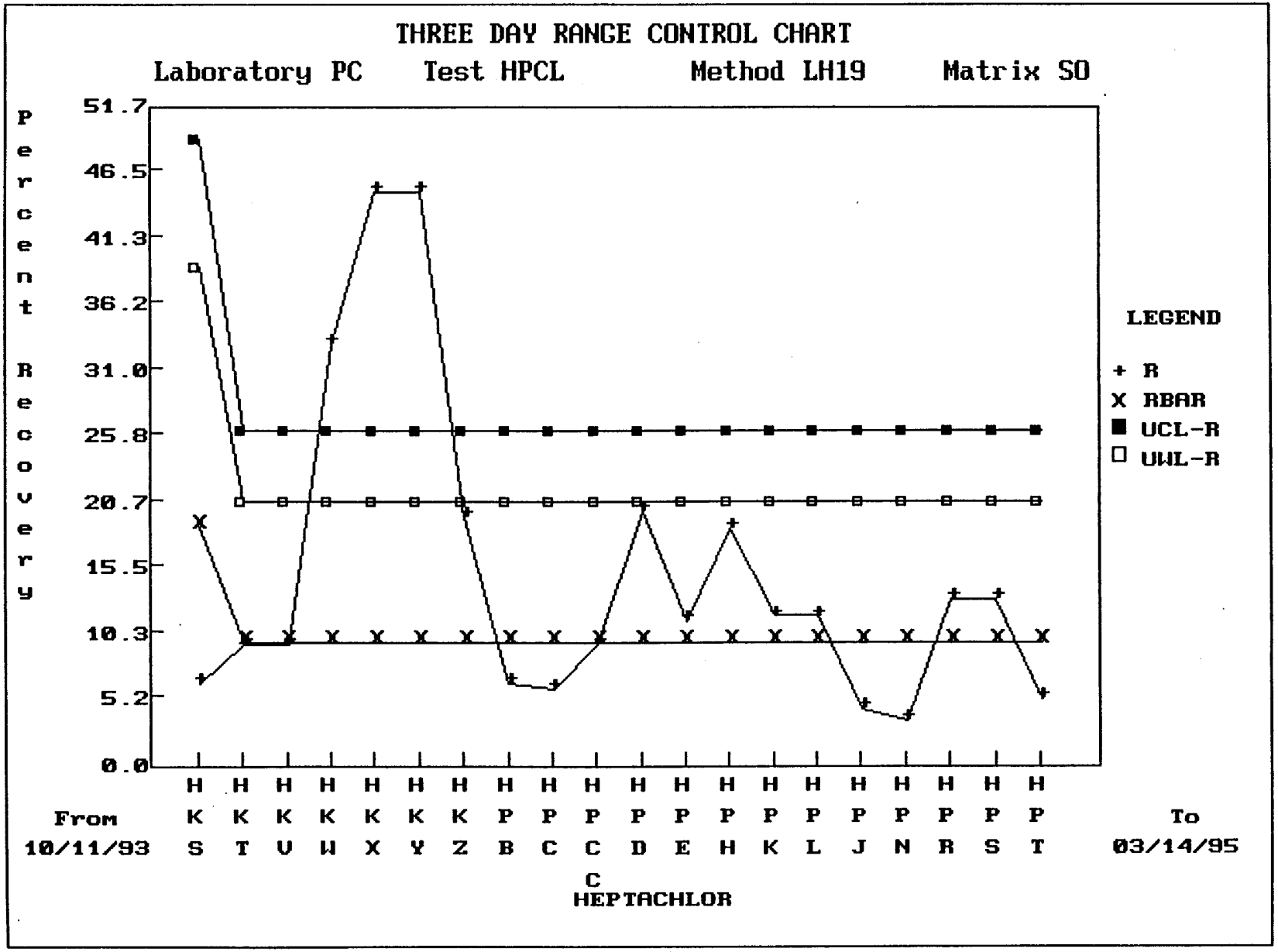

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test HPCL Method LH19 Matrix SO
Percent Recovery
115.0
109.9
104.8
99.7
94.6
89.4
84.3
79.2
74.1
69.0
63.9
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C HEPTACHLOR

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR HEPTACHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: HPCL

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.00	-2	1.69	-2	84.5	83.5	96.6	93.2	79.2	75.8	.F.
	052794	HPN	2.00	-2	1.64	-2	82.0	82.3	96.6	93.2	79.2	75.8	.F.
	082494	HPR	2.00	-2	1.91	-2	95.5	87.3	96.6	93.2	79.2	75.8	.F.
	092994	HPS	2.00	-2	1.91	-2	95.5	91.0	96.6	93.2	79.2	75.8	.F.
	031495	HPT	2.00	-2	1.81	-2	90.3	93.8	96.6	93.2	79.2	75.8	.F.

* Changes made to data

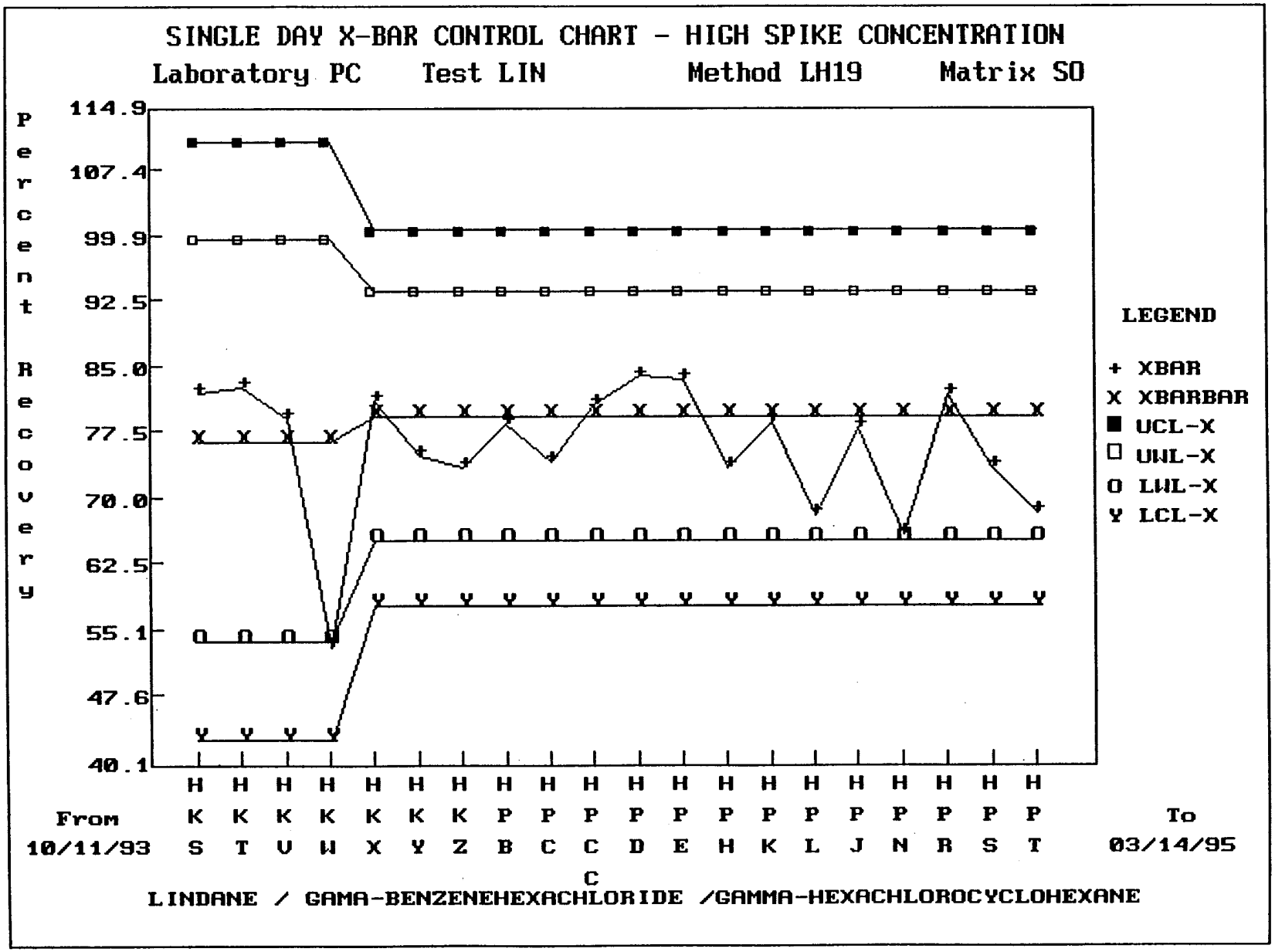

THREE DAY RANGE CONTROL CHART
Laboratory PC Test HPCL Method LH19 Matrix SO
Percent Recovery
51.7
46.5
41.3
36.2
31.0
25.8
20.7
15.5
10.3
5.2
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
HEPTACHLOR

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR HEPTACHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: HPCL

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.00	-2	1.69	-2	84.5	5.0	26.3	20.9
	052794	HPN	2.00	-2	1.64	-2	82.0	4.0	26.3	20.9
	082494	HPR	2.00	-2	1.91	-2	95.5	13.5	26.3	20.9
	092994	HPS	2.00	-2	1.91	-2	95.5	13.5	26.3	20.9
	031495	HPT	2.00	-2	1.81	-2	90.3	5.2	26.3	20.9

* Changes made to data


SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test LIN Method LH19 Matrix SO
Percent Recovery
114.9
107.4
99.9
92.5
85.0
77.5
70.0
62.5
55.1
47.6
40.1
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

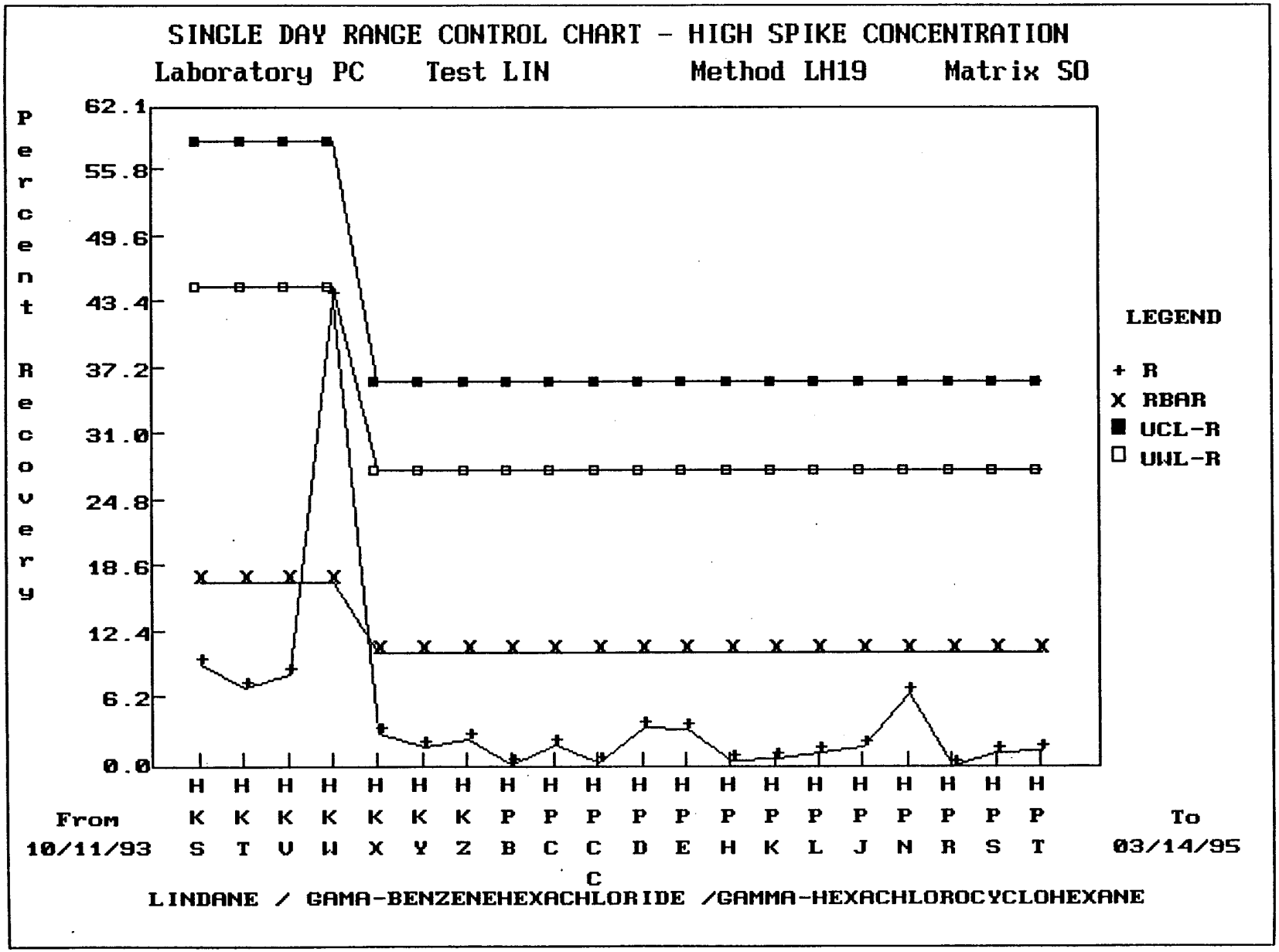
SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

Laboratory: PC	Date: 04/28/95

Method: LH19	Matrix: SO	Test Name: LIN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.41	-2	5.73	-2	5.89	-2	77.3	79.5	78.4	101.1	94.0	65.8	58.7	.F.
	052794	HPN	7.41	-2	4.68	-2	5.19	-2	63.2	70.0	66.6	101.1	94.0	65.8	58.7	.F.
	082494	HPR	7.41	-2	6.11	-2	6.11	-2	82.5	82.5	82.5	101.1	94.0	65.8	58.7	.F.
	092994	HPS	7.41	-2	5.55	-2	5.45	-2	74.9	73.6	74.2	101.1	94.0	65.8	58.7	.F.
	031495	HPT	7.41	-2	5.07	-2	5.19	-2	68.4	70.0	69.2	101.1	94.0	65.8	58.7	.F.

* Changes made to data

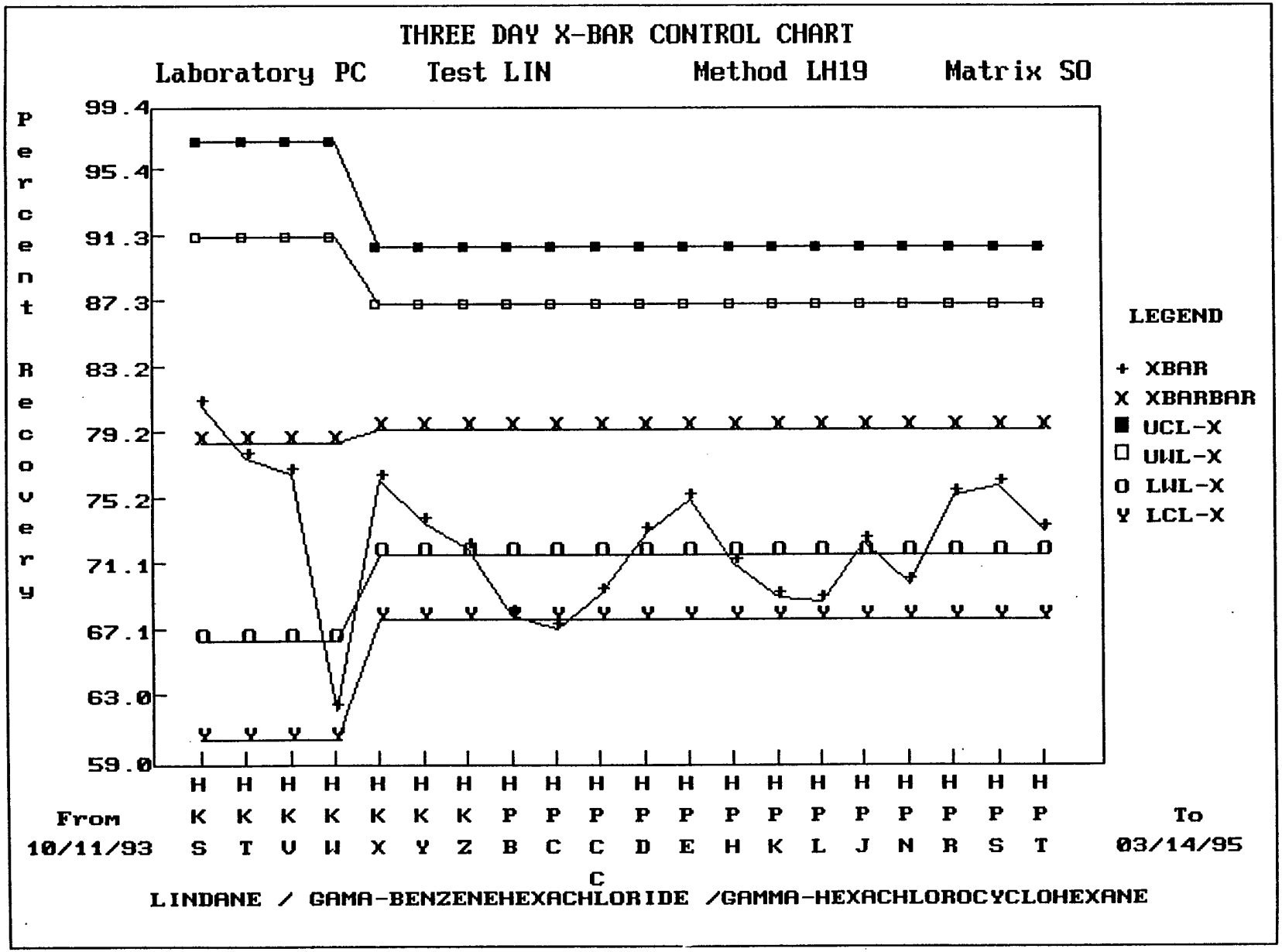

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test LIN Method LH19 Matrix SO
Percent Recovery
62.1
55.8
49.6
43.4
37.2
31.0
24.8
18.6
12.4
6.2
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: LIN

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.41	-2	5.73	-2	5.89	-2	77.3	79.5	2.2	36.9	28.4
	052794	HPN	7.41	-2	4.68	-2	5.19	-2	63.2	70.0	6.9	36.9	28.4
	082494	HPR	7.41	-2	6.11	-2	6.11	-2	82.5	82.5	0.0	36.9	28.4
	092994	HPS	7.41	-2	5.55	-2	5.45	-2	74.9	73.6	1.4	36.9	28.4
	031495	HPT	7.41	-2	5.07	-2	5.19	-2	68.4	70.0	1.6	36.9	28.4

* Changes made to data

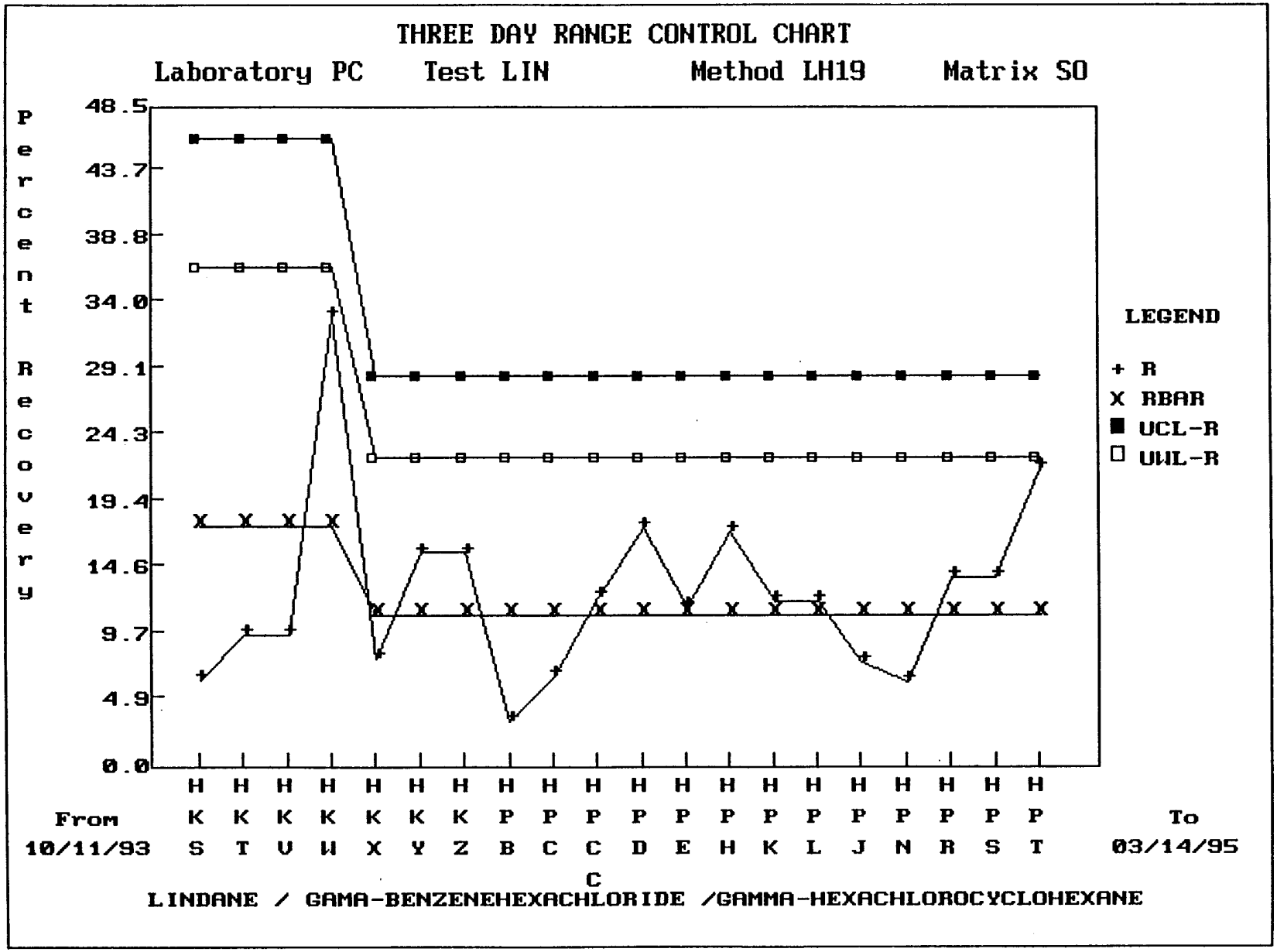

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test LIN Method LH19 Matrix SO
Percent Recovery
99.4
95.4
91.3
87.3
83.2
79.2
75.2
71.1
67.1
63.0
59.0
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: LIN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	4.00	-2	2.97	-2	74.2	72.8	91.2	87.3	71.9	68.0	.F.
	052794	HPN	4.00	-2	2.76	-2	69.0	70.4	91.2	87.3	71.9	68.0	.F.
	082494	HPR	4.00	-2	3.34	-2	83.5	75.6	91.2	87.3	71.9	68.0	.F.
	092994	HPS	4.00	-2	3.04	-2	76.0	76.2	91.2	87.3	71.9	68.0	.F.
	031495	HPT	4.00	-2	2.45	-2	61.3	73.6	91.2	87.3	71.9	68.0	.F.

* Changes made to data

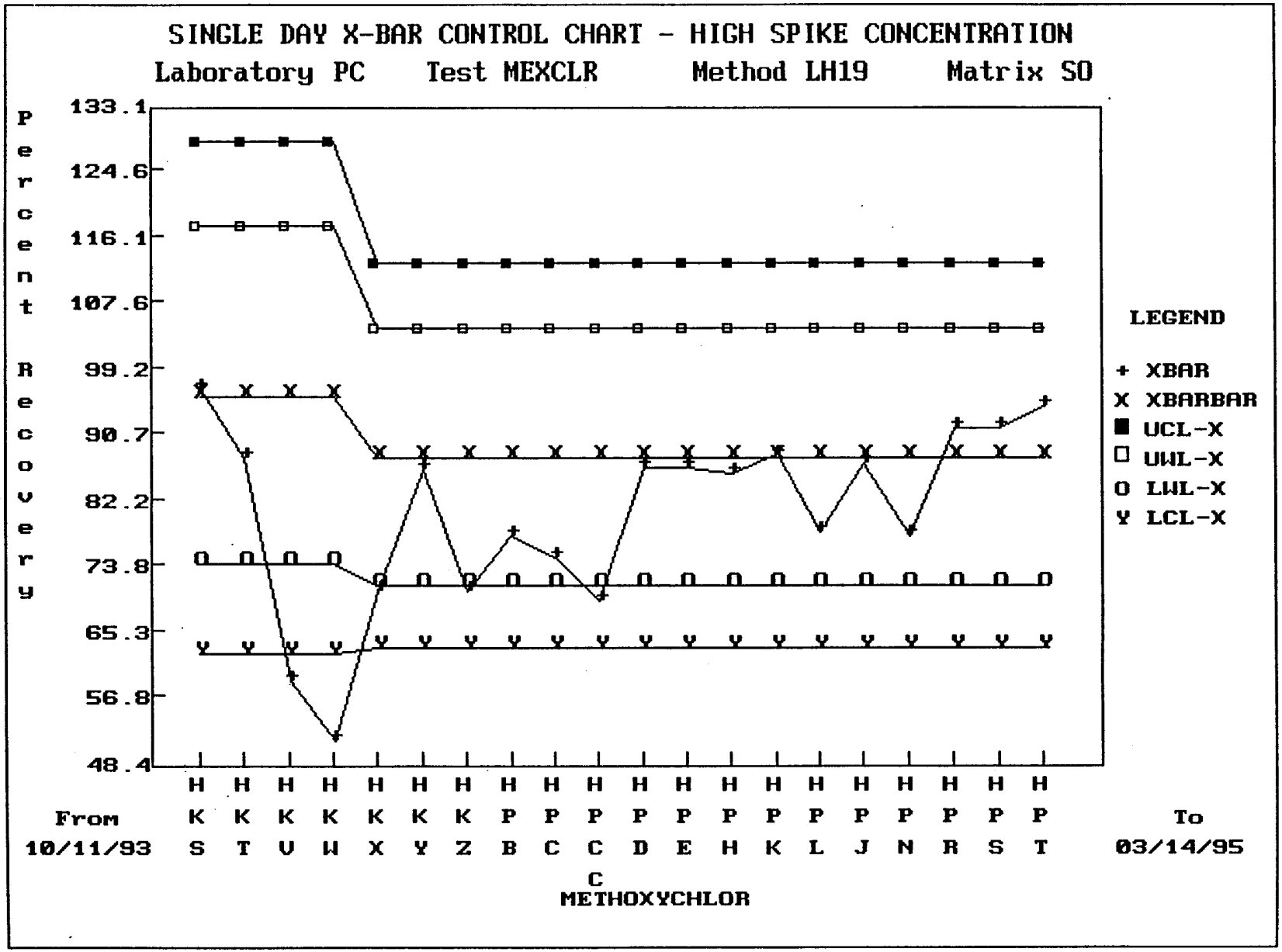

THREE DAY RANGE CONTROL CHART
Laboratory PC Test LIN Method LH19 Matrix SO
Percent Recovery
48.5
43.7
38.8
34.0
29.1
24.3
19.4
14.6
9.7
4.9
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR LINDANE / GAMA-BENZENEHEXACHLORIDE /GAMMA-HEXACHLOROCYCLOHEXANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: LIN

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	4.00	-2	2.97	-2	74.2	8.0	29.1	23.2
	052794	HPN	4.00	-2	2.76	-2	69.0	6.3	29.1	23.2
	082494	HPR	4.00	-2	3.34	-2	83.5	14.5	29.1	23.2
	092994	HPS	4.00	-2	3.04	-2	76.0	14.5	29.1	23.2
	031495	HPT	4.00	-2	2.45	-2	61.3	22.2	29.1	23.2

* Changes made to data

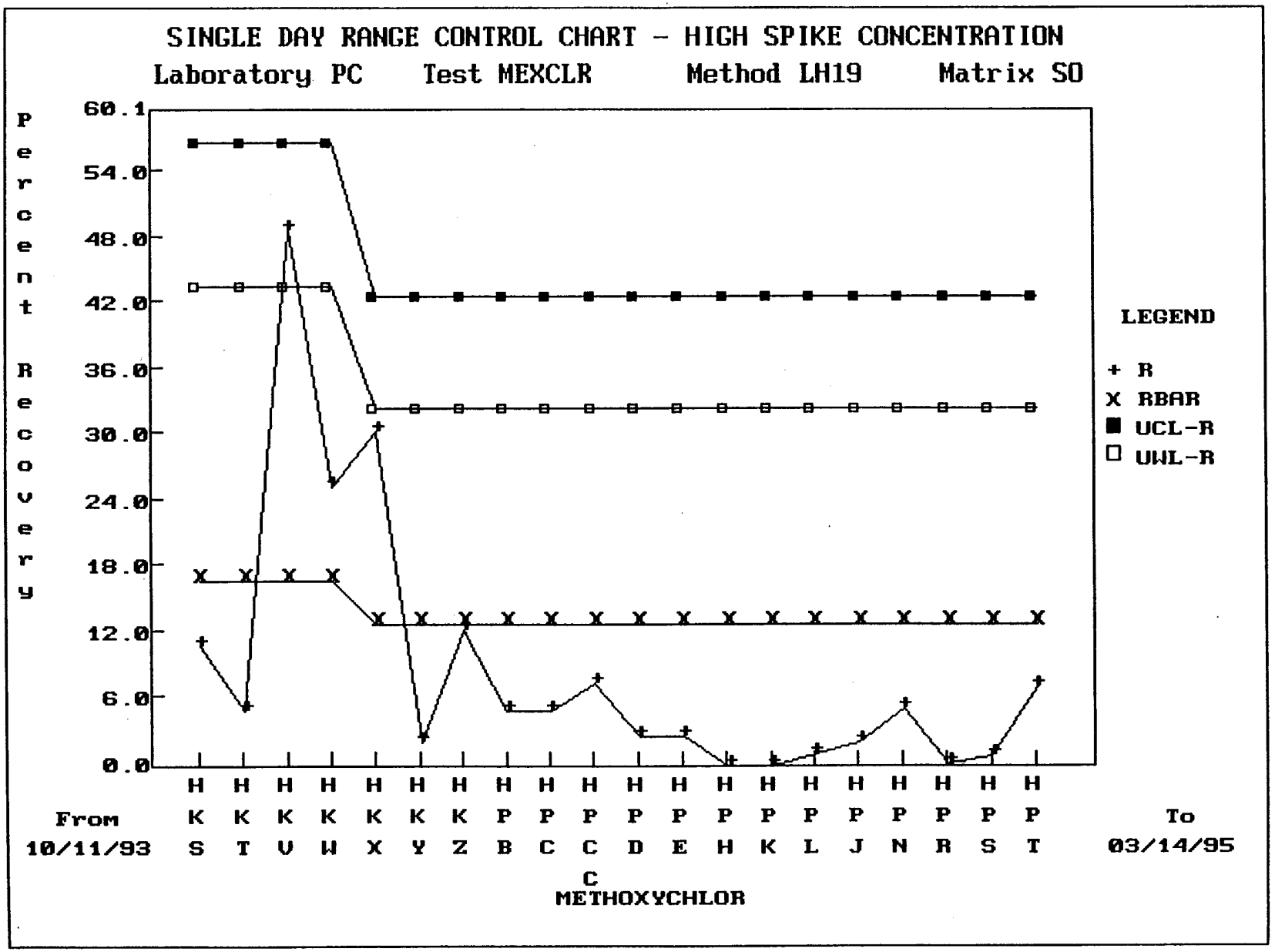

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test MEXCLR Method LH19 Matrix SO
Percent Recovery
133.1
124.6
116.1
107.6
99.2
90.7
82.2
73.8
65.3
56.8
48.4
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
C
METHOXYCHLOR

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR METHOXYCHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: MEXCLR

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	7.51	-1	6.51	-1	6.69	-1	86.7	89.1	87.9	113.5	105.3	72.5	64.3	.F.
	052794	HPN	7.51	-1	5.66	-1	6.10	-1	75.4	81.2	78.3	113.5	105.3	72.5	64.3	.F.
	082494	HPR	7.51	-1	6.92	-1	6.90	-1	92.1	91.9	92.0	113.5	105.3	72.5	64.3	.F.
	092994	HPS	7.51	-1	6.87	-1	6.95	-1	91.5	92.5	92.0	113.5	105.3	72.5	64.3	.F.
	031495	HPT	7.51	-1	6.86	-1	7.41	-1	91.3	98.6	95.0	113.5	105.3	72.5	64.3	.F.

* Changes made to data

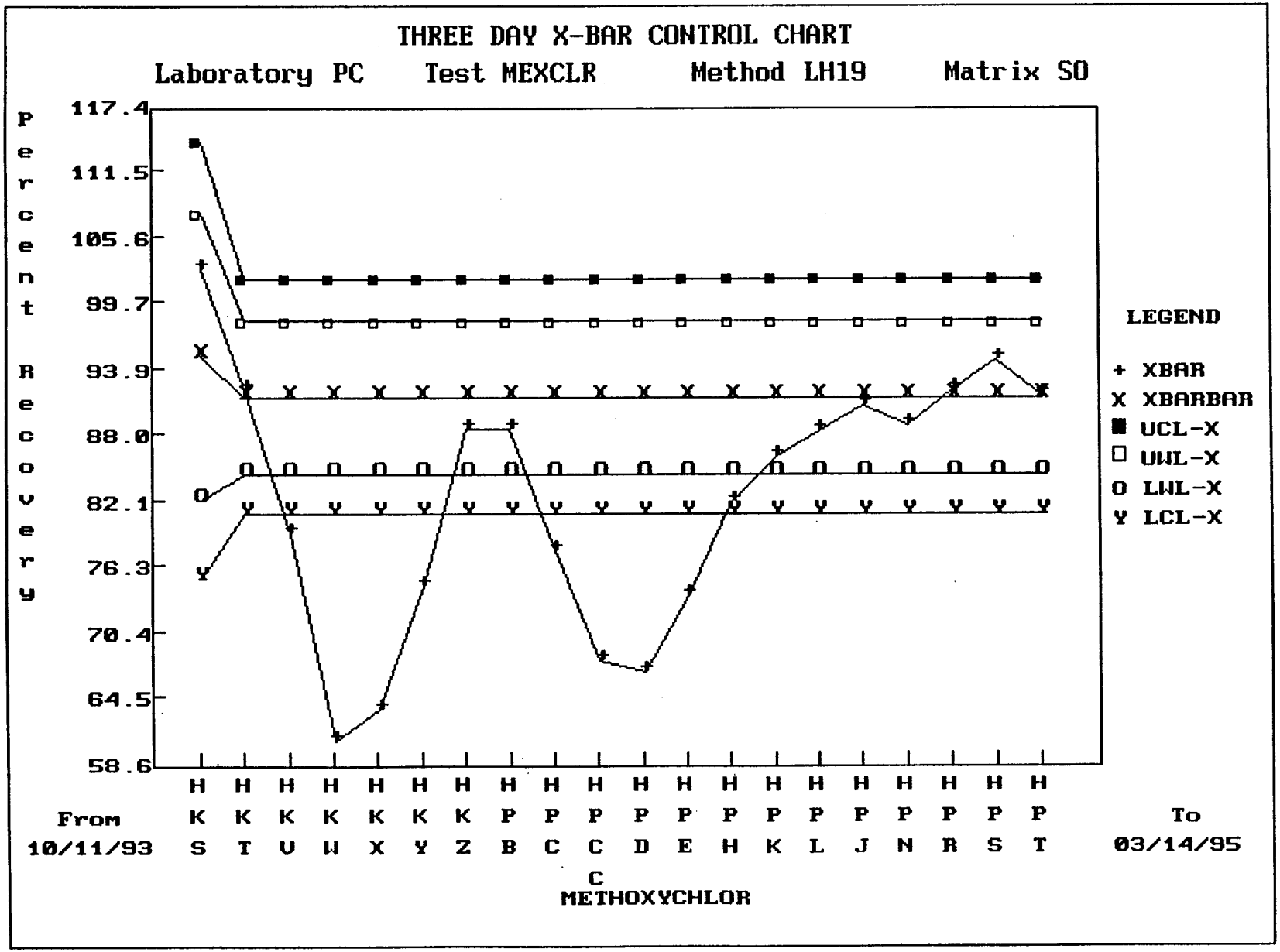

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test MEXCLR Method LH19 Matrix SO
Percent Recovery
60.1
54.0
48.0
42.0
36.0
30.0
24.0
18.0
12.0
6.0
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
METHOXYCHLOR

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR METHOXYCHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: MEXCLR

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	7.51	-1	6.51	-1	6.69	-1	86.7	89.1	2.4	42.8	32.9
	052794	HPN	7.51	-1	5.66	-1	6.10	-1	75.4	81.2	5.8	42.8	32.9
	082494	HPR	7.51	-1	6.92	-1	6.90	-1	92.1	91.9	0.3	42.8	32.9
	092994	HPS	7.51	-1	6.87	-1	6.95	-1	91.5	92.5	1.1	42.8	32.9
	031495	HPT	7.51	-1	6.86	-1	7.41	-1	91.3	98.6	7.3	42.8	32.9

* Changes made to data

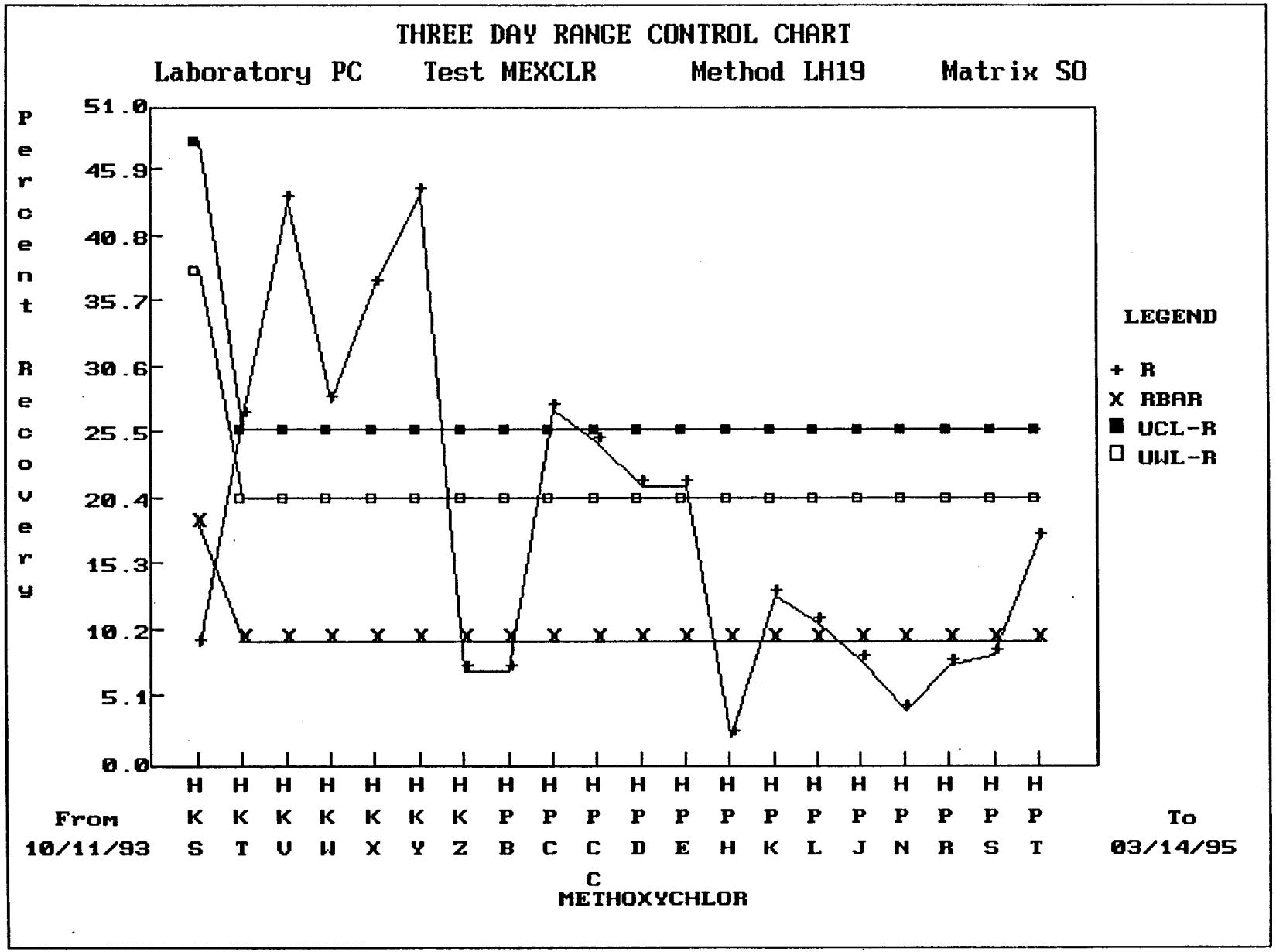

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test MEXCLR Method LH19 Matrix SO
Percent Recovery
117.4
111.5
105.6
99.7
93.9
88.0
82.1
76.3
70.4
64.5
58.6
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
METHOXYCHLOR

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR METHOXYCHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: MEXCLR

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	4.00	-1	3.66	-1	91.5	91.1	102.3	98.9	85.1	81.7	.F.
	052794	HPN	4.00	-1	3.58	-1	89.5	89.3	102.3	98.9	85.1	81.7	.F.
	082494	HPR	4.00	-1	3.90	-1	97.5	92.8	102.3	98.9	85.1	81.7	.F.
	092994	HPS	4.00	-1	3.93	-1	98.2	95.1	102.3	98.9	85.1	81.7	.F.
	031495	HPT	4.00	-1	3.22	-1	80.4	92.1	102.3	98.9	85.1	81.7	.F.

* Changes made to data

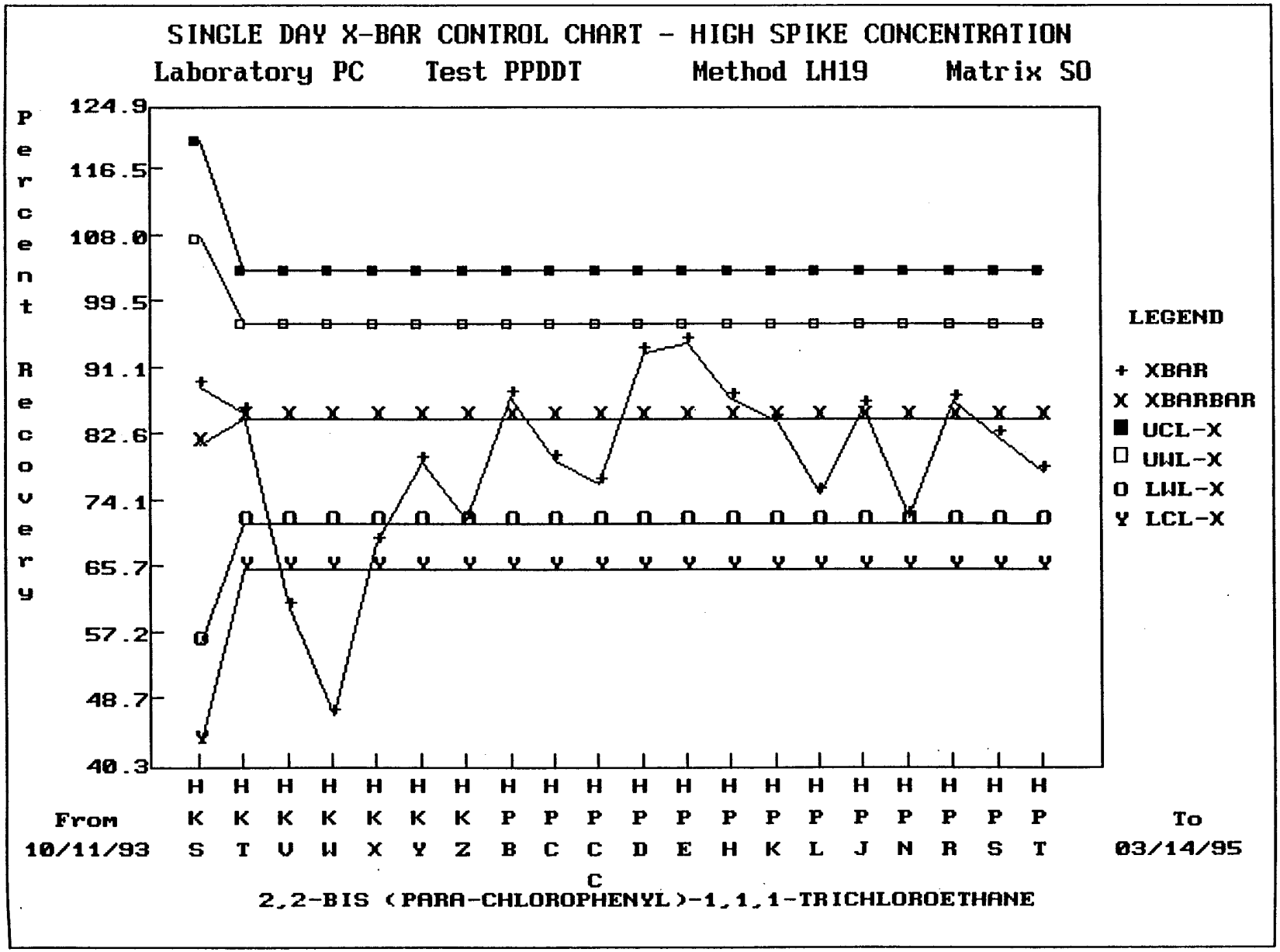

THREE DAY RANGE CONTROL CHART
Laboratory PC Test MEXCLR Method LH19 Matrix SO
Percent Recovery
51.0
45.9
40.8
35.7
30.6
25.5
20.4
15.3
10.2
5.1
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
METHOXYCHLOR

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR METHOXYCHLOR

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: MEXCLR

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	4.00	-1	3.66	-1	91.5	8.3	26.0	20.7
	052794	HPN	4.00	-1	3.58	-1	89.5	4.8	26.0	20.7
	082494	HPR	4.00	-1	3.90	-1	97.5	8.0	26.0	20.7
	092994	HPS	4.00	-1	3.93	-1	98.2	8.8	26.0	20.7
	031495	HPT	4.00	-1	3.22	-1	80.4	17.8	26.0	20.7

* Changes made to data

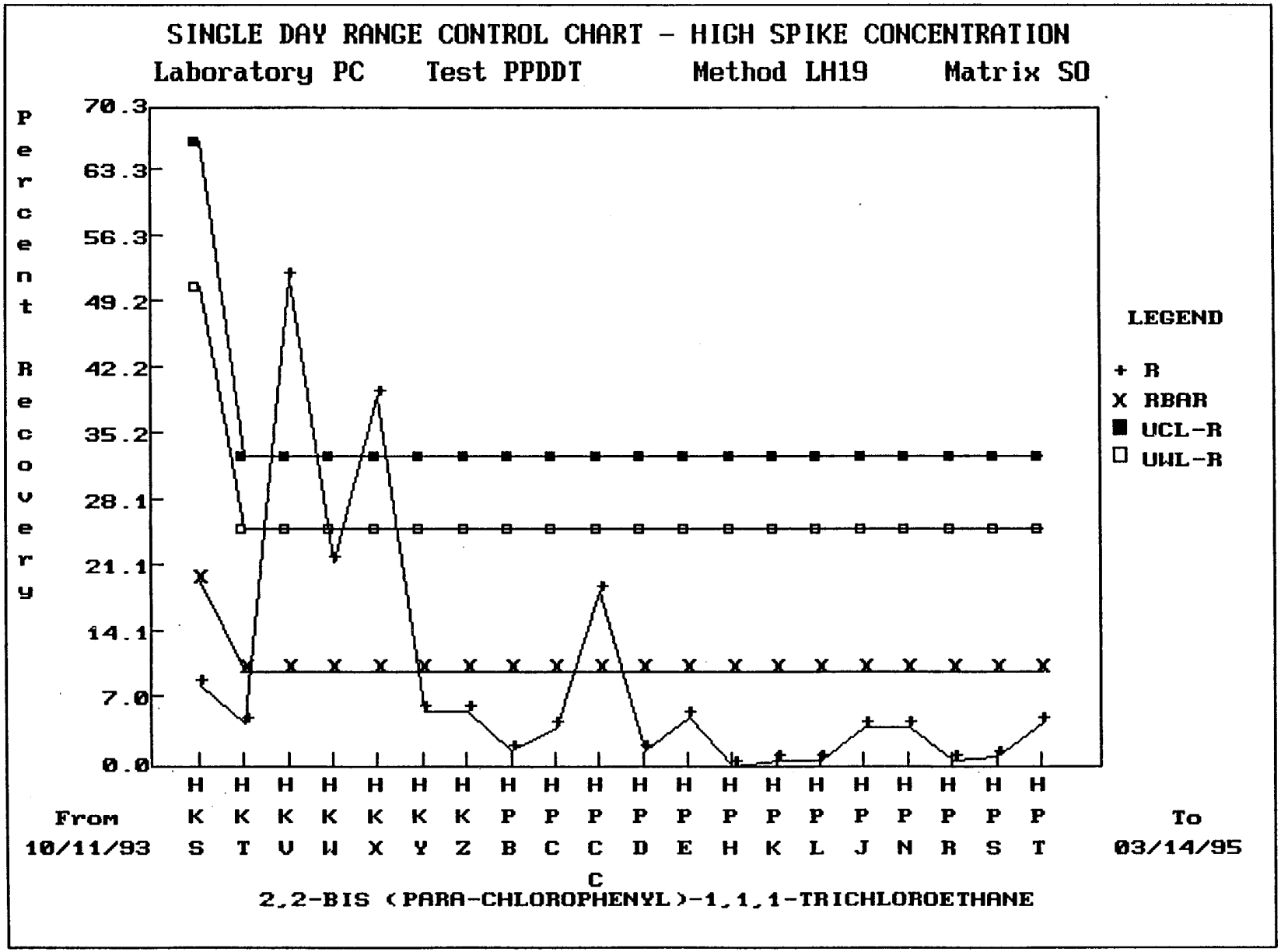

SINGLE DAY X-BAR CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test PPDDT Method LH19 Matrix SO
Percent Recovery
124.9
116.5
108.0
99.5
91.1
82.6
74.1
65.7
57.2
48.7
40.3
LEGEND
+ XBAR
X XBARBAR
■ UCL-X
□ UWL-X
0 LWL-X
Y LCL-X
From
10/11/93
To
03/14/95
2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

SINGLE DAY XBAR REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR 2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: PPDDT

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	1.50	-1	1.27	-1	1.34	-1	84.7	89.3	87.0	104.5	98.0	72.2	65.7	.F.
	052794	HPN	1.50	-1	1.06	-1	1.13	-1	70.7	75.3	73.0	104.5	98.0	72.2	65.7	.F.
	082494	HPR	1.50	-1	1.32	-1	1.31	-1	88.0	87.3	87.7	104.5	98.0	72.2	65.7	.F.
	092994	HPS	1.50	-1	1.25	-1	1.23	-1	83.3	82.0	82.7	104.5	98.0	72.2	65.7	.F.
	031495	HPT	1.50	-1	1.14	-1	1.22	-1	76.1	81.4	78.7	104.5	98.0	72.2	65.7	.F.

* Changes made to data

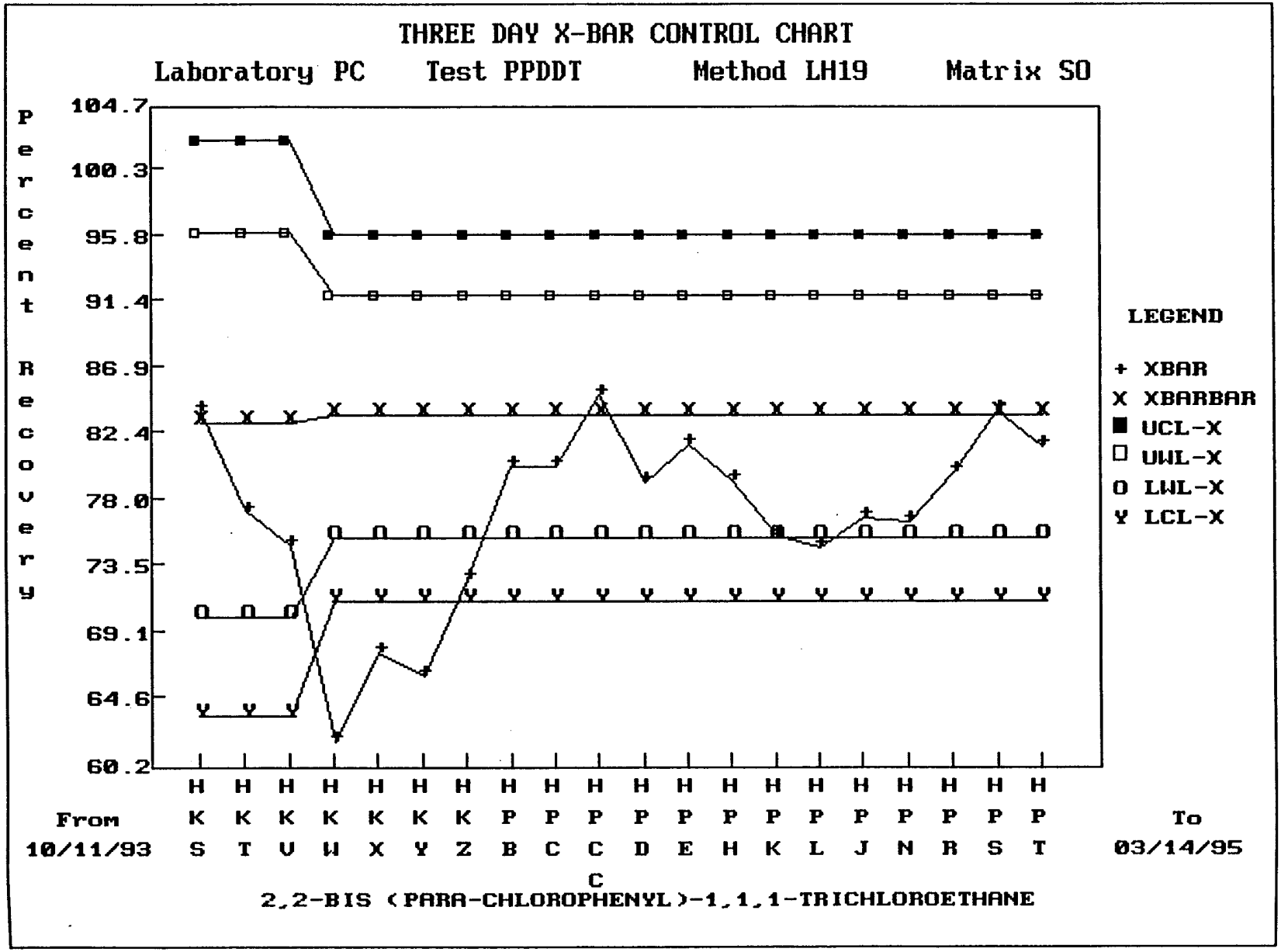

SINGLE DAY RANGE CONTROL CHART - HIGH SPIKE CONCENTRATION
Laboratory PC Test PPDDT Method LH19 Matrix SO
Percent Recovery
70.3
63.3
56.3
49.2
42.2
35.2
28.1
21.1
14.1
7.0
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From
10/11/93
To
03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

SINGLE DAY R REPORT OF PERCENT RECOVERY - HIGH CONCENTRATION
FOR 2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: PPDDT

	Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR
*	050294	HPJ	1.50	-1	1.27	-1	1.34	-1	84.7	89.3	4.7	33.7	25.9
	052794	HPN	1.50	-1	1.06	-1	1.13	-1	70.7	75.3	4.7	33.7	25.9
	082494	HPR	1.50	-1	1.32	-1	1.31	-1	88.0	87.3	0.7	33.7	25.9
	092994	HPS	1.50	-1	1.25	-1	1.23	-1	83.3	82.0	1.3	33.7	25.9
	031495	HPT	1.50	-1	1.14	-1	1.22	-1	76.1	81.4	5.3	33.7	25.9

* Changes made to data

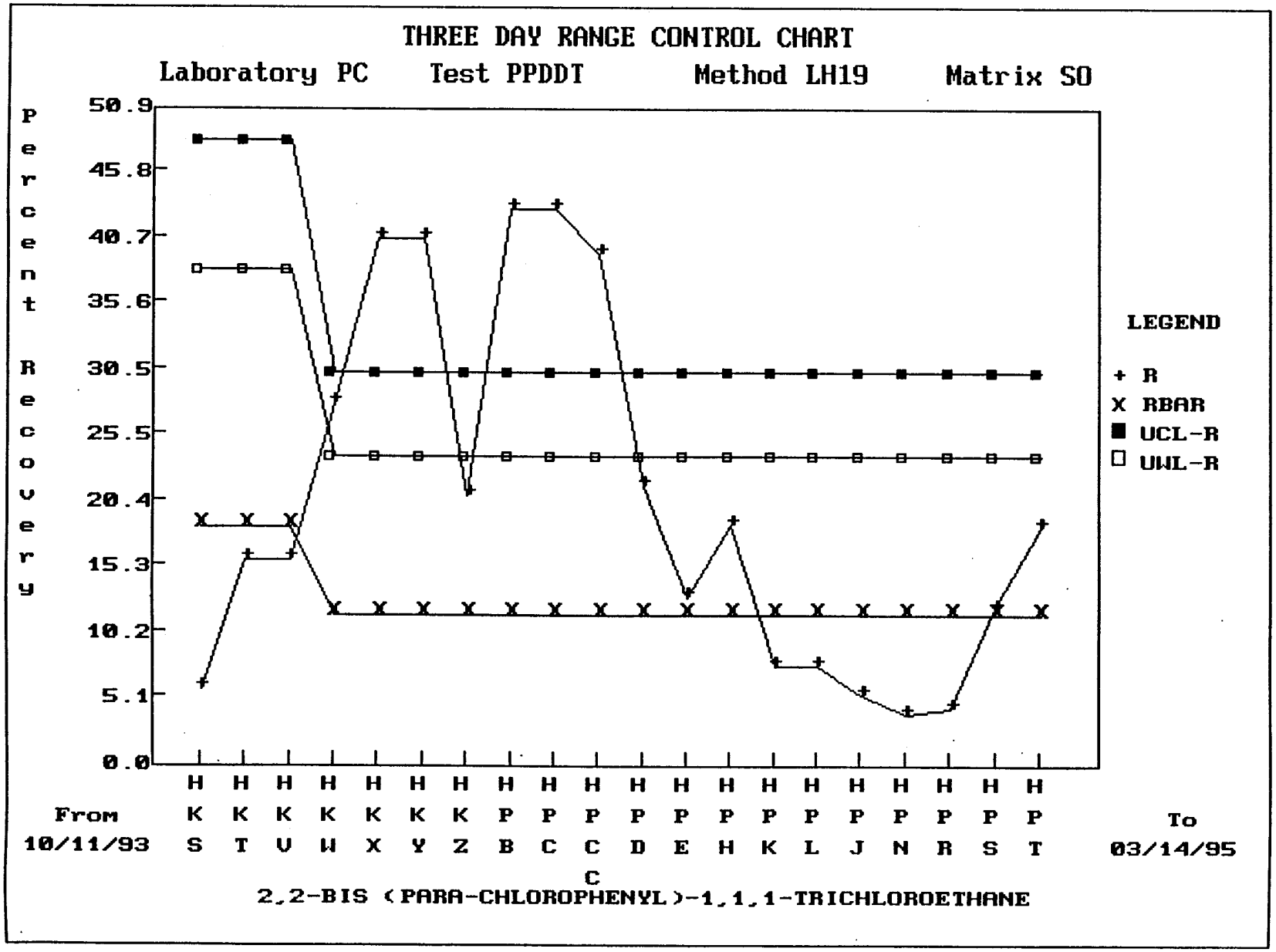

THREE DAY X-BAR CONTROL CHART
Laboratory PC Test PPDDT Method LH19 Matrix SO
Percent Recovery
104.7
100.3
95.8
91.4
86.9
82.4
78.0
73.5
69.1
64.6
60.2
LEGEND
+ XBAR
X XBARBAR
UCL-X
UWL-X
O LWL-X
Y LCL-X
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPCC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

THREE DAY MOVING AVERAGE XBAR REPORT OF PERCENT RECOVERY
FOR 2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: PPDDT

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX	OUTLIER
*	050294	HPJ	2.00	-2	1.57	-2	78.5	77.3	96.1	92.0	75.8	71.7	.F.
	052794	HPN	2.00	-2	1.57	-2	78.5	77.0	96.1	92.0	75.8	71.7	.F.
	082494	HPR	2.00	-2	1.67	-2	83.5	80.2	96.1	92.0	75.8	71.7	.F.
	092994	HPS	2.00	-2	1.82	-2	91.0	84.3	96.1	92.0	75.8	71.7	.F.
	031495	HPT	2.00	-2	1.44	-2	72.2	82.2	96.1	92.0	75.8	71.7	.F.

* Changes made to data


THREE DAY RANGE CONTROL CHART
Laboratory PC Test PPDDT Method LH19 Matrix SO
Percent Recovery
50.9
45.8
40.7
35.6
30.5
25.5
20.4
15.3
10.2
5.1
0.0
LEGEND
+ R
X RBAR
UCL-R
UWL-R
From 10/11/93
To 03/14/95
HKS HKT HKV HKW HKX HKY HKZ HPB HPC HPC HPD HPE HPH HPK HPL HPJ HPN HPR HPS HPT
2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

THREE DAY MOVING AVERAGE R REPORT OF PERCENT RECOVERY
FOR 2,2-BIS (PARA-CHLOROPHENYL)-1,1,1-TRICHLOROETHANE

Laboratory: PC	Date: 04/28/95
Method: LH19	Matrix: SO	Test Name: PPDDT

	Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR
*	050294	HPJ	2.00	-2	1.57	-2	78.5	5.5	30.6	24.4
	052794	HPN	2.00	-2	1.57	-2	78.5	4.5	30.6	24.4
	082494	HPR	2.00	-2	1.67	-2	83.5	5.0	30.6	24.4
	092994	HPS	2.00	-2	1.82	-2	91.0	12.5	30.6	24.4
	031495	HPT	2.00	-2	1.44	-2	72.2	18.9	30.6	24.4

* Changes made to data

APPENDIX D

QC CRITERIA

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TABLE D-1
SCHEDULED QUALITY CONTROL AND CALIBRATION

Procedure	Frequency of Quality Control Procedure	Acceptance Criteria			Corrective Action
Volatile Organic Compounds (VOCs)					
Initial Calibration 6-point Curve	Set-up, major maintenance, and quarterly	RRF ≥ 0.30 except bromoform ≥ 0.25 Response Factors < 30%			If RSD of the average RRF for calibration check compounds > 30%, the initial calibration must be repeated.
Daily Calibration Standard	Every 12 hours	% D for RRF ≤ 25% for 2/3 of compounds			If daily calibration standard does not meet criteria, reanalyze daily standard. If it fails a second time, perform new initial calibration.
Continuing Calibration Check	Beginning of a Sample Sequence	% D for RRF ≤ 25% for 2/3 of compounds			Samples cannot begin until this criterion is met.
Surrogate	Every Sample	4-bromofluorobenzene 1,2-dichloroethane-d_4 Toluene-d_8	Solid 89-110% 87-108% 94-109%	Aqueous 88-112% 88-116% 92-113%	If recoveries of one surrogate compounds is outside established limits, the sample must be reanalyzed. If the sample still fails upon reanalysis, document that surrogate recovery is matrix dependent (biased).
Method Blanks	Every 12 hours	"Clean"			Document source of contamination.
Tuning	Prior to Calibration	BFB key ions and ion abundance criteria in Standard Operating Procedure.			Analysis of the instrument must meet the ion abundance criteria.
Semivolatile Organic Compounds (SVOCs)					
Initial Calibration Curve	Set-up, major maintenance	RSD of RRF ≥ 35% for 2/3 of compounds			Must meet criteria prior to sample analysis.
Daily Calibration Standard	12 hours	RRF ≥ 0.05, the percent difference of the daily RRF compared to average RRF ≤ 25%.			If criteria are not met, reanalyze the daily standard. If the daily standard fails a second time, perform a new initial curve.

TABLE D-1
SCHEDULED QUALITY CONTROL AND CALIBRATION

Procedure	Frequency of Quality Control Procedure	Acceptance Criteria			Corrective Action
Semivolatile Organic Compounds (SVOCs) (Continued)					
Continuing Calibration Check	After tune, prior to sample analysis	% D for RRF ≤ 25% for 2/3 of compounds			If criteria are not met, initial calibration must be repeated.
Internal Standards	Every Analysis	Retention time ±30 seconds. Area changes by a factor of two (-50% to +100%).			Inspect for malfunction. Demonstration system is functioning properly. Reanalyze samples with standards outside criteria.
Tuning DFTPP	12 hours	Must meet tuning criteria in USEPA CLP OLMO1.8.			Re-tune, recalibrate.
Method Blanks	12 hours	"Clean"			Document source of contamination.
Surrogate Spikes	Every Sample		Solid	Aqueous	If recoveries of two surrogate compounds (2 acids or 2 base/neutrals) are not met, the extract must be reanalyzed. If extract fails upon reanalysis, document that surrogate recovery is matrix dependent.
		2-fluorophenol	31-88.6%	36-66%	
		Phenol-d_6	33.7-89.1%	24-40%	
		2,4,6-Tribromophenol	47.9-87.2%	57-100%	
		Nitrobenzene-d_5	21.5-85.5%	60-88%	
		2-Fluorobiphenyl	34.1-92.9%	54-80%	
		p-Terphenyl-d_{14}	54.7-99.1%	64-99%	
Pesticides/Polychlorinated Biphenyls (PCBs)					
Initial Calibration Curve Single Component, Multi-component	Set-up, major maintenance	2/3 of compounds have ≥ 0.995			Must meet criteria prior to sample analysis.
Daily Calibration Standard	12 hours	% D for RRF ≤ 25% for 2/3 of compounds			If criteria are not met, reanalyze the daily standard. If the daily standard fails a second time, perform a new initial curve.

TABLE D-1
SCHEDULED QUALITY CONTROL AND CALIBRATION

Procedure	Frequency of Quality Control Procedure	Acceptance Criteria			Corrective Action
Pesticides/Polychlorinated Biphenyls (PCBs) (Continued)					
Independent Reference Standard (Calibration Check)	Weekly	Recovery ±25%			Initiate investigation and document actions taken.
Performance Evaluation Mixture	12 hours, after analytical run	Endrin/4,4-DDT degradation < 30%			If criterion is not met, system must be deactivated and the affected sample reanalyzed if endrin or 4,4-DDT or their degradation products are detected in the samples.
Instrument Blank	12 hours, after analytical run	"Clean"			Demonstrated "clean". Affected sample will be analyzed.
Method Blanks	12 hours	"Clean"			Document source of contamination.
Surrogate Spikes[1]	Every Sample		Solid	Aqueous	Investigate to determine cause and document actions taken; data are acceptable.
		Tetrachloro-m-xylene	41.9-129%	63-109%	
		Decachlorobiphenyl	66.9-148%	34-133%	
Standard Spikes[1]	One low spike, two high spikes per sample lot	LWL < x < UWL			Investigate to determine cause and document actions taken; data are acceptable.
Target Analyte List (TAL) Metals					
Initial Calibration Curve 2-point Curve	Major maintenance, instrument modification, replacement of the torch, replacement of the mirror	r > 0.995 for all elements			If r < 0.995 for any element, the standards for that element must be prepared again and/or lower upper range standard must be used.

TABLE D-1
SCHEDULED QUALITY CONTROL AND CALIBRATION

Procedure	Frequency of Quality Control Procedure	Acceptance Criteria	Corrective Action
Target Analyte List (TAL) Metals (Continued)			
Daily Calibration Standard (calibration blank & calibration verification)	12 hours	Slope within 10% of initial calibration recovery ±5% of true value.	If criteria are not met, reanalyze the daily standards. If the daily standard fails a second time, perform an initial calibration.
Interference Check	Beginning and end of each sample analytical run	Recovery ±20% of true value.	Terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.
Continuing Calibration Verification (CCV)	Every 15 samples, end of analytical run	Recovery ±10% of true value.	Reanalyze CCV. If the CCV fails second time, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to continuing sample analyses.
Continuing Calibration Blank (CCB)	Every 15 samples, end of analytical run	Concentration $< 3 \times s$ of the background mean.	If the average in not within criteria, terminate the analysis, correct the problem, recalibrate, and reanalyze all samples analyzed since the last acceptable CCB.
Preparation Blank	1 per 20 samples	"Clean"	Document source contamination.
Control Spikes	Four spikes per 20 samples	± 30% for low spikes and ±20% for high spikes.	Initiate investigation, document actions taken; data are acceptable.

TABLE D-1
SCHEDULED QUALITY CONTROL AND CALIBRATION

Procedure	Frequency of Quality Control Procedure	Acceptance Criteria	Corrective Action
Total Petroleum Hydrocarbons (TPHs)			
Initial and Daily Calibration Curve 6-point Curve	Major maintenance or instrument modification	$r > 0.995$ for each compound.	If $r < 0.995$ for any element, the standards for that element must be prepared again and/or lower upper range standard must be used.
Independent Reference	Weekly	Recovery within ±25% of true value.	No corrective action cited.
Continuing Calibration Verification (CCV)	Every 10 samples, end of analytical run	Recovery ±25% of true value.	Reanalyze CCV. If the CCV fails second time, the samples must be reanalyzed or documentation provided by the analyte as to why the sample data should be acceptable.
Method Blank	1 per 20 samples	"Clean"	Documented source of contamination.
Standard Spikes	One low and two high spikes per sample lot		Investigate to determine cause and document action taken; data are acceptable.

(1) Total discussion of control criteria and corrective action is provided in Section 8.7 of the USAEC Guidelines (USAEC, 1993).

TABLE D-2
MATRIX SPIKE AND MATRIX SPIKE DUPLICATE QUALITY CONTROL CRITERIA

Compounds	Solid		Aqueous	
	Percent Recovery Criteria (%)	Relative Percent Difference Criteria	Percent Recovery Criteria (%)	Relative Percent Difference Criteria
Volatile Organic Compounds (VOCs)				
1,1-Dichloroethane	59 - 155	30	59 - 155	30
Toluene	79 - 120	16	62 - 125	43
Trichloroethylene	76 - 117	19	60 - 125	40
Benzene	72 - 128	17	60 - 115	29
Chlorobenzene	78 - 122	17	59 - 126	45
Semivolatile Organic Compounds (SVOCs)				
Phenol	50 -102	12	43 - 85	55
2-Chlorophenol	63 - 98	11	57 - 90	42
1,4-Dichlorobenzene	7 - 105	24	31 - 74	27
N-nitroso-di-n-propylamine	30 - 110	21	23 - 117	32
1,2,4-Trichlorobenzene	33 - 96	16	28 - 79	26
4-Chloro-3-methylphenol	63 - 100	17	55 - 99	53
Acenaphthene	57 - 106	19	48 - 99	21
4-Nitrophenol	23 - 139	77	60 - 145	42
2,4-Dinotrotoluene	13 - 116	55	44 - 86	21
Pentachlorophenol	33 - 120	50	60 - 99	33
Pyrene	19 - 156	83	55 - 102	21

TABLE D-3
LOW AND HIGH MATRIX SPIKE QUALITY CONTROL CRITERIA

Compounds	Solid		Aqueous	
	Percent Recovery Low Spike	Percent Recovery High Spike	Percent Recovery Low Spike	Percent Recovery High Spike
Pesticides				
Endosulfan I	78.4 - 101.4	67.9 - 113.1	72.1 - 96.7	58.0 - 106
Aldrin	70.5 - 91.5	62.8 - 102.6	52.7 - 75.7	42.2 - 83.6
Dieldrin	76.1 - 96.7	63.1 - 110.1	65.3 - 82.7	56.6- 89.6
Endrin	68.1 - 89.7	95.8 - 60.0	65.5 - 87.1	56.2 - 94.2
Heptachlor	75.8 - 96.6	65.5 - 104.3	59.8 - 78.6	49.3 - 87.7
Lindane	68.0 - 91.2	58.7 - 101.1	63.7 - 79.5	54.2 - 87.0
Methoxychlor	81.7 - 102.3	64.3 - 113.5	79.8 - 97.4	73.3 - 104.9
pp-DDT	71.7 - 96.1	65.7 - 104.5	68.0 - 87.6	58.4 - 96.8

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