RESULTS OF A MICROBIAL WEATHERING STUDY OF COMPOSTED EXPLOSIVES-CONTAMINATED SOIL OBTAINED FROM THE UMATILLA ARMY DEPOT ACTIVITY

Umatilla, Oregon

Interim Report

(September 1996 to September 1998)

Prepared for

U.S. Army Environmental Center

Aberdeen Proving Ground, Maryland 21010-5401

Prepared by

Tennessee Valley Authority

Environmental Research Center

Muscle Shoals, Alabama 35662-1010

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Prepared for

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This report describes the interim results (September 1996 through September 1998) of a Microbial Weathering Study conducted to determine if composted explosives-contaminated soil would leach explosives or explosive by-products. The three-year study was conducted using compost produced during the remediation of an explosives-contaminated site at the U.S. Army's Umatilla Army Depot Activity at Umatilla, Oregon. This compost was shipped to the Tennessee Valley Authority's Environmental Research Facility in Muscle Shoals, Alabama, where the study was conducted. At this juncture, two years' worth of data have been collected. The report concludes that the compost had not leached TNT, but had leached as much as 31.5 and 26.4 ppb of HMX and RDX, respectively. These results suggest that these explosives were not fully mineralized. However, the concentrations leached were well below the state of Oregon's action limit of 30 ppm.

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EXECUTIVE SUMMARY

This report summarizes the first two years (September 1996 through September 1998) of a study examining the microbial weathering of compost produced for the remediation of explosives-contaminated soil at the Umatilla Army Depot Activity (UMADA), Umatilla, Oregon. The Microbial Weathering Study is part of a larger study examining whether or not the compost produced from remediating explosives-contaminated soils contained residual explosives or explosive by-products which might be of concern. Specifically, the larger study was to determine if these chemicals could be:

- Leached from the compost when stockpiled or land-applied.
- Taken up by plants which, in turn, might be consumed by livestock or people.

The larger study involved the measurement of the uptake of explosive residues by plants, as well as the development of analytical methods for detecting explosives and explosive by-products in compost. A detailed description of the larger study and its results are provided in the final report, *Results of a Study Investigating the Plant Uptake of Explosive Residues from Compost of Explosives-Contaminated Soil Obtained from the Umatilla Army Depot Activity.*[Ref. 1] The Microbial Weathering Study was limited to determining if the explosives or explosive by-products would leach. The three-year Microbial Weathering Study described herein began on September 15, 1996, and is scheduled to end on September 15, 1999. This report describes the Microbial Weathering Study's interim results after two years of study.

The compost used during the Microbial Weathering Study was obtained from UMADA in 1996. At that time, the Army was remediating explosives-contaminated soil at UMADA using windrow composting. Previous treatability studies conducted by the Army at UMADA indicated that this treatment method was both an effective and economical method for reducing TNT and RDX to levels below the state of Oregon's action limit of 30 ppm for each explosive. Analysis of the soil prior to remediation indicated that it contained between 6,000-8,000 ppm total explosives. Approximately 90% of this was TNT, 8% RDX, and 2% other explosives.

To conduct the Microbial Weathering Study, compost was placed in six large aboveground plastic bins and exposed to the environment. The bins were equipped with drainage and

leachate collection systems to facilitate leachate collection. Three of these bins were filled with immature compost from the UMADA remediation project and three bins were filled with uncontaminated soil from UMADA and amended with immature compost mixed in the top six inches. The term 'immature' means that the compost was taken from the UMADA remediation activity shortly after treatment, but before microbial activity reached low levels. During the study, rainfall amounts at the site and leachate volumes collected in the bins were recorded. Leachate samples were also collected and composited for analysis once every two weeks during the study's first year and once every two months during the second year. Leachate collected during the first year was analyzed for explosives, explosive by-products, nutrients, organic carbon, electrical conductivity, and pH. Only explosives and explosive by-products were analyzed during the second year. Analysis for the other chemical characteristics was suspended since their levels had stabilized.

The compost itself was analyzed for explosives and explosive by-products prior to use and on an annual basis thereafter. These analyses revealed that the compost received by TVA initially had very low levels of explosives. TNB, TNT, and RDX had average concentrations of 245, 64, and 20 ug/Kg (ppb), respectively. The only other explosive analyte detected was the TNT breakdown product 2-amino-4,6-dinitrotoluene, at a level of 8.2 ug/Kg. After being weathered for one year, a small amount of TNB (121 ug/Kg) was detected in only one of the bins. No other explosive analytes were detected.

Analyses of the leachate revealed that HMX and RDX were released from the compost and that the dilution of compost with soil appeared to cause the release of HMX. The HMX and RDX concentrations in the leachate peaked at 31.5 and 26.4 ug/L (ppb), respectively. The concentrations of HMX and RDX leached were well below the state of Oregon's action limit of 30 ppm (30,000 ppb) for each explosive. However, the fact that HMX and RDX were leaching suggests that these explosives were tightly bound or were not fully mineralized in the composting process.

The leachate analyses also suggested that the levels and leaching pattern of nutrient organic carbon and salts (indicated by the electrical conductivity measurements) were consistent with the decomposition of organic matter. Nitrogen leached from the pure compost was primarily in the organic form. Nitrogen leached from the soil amended with compost was primarily in the

nitrate form, indicating that the ammonium and organic nitrogen was nitrified by microbes in the soil.

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ABBREVIATIONS

2-ADNT	2-Amino-4,6-dinitrotoluene
4-ADNT	4-Amino-2,6-dinitrotoluene
2,4-DANT	2,4-Diamino-6-nitrotoluene
2,6-DANT	2,6-Diamino-4-nitrotoluene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
BSI	Bioremediation Services, Inc.
CEB	Chemical Engineering Building
cm	centimeter
DNT	Dinitrotoluene
DoD	Department of Defense
EC	Electrical Conductivity
EPA	Environmental Protection Agency
ERC	Environmental Research Center
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High Performance Liquid Chromatography
K	Potassium
MDL	Method Detection Limit
N	Nitrogen
ND	Not Detected
NH_4-N	Ammonium Nitrogen
NO_3	Nitrate
(NO_3+NO_2)-N	Nitrate + Nitrite Nitrogen
P	Phosphorus
PO_4	Orthophosphate
PO_4-P	Orthophosphate - Phosphorus
QA	Quality Assurance
QC	Quality Control
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
TKN	Total Kjeldahl Nitrogen
TNB	Trinitrobenzene
TNT	2,4,6 Trinitrotoluene
TOC	Total Organic Carbon
TVA	Tennessee Valley Authority
UMADA	Umatilla Army Depot Activity
USAEC	U.S. Army Environmental Center

SECTION 1.0
INTRODUCTION

1.1 Background

Contamination of soils and sediments with explosives is a concern at many military facilities where explosives have been produced and handled. Over time, the soils and sediments at these installations became contaminated with a variety of explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3.5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and n-methyl-n-2,4,6-tetranitroaniline (tetryl). Incineration methods can be used to remediate the soils at these sites. However, the U.S. Army Environmental Center (USAEC) is investigating alternative remediation technologies because of public resistance to the use of incineration and because such remediation costs are high. Among the most promising of these alternatives is composting.

Previous USAEC studies have indicated that soil remediation using composting techniques is cost-effective; that removal efficiencies for TNT, RDX, and HMX were high; and little or no toxicity was produced.[Refs. 2,3] However, the USAEC was concerned that undetected explosive residuals may be present within the compost and that these residuals could represent potential risk to the health of individuals or livestock which come into contact with the compost. Specific concerns were:

- That explosive material residuals may be taken up by plants which might be consumed by humans or livestock, and.
- That land-applied compost would leach explosive residuals.

These concerns were based on the difficulty of detecting explosive materials in compost and the consequent difficulty in establishing that the explosives have indeed been destroyed. The USAEC felt that these concerns should be addressed before it could recommend unrestricted use of the composted soil. Therefore, the USAEC funded this project to study the potential for the explosive uptake by plants and leaching of explosives from composted soil.

The Microbial Weathering Study was conducted to determine if the compost would leach explosive residuals over time. The findings on plant uptake are documented in a separate report. During the Microbial Weathering Study, the Tennessee Valley Authority (TVA) exposed compost and compost + soil mixtures to the environment at TVA's Environmental Research Center (ERC) at Muscle Shoals, Alabama. The Microbial Weathering Study was designed to simulate two conditions:

- A pile of immature composted explosives-contaminated soil placed outside (simulated by the bins containing compost only). The term 'immature' means that the compost was taken from the UMADA remediation activity shortly after treatment, but before microbial activity reached low levels.

- Land-applied immature compost which would typically be tilled into the top six inches of soil (simulated by the bins containing the compost + soil mixture)

Over the course of the study, leachates from the compost and compost + soil mixture were periodically collected and subjected to chemical analysis to determine if explosive residuals were leaching from the composts. The Microbial Weathering Study is scheduled to be run for three years from September 15, 1996, to September 15, 1999. This report summarizes the results of the first two years of data.

This project was executed under an agreement between the USAEC and the Tennessee Valley Authority (TVA). The USAEC was the lead agency while the TVA provided technical expertise in composting and explosives residue analysis. The compost used was obtained from the Umatilla Army Depot Activity (UMADA) in Umatilla, Oregon. This compost was produced as part of a soil remedial action program conducted at UMADA. All of the test work was conducted at TVA's facilities in Muscle Shoals, Alabama.

1.2 Project Objectives

The objective of the Microbial Weathering Study was:

- To assess changes in compost leachate or in the composition of the compost as it weathers in the environment.

Assessment of the weathering of the compost was based on an analysis of:

- Specific explosives;
- Known explosive transformation products;
- Nutrient content (nitrogen, phosphate, and organic carbon);
- Electrical conductivity and;
- pH.

1.3 Approach

The Microbial Weathering Study was conducted during Phase III of a six-phase project. These phases were:

- Planning, Permitting, and Materials Acquisition (Phase I). During this phase, a test plan was written and approved; an environmental review was conducted and the state of Alabama was notified about the project; and compost produced from contaminated soil, uncontaminated soil, and compost amendments were obtained from UMADA.

- Compost Production and Maturity Study (Phase II). During this phase, a control compost was produced at TVA's facility and both the control and treated composts were monitored to determine when they had matured. The control compost was made by TVA from uncontaminated soil and amendments obtained from UMADA.

- Microbial Weathering Study (Phase III). During this phase, the treated compost and compost + soil mixtures were exposed to the weather to determine if the treated compost would leach explosives over a long period of time.

- Analytical Methods Development (Phase IV). During this phase, analytical methods were developed for extracting TNT residues from compost, compost leachate, and plant materials. Phase IV was conducted concurrently with Phases II and III.

- Plant Uptake Study (Phase V). During this phase, plants were grown in mature compost, harvested, and analyzed for TNT residues. Soil, compost, and leachate samples were also collected and analyzed during this period. The purpose of this study was to determine if specific plants would take up and store explosive compounds.

- Final Report (Phase VI). During this phase, the final plant uptake study report was written.

The project began on June 17, 1996. On July 17, 1996, compost, compost amendments, and uncontaminated soil obtained from UMADA arrived at TVA's facility in Muscle Shoals, Alabama (Figure 1-1), where the project was conducted. Project operations took place in the main ERC building and the Chemical Engineering building (CEB), the ERC composting facility, and the ERC greenhouses and growth chamber, each located approximately one mile from the main buildings. The Microbial Weathering Study took place near the ERC greenhouses and growth chamber. Treated compost obtained from UMADA was stored on-site. Control compost was produced at the ERC from uncontaminated soil and compost amendment obtained from UMADA.

The treated compost was produced at UMADA by Bioremediation Services, Inc. (BSI), in late June 1996. At that time, BSI was under contract with the DoD to remediate explosives-(TNT, HMX, and RDX) contaminated soil at UMADA. The treated compost was produced by thoroughly mixing a volume ratio of 70% organic amendment to 30% contaminated soil using method and amendment recipes developed by BSI. The treated compost was then stored in bulk bags and transported by truck to TVA's ERC in Muscle Shoals, Alabama. Upon arriving at TVA, a treated compost pile was constructed. Monitoring of the treated compost pile began on August 13, 1996. The treated compost was estimated to be approximately 30 days older than the control compost. On September 15, 1996, a portion of the treated compost was taken from the treated compost pile for use in the Microbial Weathering Study.

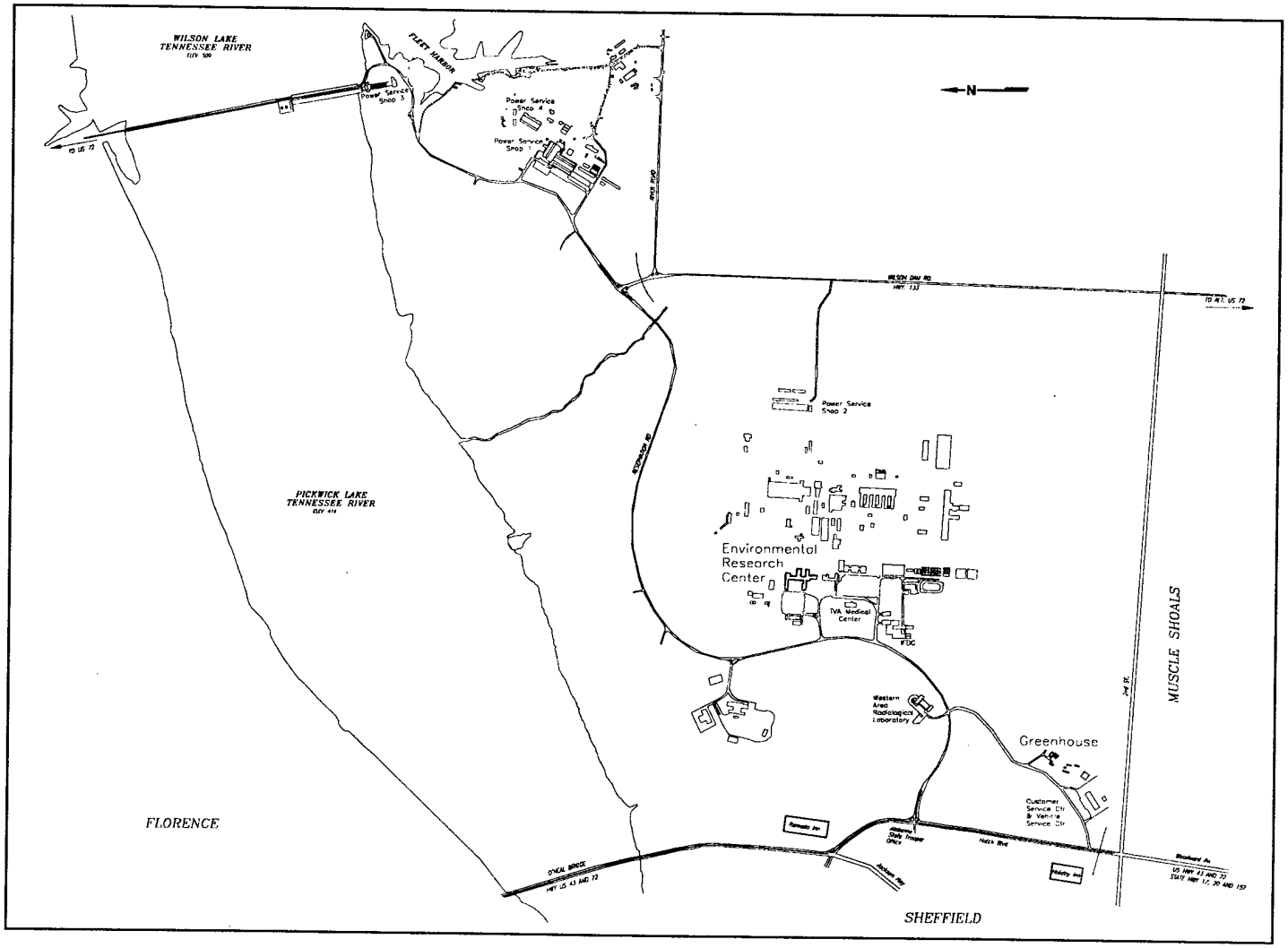


Figure 1-1

Location of TVA's Environmental Research Center

The compost used in the Microbial Weathering Study was placed in aboveground bins (Section 3.1 and Figure 3-1) and placed outdoors to be exposed to the weather. During the course of the study, the amount of rainfall which fell on the compost was recorded, as was the volume of leachate produced. Leachate samples were analyzed periodically for explosives, explosive by-products, nutrients, pH, and conductivity. Compost was also analyzed before being placed in bins and was sampled and analyzed annually, thereafter.

1.4 Schedule

The study began in July 1996 with acquisition of the compost from UMADA. The test plan was finalized in September 1996. The weathering study began when the compost was placed in the bins on September 15, 1996. The weathering study was scheduled for three years, with the compost to be exposed to the elements from September 15, 1996, through September 15, 1999. This report covers the exposure period from September 15, 1996, through September 15, 1999. A detailed schedule of the weathering study is provided Figure 1-2.

ID	Task Name
1	**Receive Funding**
2	**Phase I - Planing, Permits, and Matl. Acquisition**
3	**Task 1 -- Develop Detailed Project Plan**
4	Write Draft Test Plan
5	Consolidate/Format/Edit Draft Test Plan
6	AEC Reviews Test Plan
7	Write Final Test Plan
8	Final Test Plan Issued -- Task 1 complete
9	**Task 2 -- Environmental Permit Acquisition**
10	Permit Acquisition Started
11	Analysis of Cont. Soil and Treated Compost Received
12	Acquire Project Information & Regulatory Reqd.
13	EDR Submitted to TVA Envir. Compliance Staff
14	TVA OGC Office Reviews ERC Approach
15	State Contacted for First Time
16	State Notification Written and Received
17	All Permits Acquired - Task 2 Complete
18	**Task 3 -- Materials Acquisition**
19	Feedstocks Acquisition Starts
20	Obtain Soil Amendments and Clean Soil
21	Clean Soil and Amendments Arrive at Muscle Shoals
22	Obtain Treated Compost
23	Treated Compost Arrives at Muscle Shoals
24	All Study Feedstocks Obtained - Task 3 Complete
25	Phase I Complete

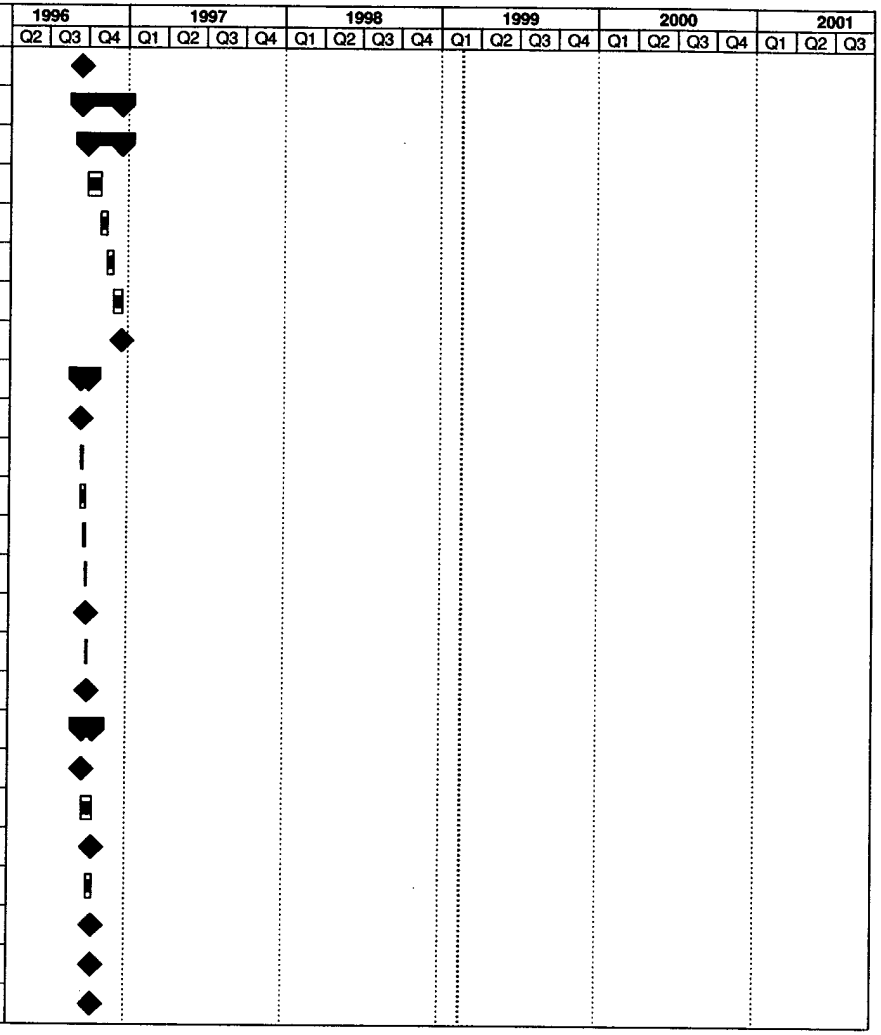


Figure 1-2

Gannt Chart for Plant Uptake Study

ID	Task Name
26	**Phase II - Compost Production & Maturity Test**
27	Earliest Maturity Period
28	Additional Curing
29	Sample and Monitor Control Compost
30	Data Analysis
31	Phase II Complete
32	**Phase III - Microbial Weathering Test**
33	Prepare Bins
34	Compost Placed in Bins and Exposed to the Elements
35	Data Collection and Sampling
36	Data Analysis
37	Write Draft Interim Weathering Report
38	Format/Draft Interim Weathering Report
39	AEC Reviews Interim Weathering Report
40	Finalize Interim Weathering Report
41	Develop Scope of Work for 98/99 Extension
42	Data Collection for 98/99 Extension
43	Data Analysis for 98/99 Extension
44	Write Draft Final Weathering Report
45	Format/Draft Final Weathering Report
46	AEC Reviews Final Weathering Report
47	Finalize Final Weathering Report
48	Phase III Complete

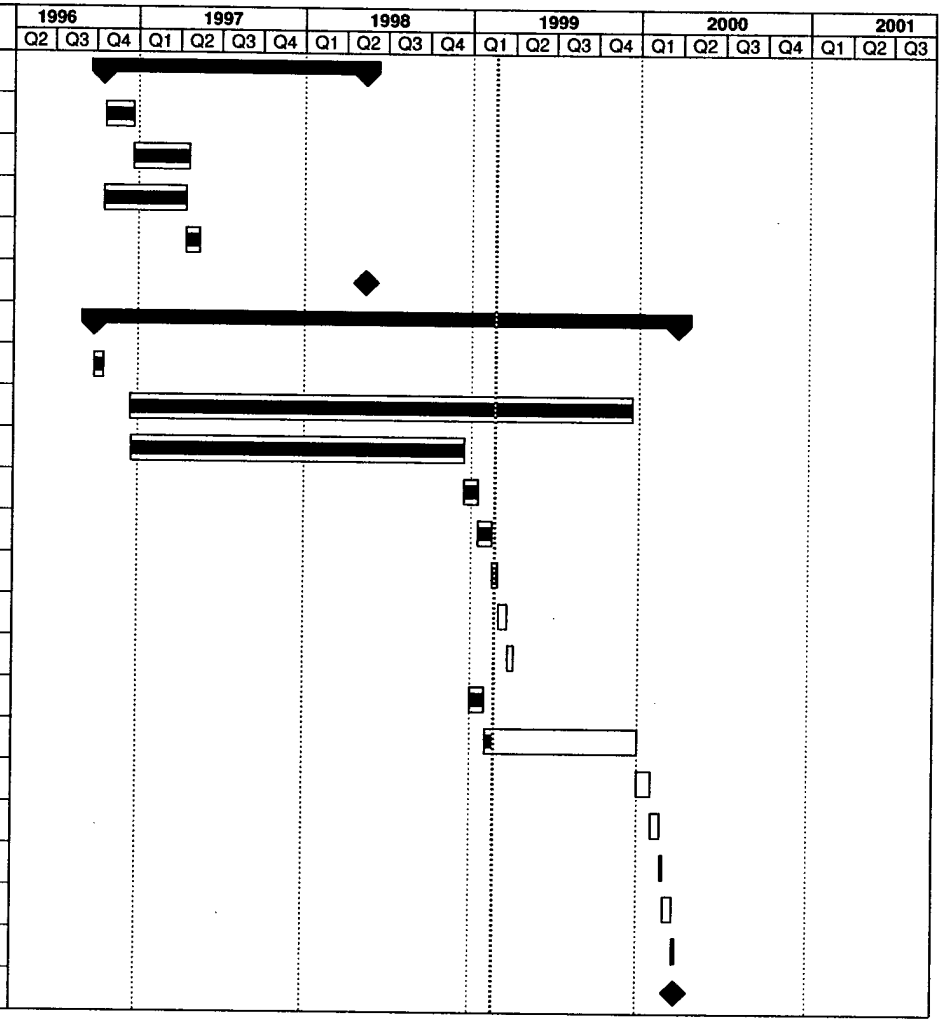


Figure 1-2

Gannt Chart for Plant Uptake Study

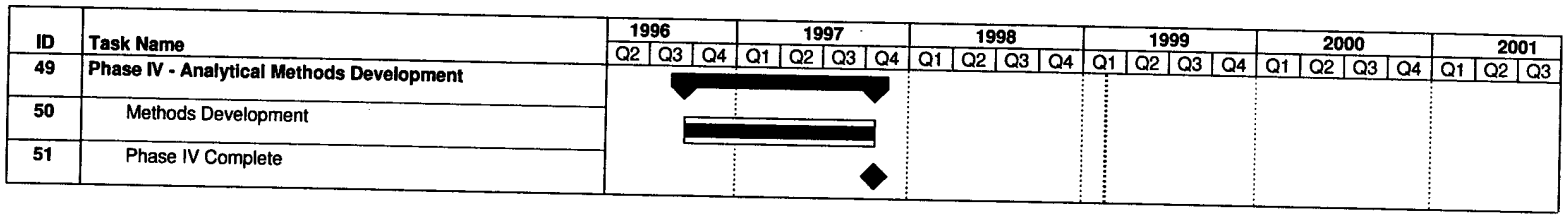


Figure 1-2

Gannt Chart for Plant Uptake Study

SECTION 2.0
COMPOST DESCRIPTION

The compost used during this project was obtained from UMADA in 1996. At that time, the Army was remediating explosives-contaminated soil at UMADA using windrow composting. The soil at UMADA became contaminated with explosives when wastewater from an ammunition loading and unloading facility was routed to two lagoons resulting in a contamination of the lagoon's sediment and surrounding soil. The level of explosives in the soil and sediments ranged from 6,000-8,000 ppm total explosives and further analysis revealed the mix of explosives in the soil to be approximately 90% TNT, 8% RDX, and 2% other explosives.

To identify an effective remediation method for the site, both the USAEC and UMADA conducted field-scale pilot tests of several composting technologies.[Ref. 2] The goal was to remove TNT and RDX to below the state of Oregon's action limit of 30 ppm for each explosive. Of the methods examined, windrow composting was found to be the most effective and economical. The treatability studies also indicated that the compost was non-leaching.

Bioremediation Services was employed to remediate the UMADA site using the windrow composting method. During the remediation process, excavated soil contaminated with explosives was screened to remove large rocks and debris and transported to a soil storage building. There the contaminated soil was combined with:

- Biodegradable carbon sources such as alfalfa, potato culls, chicken manure, and cow manure;
- Bulking agents such as wood chips and sawdust to increase porosity and oxygen content; and
- Water.

The mixture was placed in windrows (long piles) within a treatment building to prevent windblown contaminant migration and to protect the piles from the weather. The windrows were periodically mixed and aerated with a compost turner. Moisture, temperature, and explosive concentrations were monitored throughout the composting process. The

biodegradable contaminants were degraded by microorganisms which produce organic and inorganic transformation products and heat during the process. Following treatment, all of the compost was tested and certified to contain less than the action levels, 30 ppm TNT and 30 ppm RDX. Once the concentration of contaminants dropped below the action levels, the compost was removed from the treatment building and stored in a pile. This compost was later used as part of the vegetative cover on the installation's solid waste landfill.

The treated compost used in this project was produced at UMADA by Bioremediation Services in late June 1996. The treated compost was produced by thoroughly mixing a volume ratio of 70% organic amendment to 30% soil using methods and amendment recipes developed by Bioremediation Services. The treated compost was then stored in bulk bags and transported by truck to TVA's Environmental Research Center in Muscle Shoals, Alabama.

Upon arriving at TVA, a treated compost pile was constructed and monitored for oxygen content and temperature. All composting activities took place inside an enclosed building for control of weather-related variables. Monitoring of the treated compost pile began on August 13, 1996. Whenever the oxygen levels in the pile fell below 5%, the pile was aerated (turned) with a compost turner. Initially, the pile had to be aerated daily to maintain oxygen levels; however, as the pile matured, it was aerated less frequently. The treated compost pile was aerated a total of ten times prior to conducting the Microbial Weathering Study. Upon arriving at TVA, a sample of the treated compost was taken to identify the amount of water which should be periodically added to adequately wet the compost prior to aeration. Based on these measurements, it was established that compost should contain approximately 20% moisture on a dry weight basis. Therefore, prior to aerating the pile, water was added to bring the moisture up to this level while taking care not to exceed the compost's saturation level. On September 15, 1996, a portion of the treated compost was diverted from the treated compost pile for use in the Microbial Weathering Study. The remaining compost was used during the Plant Uptake Study.

SECTION 3.0
EXPERIMENTAL DESIGN

3.1 Introduction

The goal of the Microbial Weathering Study was to determine if leachate derived from the compost of explosives-contaminated soil would contain explosives or other toxic compounds. Also, the changes in the composition of the compost over time were measured.

During the Microbial Weathering Study, treated compost and soil with additions of treated compost were placed in six large plastic bins and exposed to ambient weather conditions. The bins were reinforced plastic watering troughs with a capacity of approximately 265 liters (70 gallons). A diagram of the bins and the leachate collection system is shown in Figure 3-1. Three bins each contained 450 pounds of immature treated compost only. Three additional bins contained 600 pounds of clean UMADA soil with 4 pounds of dry immature treated compost mixed into the top six inches. This amount of compost was equivalent to 28,000 pounds per acre and would supply around 150 pounds of nitrogen per acre. An immature compost, particularly under moist, anaerobic conditions, produce compounds which inhibit seed germination, inhibit plant growth, and produce undesirable odors. The compost used had been treated long enough for the levels of TNT and RDX to fall below the state of Oregon's action level of 30 ppm.

The bins were placed near the ERC greenhouse for monitoring by greenhouse staff. The bins were elevated to facilitate leachate collection. Leachate was collected in 3.78-liter (1-gallon) amber glass bottles contained inside a larger (e.g., 18.9-liter [5-gallon]) closed container to provide leachate containment in the event the primary collector overflowed. The leachate collection piping and containers were wrapped in aluminum foil to prevent photo degradation. Within 24 hours of a rain event, leachate from each bottle was collected and the volume measured. Leachate was collected and composited over two-week periods during the first year and analyzed for explosives, explosive degradation products, nutrient content

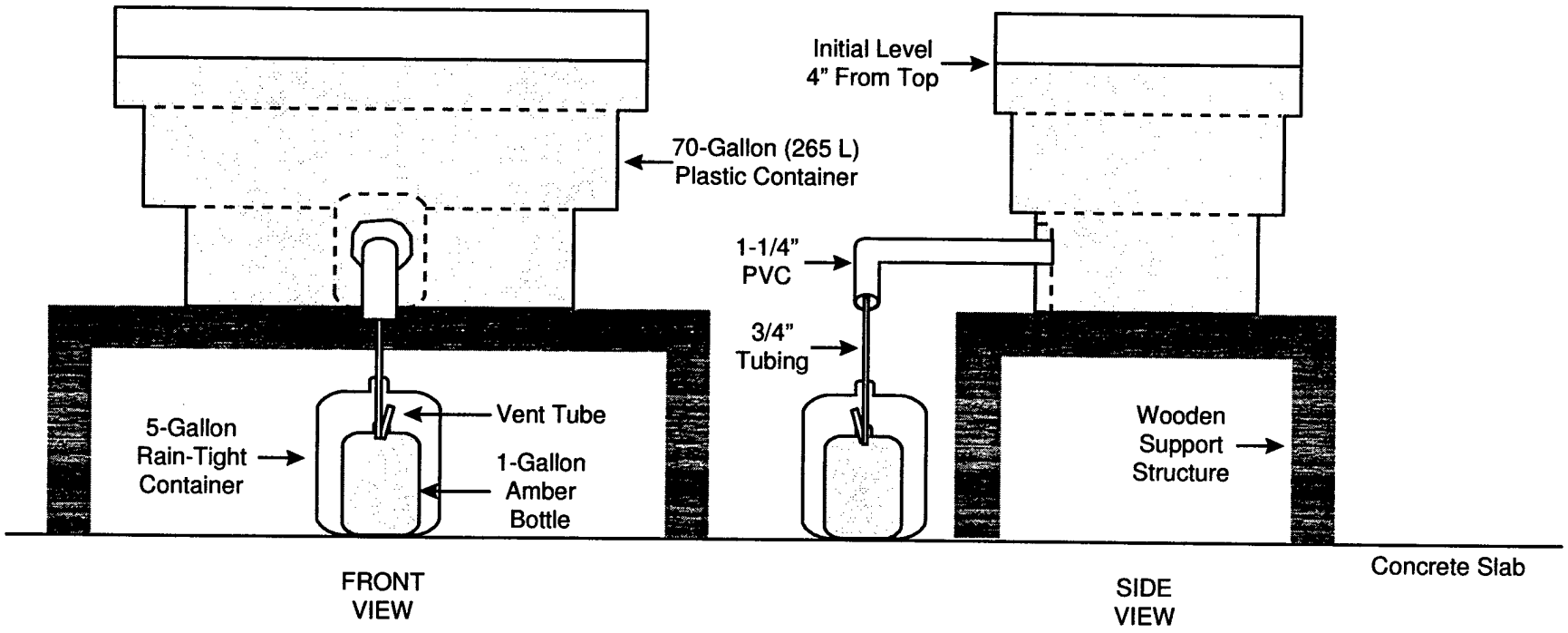


Figure 3-1

Compost Weathering Bins

(nitrogen, phosphate, and organic carbon), pH, conductivity, and metals (if detected in the compost at levels 50% above the EPA toxicity characterization leaching procedure limits).

Since the concentrations of metals in the compost were below 50% of the EPA limits, leachates were not analyzed for metals. In the second year, leachate samples were composited over two-month periods and analyzed only for explosives and explosive degradation products. A summary of the leachate sampling and analyses schedule is given in Table 3-1. Compost samples were collected as cores from each replicate after one and two years to provide a basis for comparing differences in the leachate and compost composition over time.

In support of the weathering study, analytical methods were developed for analyzing the explosives content of compost-derived leachate. The goal of this work was to find improved methods for analyzing the explosives content of these materials. Details of the methods development are given in the Plant Uptake Study final report.[Ref. 1]

3.2 Sampling Methods

3.2.1 Leachate Sampling

During the first year, compost samples were collected at two-week intervals. During the second year, they were collected at two-month intervals. Within 24 hours of the first rain event in each two week or two month interval, the leachate which had accumulated in each 3.78-liter (1-gallon) amber glass collection bottle was measured by pouring the leachate into a pre-cleaned graduated cylinder. Based on the collectors judgment as to the likelihood of the amount of rain likely to occur during the collection interval, a portion of the leachate collected during the first rain event would be poured into a 250-ml amber glass bottle, sealed with a Teflon-lined lid, and wrapped in aluminum foil. Between 5 and 100% of the first sample obtained would normally be collected. The remaining liquid was disposed of. All sample containers were labeled to identify date collected, location, and project identification. All of the containers were then stored in a laboratory refrigerator at TVA's greenhouse.

Table 3-1

Analysis of Leachate

Parameter Measured	Frequency[1]		Method
	First Year	Second Year	
TNT (2,4, 6 Trinitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
TNB (Trinitrobenzene)	Every Two Weeks	Every Two Months	Method AP-0062
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)	Every Two Weeks	Every Two Months	Method AP-0062
RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine)	Every Two Weeks	Every Two Months	Method AP-0062
2,4 DNT (2,4-Dinitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
2,6 DNT (2,6-Dinitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
2A-DNT (2-Amino-4,6-dinitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
4A-DNT (4-Amino-2,6-dinitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
2,6 DANT (2,6-Diamino-4-nitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
2,4 DANT (2,4-Diamino-6-nitrotoluene)	Every Two Weeks	Every Two Months	Method AP-0062
Total Organic Carbon (TOC)	Every Two Weeks	Not Analyzed	415 Series
NH_4-N	Every Two Weeks	Not Analyzed	AP-0059
Total Kjeldahl Nitrogen	Every Two Weeks	Not Analyzed	AP-0064
$(NO_3 + NO_2)$-N	Every Two Weeks	Not Analyzed	AP-0058
$(PO_4$-P)	Every Two Weeks	Not Analyzed	AP-0060
pH	Every Two Weeks	Not Analyzed	150 Series
Electrical Conductivity	Every Two Weeks	Not Analyzed	120 Series for liquids

(1) Leachate was collected after every rain event and after thorough mixing, 5 to 100% of each collection was placed in a designated sample bottle and placed in cold storage. This procedure was followed for each rain event with the same proportion composited that was composited from other samples taken during the sampling period.

(2) See Appendix A for details on methods and procedures.

After 24 hours of any subsequent rain event in a collection interval, any leachate collected in the same 3.78-liter collection bottle was again measured by pouring the leachate into a pre-cleaned graduated cylinder. Then the same percent of the total volume collected after the first rain event would be poured into a 250-ml amber glass sample bottle. For example, if 5% of the sample was collected during the first sampling event, then 5% of any samples from any subsequent rain events would be collected for analysis. If more than one 250-ml sample bottle per replicate was filled over this interval, the samples for each replicate were composited prior to being sent to the laboratory. The samples were composited by measuring a portion from each related sample bottle into a pre-cleaned graduated cylinder and then by pouring a sample into a 250-ml amber glass bottle. All of the sampling bottles were sealed with a Teflon-lined lid and wrapped in aluminum foil. All of the 250-ml containers were then stored in a laboratory refrigerator at TVA's greenhouse.

At two-week intervals during the first year and at two-month intervals during the second year, the sample bottles were sent to TVA's analytical laboratory. The samples were quickly transported to the laboratory in the custody of a TVA employee. All samples were refrigerated upon arrival at the lab. The leachate samples submitted to the analytical laboratory were analyzed for explosives, explosive by-products, EC, pH, and nutrient content (N, P, and K), as outlined in Table 3-1. All samples received from the greenhouse were handled in accordance with TVA's Chain of Custody procedure (Appendix A-1).

3.2.2 Sampling of Compost Prior to the Microbial Weathering Study

The treated compost pile was sampled prior to using it in the Microbial Weathering Study. Samples of approximately 4 liters' volume were collected by digging into random positions around the perimeter of the treated compost pile with a shovel and placing the compost in buckets. Three independent samples were collected from both the control and treated compost. After thorough mixing, a subsample of each larger sample was placed in a 250-ml foil-wrapped amber glass bottle, sealed with a Teflon-lined lid, and submitted to TVA's analytical laboratory for chemical analysis (Table 3-2). All samples received from the test site were handled in accordance with TVA's Chain of Custody procedures (Appendix A-1).

Table 3-2

Analysis of Compost

Compost Parameters Measured	Frequency	Method[1]
TNT	Annually	Method AP-0062
2,4 DNT	Annually	Method AP-0062
2,6 DNT	Annually	Method AP-0062
2A-DNT	Annually	Method AP-0062
4A-DNT	Annually	Method AP-0062
2,6 DANT	Annually	Method AP-0062
2,4 DANT	Annually	Method AP-0062
Total Organic Carbon (TOC)	Annually	415 Series
NH_4-N	Annually	AP-0059 (Analyze 2N KCl extract)
Total Kjeldahl Nitrogen	Annually	AP-0064
$(NO_3 + NO_2)$-N	Annually	AP-0058 (Analyze 2N KCl extract)
Total P	Annually	ASA 24-2.3 perchloric acid digestion or Kjeldahl digestion followed by 6010B
Inorganic P	Annually	ASA 24-3.3.3 (extraction with 1N H_2SO_4 only) followed by Lachat 10-115-01
Organic P	Annually	Calculated (Total P - Inorganic P)
pH	Annually	ASA 12-2.6
Metals	Annually	6010B (7470A/71A for Hg, 7740 for Se, 7060A for As) digestion for 6010B by 3050B
Ash	Annually	Method AP-0022
Moisture	Annually	ASTM E 871

(1) See Appendix A for details on methods and procedures.

3.2.3 Sampling of Compost and Compost + Soil Mixtures During the Microbial Weathering Study

At the end of each year, core samples of each replicate of the compost and compost + soil mixture were taken from each bin for chemical analysis as outlined in Table 3-2. Each bin containing the compost or compost + soil mixture was cored at two locations during each sampling event. The first core was left intact as a full depth core sample. The second core sample was divided into three segments by depth; the top 15 cm, the middle 15 cm, and the bottom 15 cm. Each of the four core samples were then placed in individual 250-ml foil-wrapped amber glass bottles, sealed with a Teflon-lined lid, and sent to TVA's analytical laboratory for analysis. If explosives or explosive by-products were detected in the full depth core sample, then the segmented core samples were analyzed to determine at what depth explosives or explosive by-products were present. The core sampler was wiped clean between each sampling. At the end of sampling, the sample holes were filled with an appropriate length and diameter of PVC pipe which had been capped at both ends. All samples received from the test site were handled in accordance with TVA's Chain of Custody procedures (Appendix A-1).

3.3 Laboratory Procedures

The standard analytical procedures used during this project are provided in Appendices A-1 through A-19.

3.4 Laboratory Analytical Equipment

A list of the laboratory equipment used during this project is provided in Table 3-3.

3.5 Quality Assurance

Details of the Quality Assurance Program used during this project are provided in Appendix B.

Table 3-3

Equipment Used for Data Collection

Laboratory Data	Equipment
Explosives and Related By-Products	Varian HPLC
TKN, NH_4, NO_3, and PO_4	Lachat Quick Chem 8000 or Technicon AutoAnalyzer II
Total Organic Carbon	Dohrmann DC 190
pH	Orion Meter
Electrical Conductivity	Orion
Metals	Varian Cold Vapor AA, Varian Graphite Furnace AA, and Perkin Elmer or Thermo Jarrel Ash ICP

3.6 Advantages and Limitations of the Experimental Design

The one disadvantage of the weathering study is that it was done in a humid and warm climate that may not be typical of all sites where composting will be used to remediate explosives-contaminated soil. The high amount of rainfall which occurred during the study, however, was advantageous since it represented the worst case in terms of the amount of precipitation that would normally be encountered at military sites in the continental U.S. One other limitation of the system was that the overflow collection containers were not large enough to collect all the leachate associated with the largest rainfall events. Early during the study, the water-holding capacity of the compost was relatively high and leachate was not lost from the system. However, after the compost had weathered for several months, the rainfall passed so rapidly through the compost that some leachate was lost from heavy rains occurring over weekends.

SECTION 4.0
STUDY RESULTS

4.1 Initial Compost Composition

To determine initial concentration of explosives, nutrients, and metals in the treated compost, three cores were taken from the compost after it arrived at TVA's facility. TNT, TNB, RDX, and 2-ADNT were detected in the compost (Table 4-1). TNT was found in all three samples, TNB was above the detection limit in only two samples, and RDX and 2-ADNT were above the detection limit in only one of the three samples. Arsenic, barium, cadmium, and chromium were found, but not at levels high enough to warrant the analyses of metals in the leachate.

4.2 Rainfall

Rainfall was measured manually using a rain gauge located approximately 15 meters (50 feet) west of the weathering bins. Rainfall amounts were recorded daily and measured to the nearest one-hundredth inch. The rainfall events and the amount of rain in each event are shown, respectively, for the first and second year of the weathering study in Figures 4-1 and 4-2. The rainfall data is tabulated in Appendix C. The compost and soil amended with compost were placed in the weathering bins on September 15, 1996. This date marks the first day of each year of the study. The first year of the study, the total rainfall was 71.69 inches (182.1 cm). This is 17.84 inches (45.3 cm) more than the average annual rainfall of 53.85 inches (136.8 cm), based on 1960 through 1990 records.

The second year was slightly drier, but still above normal. Total rainfall in the second year was 61.19 inches (155.4 cm). The first year had seven events which exceeded 2 inches (5 cm) and the second had 6 events which exceed 2 inches (5 cm). The longest period with no rain was in the last four weeks of the study from August 18 to September 15, 1998.

Table 4-1

Initial Compost Analysis

Analyte	Sample 1	Sample 2	Sample 3	Average
Explosives				
HMX (mg/kg)	ND (0.0589)	ND (0.0608)	ND (0.0593)	ND
RDX (mg/kg)	0.0704	ND (0.0041)	ND (0.0040)	0.0248*
TNT (mg/kg)	0.0442	0.0500	0.0974	0.064
TNB (mg/kg)	0.1820	ND (0.0485)	0.5520	0.252*
2,6-DA-4-NT (mg/kg)	ND (0.0272)	ND (0.0281)	ND (0.0274)	ND
2,4-DA-6-NT (mg/kg)	ND (0.00495)	ND (0.00511)	ND (0.00498)	ND
2,6-DNT (mg/kg)	ND (0.0243)	ND (0.0250)	ND (0.0244)	ND
2,4-DNT (mg/kg)	ND (0.0114)	ND (0.0118)	ND (0.0115)	ND
2-ADNT (mg/kg)	ND (0.0104)	ND (0.0107)	0.0245	0.012*
4-ADNT (mg/kg)	ND (0.0193)	ND (0.0199)	ND (0.0194)	ND
Nutrients and Moisture				
Moisture (%)	21.9			
Phosphorus (%)	0.31			
Potassium (%)	0.78			
Total Nitrogen (%)	0.55			
Metals				
Arsenic (ug/kg)	981	1,140	1,330	1,150
Barium (mg/kg)	59	57.1	57.7	57.9
Cadmium (mg/kg)	1.2	1.39	1.22	1.27
Chromium (mg/kg)	5.09	5.52	6.08	5.56
Lead (mg/kg)	ND (1.5)	ND (1.5)	ND (1.5)	ND
Mercury (ug/kg)	ND (115)	ND (115)	ND (115)	ND
Selenium (ug/kg)	ND (600)	ND (600)	ND (600)	ND
Silver (mg/kg)	ND (0.1)	ND (0.1)	ND (0.1)	ND

ND = Not detected above the detection limit shown in parentheses.

* One half times the detection limit used for ND when averaging.

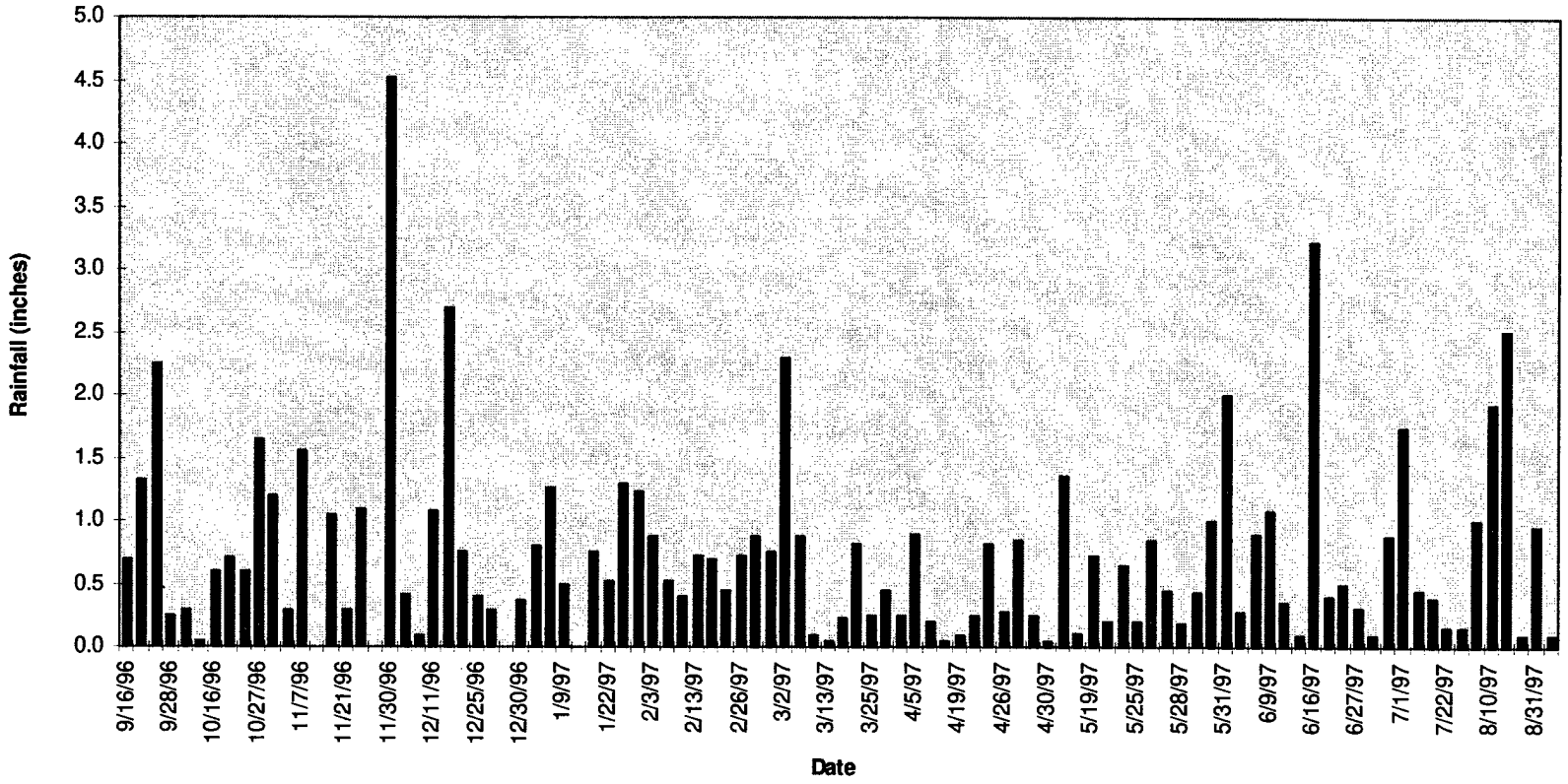


Figure 4-1

Rainfall Pattern for the First Year

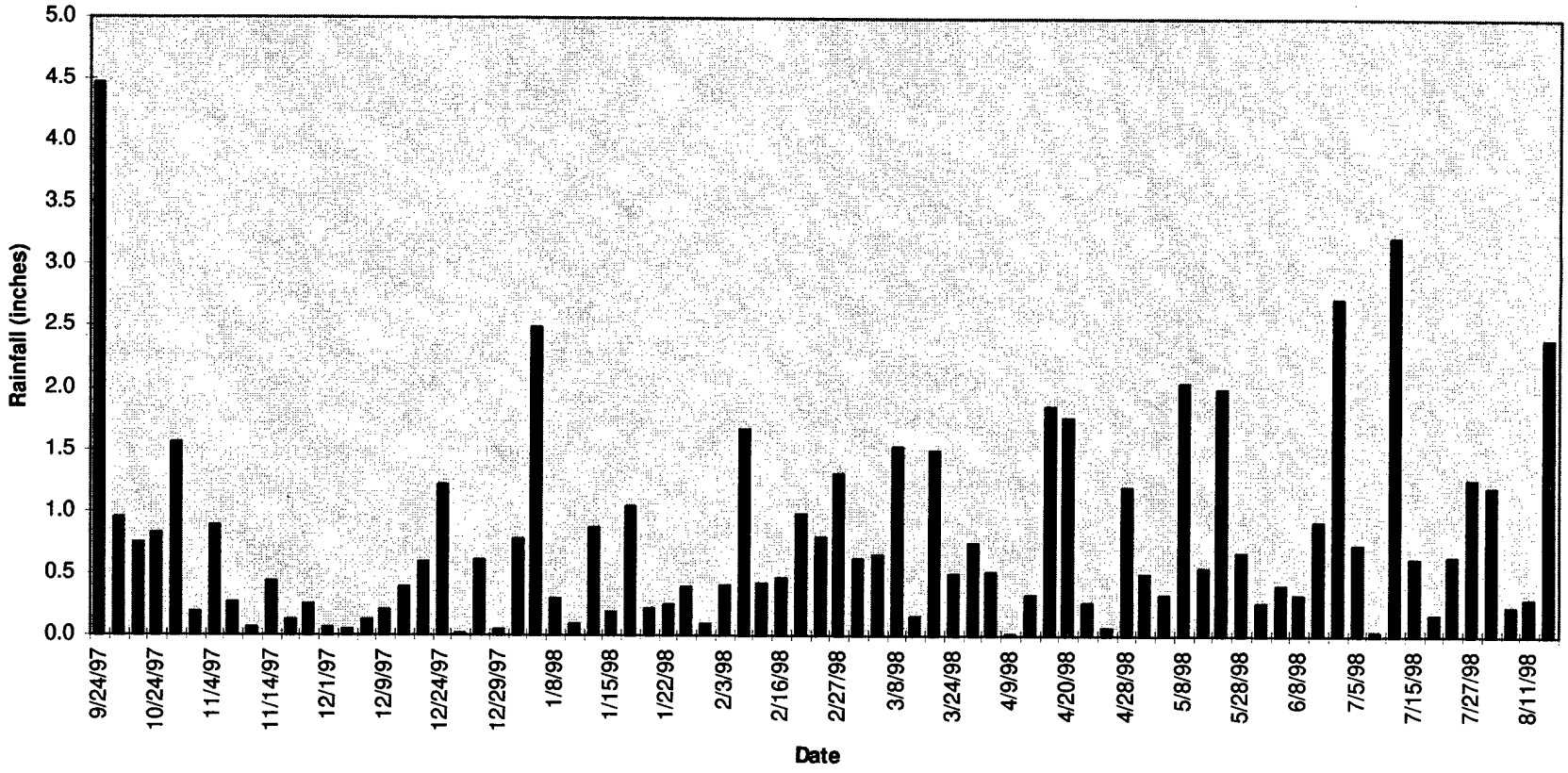


Figure 4-2

Rainfall Pattern for the Second Year

4.3 Leachate Volume

To simplify the discussion of the data, the leachate from the three bins containing compost (Bins 1-3) and the three containing soil amended with compost (Bins 4-6) were averaged for reporting and plotting. Figure 4-3 shows the average monthly leachate volumes collected from the two groups of bins (compost only and compost + soil mixture). The volumes of leachate collected from all six bins are tabulated in Appendix D. There were two trends in the monthly leachate volume data; 1) the compost only produced more leachate than did the compost + soil mixture, and 2) more leachate was produced in the winter months. June 1997 was the only summer month in which leachate volumes approached those of the winter months. This was due to the unusually high rainfall of 8.1 inches (20.6 cm) which fell that month (see rainfall data in Appendix C).

The bins containing only compost produced more leachate mainly because the compost had a lower moisture-holding capacity and precipitation passed through the material fairly rapidly. Conversely, precipitation sometimes pooled on the surface of the compost + soil mixtures and was subject to evaporation. Absorbed precipitation was subject to loss by evaporation and transpiration. Eight months into the study, weeds began to grow in the weathering bins. Willow trees (*Salix nigra)*, which grew only in the bins containing the compost + soil mixture, may also have contributed to the lower leachate volumes from the bins containing the compost + soil mixture.

The higher leachate volumes in the colder months are attributable to lower rates of evapotranspiration. The three parameters that enhance evapotranspiration (temperature, sunlight, and plant growth) are reduced in winter months.

4.4 Explosive Residues in Leachate

Explosives and their transformation products were analyzed on two-week intervals during the first year of the study and then on two-month intervals in the second year. The average concentration of explosives in the leachate from the three bins containing only compost is shown in Table 4-2.

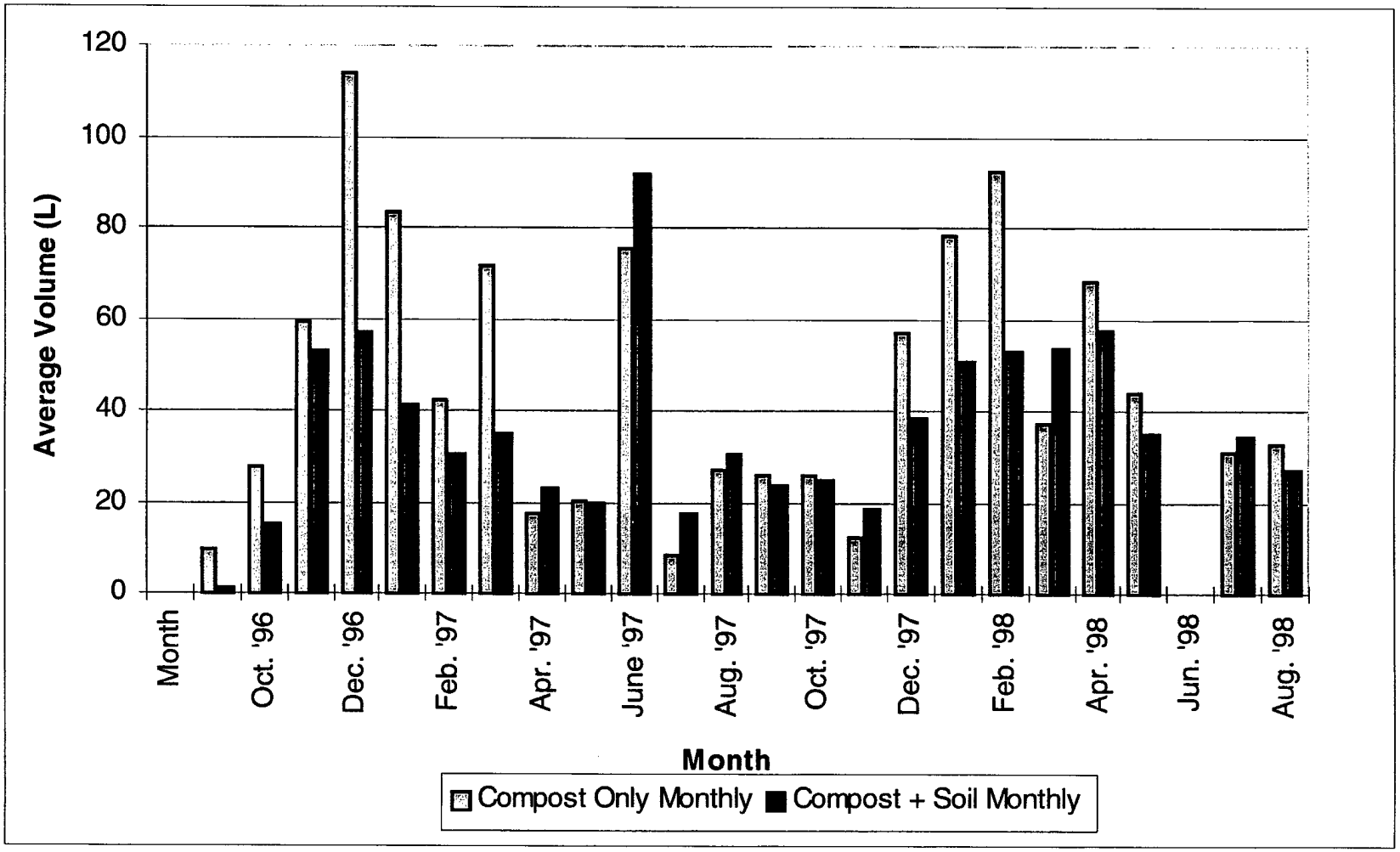


Figure 4-3

Monthly Leachate Volume

Table 4-2

Leachate From Compost Only Bins

Average Explosives Analysis											
Date	Leachate Volume (Liters)	HMX (mg/L)	RDX (mg/L)	TNT (mg/L)	TNB (mg/L)	2,6-DANT (mg/L)	2,4-DANT (mg/L)	2,6-DNT (mg/L)	2,4-DNT (mg/L)	2-ADNT (mg/L)	4-ADNT (mg/L)
9/22/96	4.1	ND	11.86	ND	ND	ND	ND	ND	ND	ND	ND
9/27/96	5.4	ND	24.18	ND	ND	ND	ND	ND	ND	ND	ND
10/8/96	1.4	ND	8.66*	ND	ND	ND	ND	ND	ND	ND	ND
11/3/96	17.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11/20/96	4.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12/3/96	9.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12/16/96	41.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12/31/96	56.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1/13/97	11.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1/29/97	69.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2/13/97	21.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2/27/97	20.7	ND	1.87	ND	ND	ND	ND	ND	ND	ND	ND
3/13/97	62.4	ND	1.48	ND	ND	0.295*	ND	ND	ND	ND	ND
3/31/97	8.9	ND	2.74	ND	ND	ND	ND	ND	ND	ND	ND
4/15/97	4.9	0.922*	4.15	ND	ND	ND	ND	ND	ND	ND	ND
4/30/97	12.4	0.566*	4.34 **	ND	ND	ND	ND	ND	ND	ND	ND
5/15/97	11.9	1.33*	3.73	ND	ND	ND	ND	ND	ND	0.349*	0.526*
5/29/97	8.4	0.840**	2.62**	ND	ND	ND	ND	ND	ND	ND	0.398*
6/16/97	54.7	1.35**	1.38	ND	ND	ND	ND	ND	ND	ND	ND
6/30/97	45.5	0.835*	0.475*	ND	ND	ND	ND	ND	ND	ND	ND
7/14/97	17.4	0.895*	1.36**	ND	ND	ND	ND	ND	ND	ND	ND
8/28/97	27.0	0.876*	1.33**	ND	ND	ND	ND	ND	ND	ND	ND
9/15/97	2.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9/29/97	23.5	ND	2.81	ND	ND	ND	ND	ND	ND	ND	ND
12/4/97	61.8	ND	1.25*	ND	ND	ND	ND	ND	ND	ND	ND
2/5/98	148.9	ND	1.02**	ND	ND	ND	ND	ND	ND	ND	ND
4/9/98	111.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6/29/98	42.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7/31/98	30.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not Detected (below detection limits)

*One or more samples below detection limit and average based on one-half of detection limit.

**On one or more samples, associated quality control sample was out of limits.

Table 4-3 lists the average values for explosives found in leachate from the three bins containing the compost + soil mixture. The values marked with an asterisk are based on readings made when an associated quality control sample was out of limits. A review of the data revealed that the instrument calibration always drifted downward indicating that the actual concentrations were higher than the measured values. Most of the analytical results were below detection levels. A list of the detection levels for all the leachate analysis is given in Appendix E.

4.4.1 TNT and Related Degradation Products

TNT was never detected in the leachate containing the compost only (Table 4-2) or the compost + soil mixture (Table 4-3). Indeed, the only explosive analytes detected in the leachate from more than one bin in a given sampling period were HMX and RDX. This was true for both the compost only and the compost + soil mixture. The values shown in Tables 4-2 and 4-3 are an average of the data from three bins. A detailed listing of these values is provided in Appendix F.

TNT degradation products were not detected in the leachate from the bins containing the compost + soil mixture. However, TNT degradation products were detected in the leachate from the bins containing compost only: 4-ADNT was detected twice; 2,6-DANT and 2-ADNT were detected once; and 2,4-DANT and 2,4-DNT were never detected (Table 4-4). In each case, the analyte was detected from only one of the three bins; either Bin 1 or Bin 2. No degradation products were detected in the leachate from Bin 3. The low levels of these TNT degradation products indicate that TNT was effectively treated in the Umatilla composting process.

4.4.2 HMX and RDX

Unlike TNT and its related compounds, HMX and RDX were detected in leachate samples from all bins for several sampling events. Figures 4-4 and 4-5 show, respectively, the average change in the concentration of HMX and RDX over time from both the bins containing compost only and the compost + soil mixture. All of the HMX and RDX analytical data is presented, respectively, in Tables 4-5 and 4-6. The values marked with two asterisks are based

Table 4-3

Leachate From Bins Containing Compost + Soil Mixtures

Average Explosives Analysis											
Date	Leachate Volume (Liters)	HMX (mg/L)	RDX (mg/L)	TNT (mg/L)	TNB (mg/L)	2,6-DANT (mg/L)	2,4-DANT (mg/L)	2,6-DNT (mg/L)	2,4-DNT (mg/L)	2-ADNT (mg/L)	4-ADNT (mg/L)
9/22/96	0.005	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9/27/96	1.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10/8/96	0.1	31.5	26.4	ND	ND	ND	ND	ND	ND	ND	ND
11/3/96	12.8	18.3	14.5	ND	ND	ND	ND	ND	ND	ND	ND
11/20/96	4.0	16.4	8.62	ND	ND	ND	ND	ND	ND	ND	ND
12/3/96	6.9	12.1 **	3.91	ND	ND	ND	ND	ND	ND	ND	ND
12/16/96	15.7	11.6 **	3.18 **	ND	ND	ND	ND	ND	ND	ND	ND
12/31/96	24.6	8.85	ND	ND	ND	ND	ND	ND	ND	ND	ND
1/13/97	10.9	7.52 **	ND	ND	ND	ND	ND	ND	ND	ND	ND
1/29/97	29.5	4.22	ND	ND	ND	ND	ND	ND	ND	ND	ND
2/13/97	14.7	4.26	ND	ND	ND	ND	ND	ND	ND	ND	ND
2/27/97	15.9	2.93	ND	ND	ND	ND	ND	ND	ND	ND	ND
3/13/97	17.0	2.71	ND	ND	ND	ND	ND	ND	ND	ND	ND
3/31/97	18.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4/15/97	13.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4/30/97	9.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5/15/97	8.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5/29/97	10.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6/16/97	46.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6/30/97	45.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7/14/97	17.4	ND	1.40**	ND	ND	ND	ND	ND	ND	ND	ND
8/28/97	30.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9/15/97	0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9/29/97	23.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12/4/98	60.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2/5/98	128.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4/9/98	91.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6/29/98	35.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7/31/98	34.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not Detected (below detection limits)

**On one or more samples, associated quality control sample was out of limits.

Table 4-4

Detection of TNT Degradation Products in Leachate

Analyte	Date	Bin Number	Concentration (ug/l)
2,6-Diamino-4-nitrotoluene	3/13/97	2	0.493
2-Amino-4,6-dinitrotoluene	5/15/97	1	0.543
4-Amino-2,6-dinitrotoluene	5/15/97	1	1.07
4-Amino-2,6-dinitrotoluene	5/29/97	1	0.745

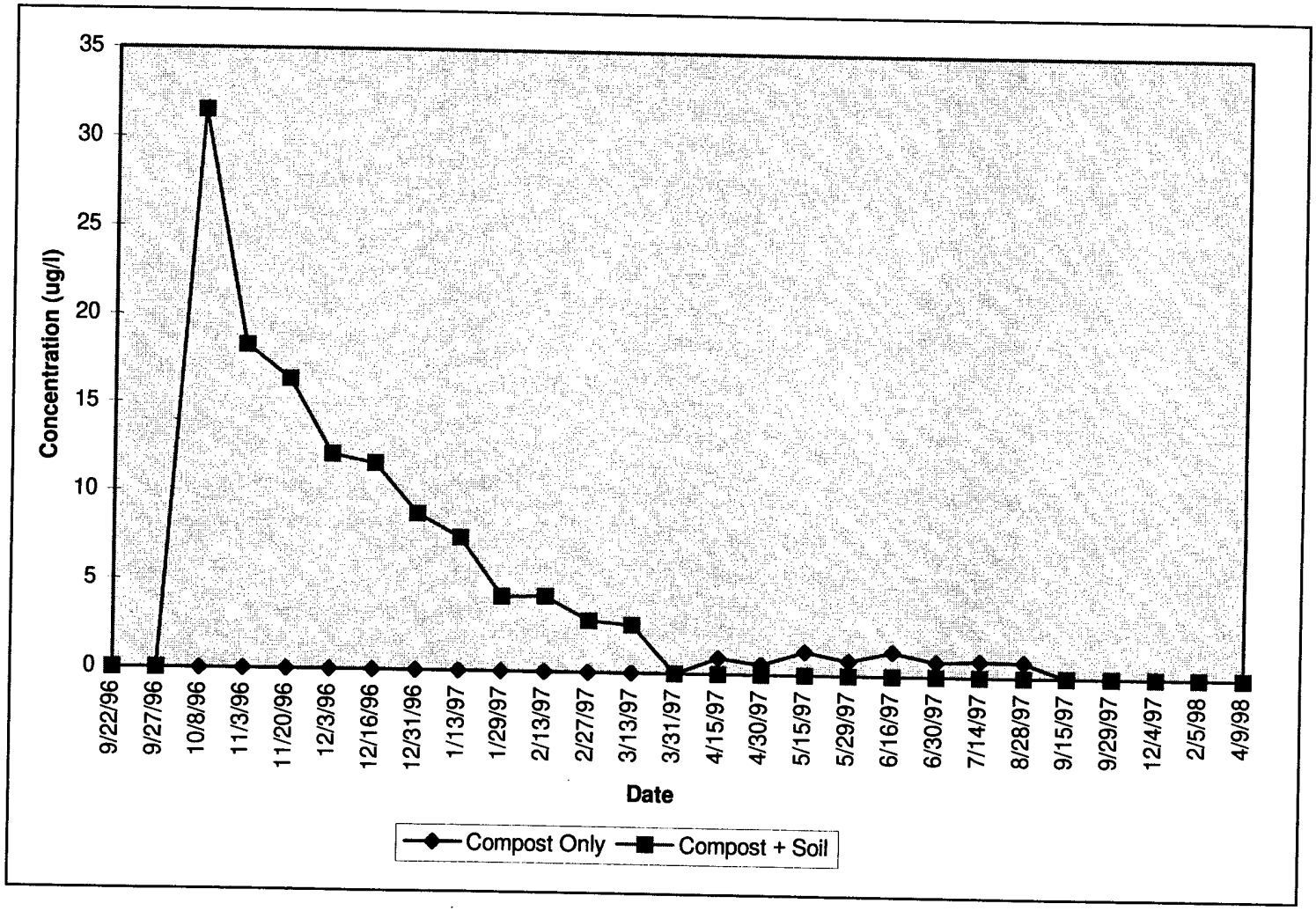


Figure 4-4

Average HMX Concentrations in Leachate

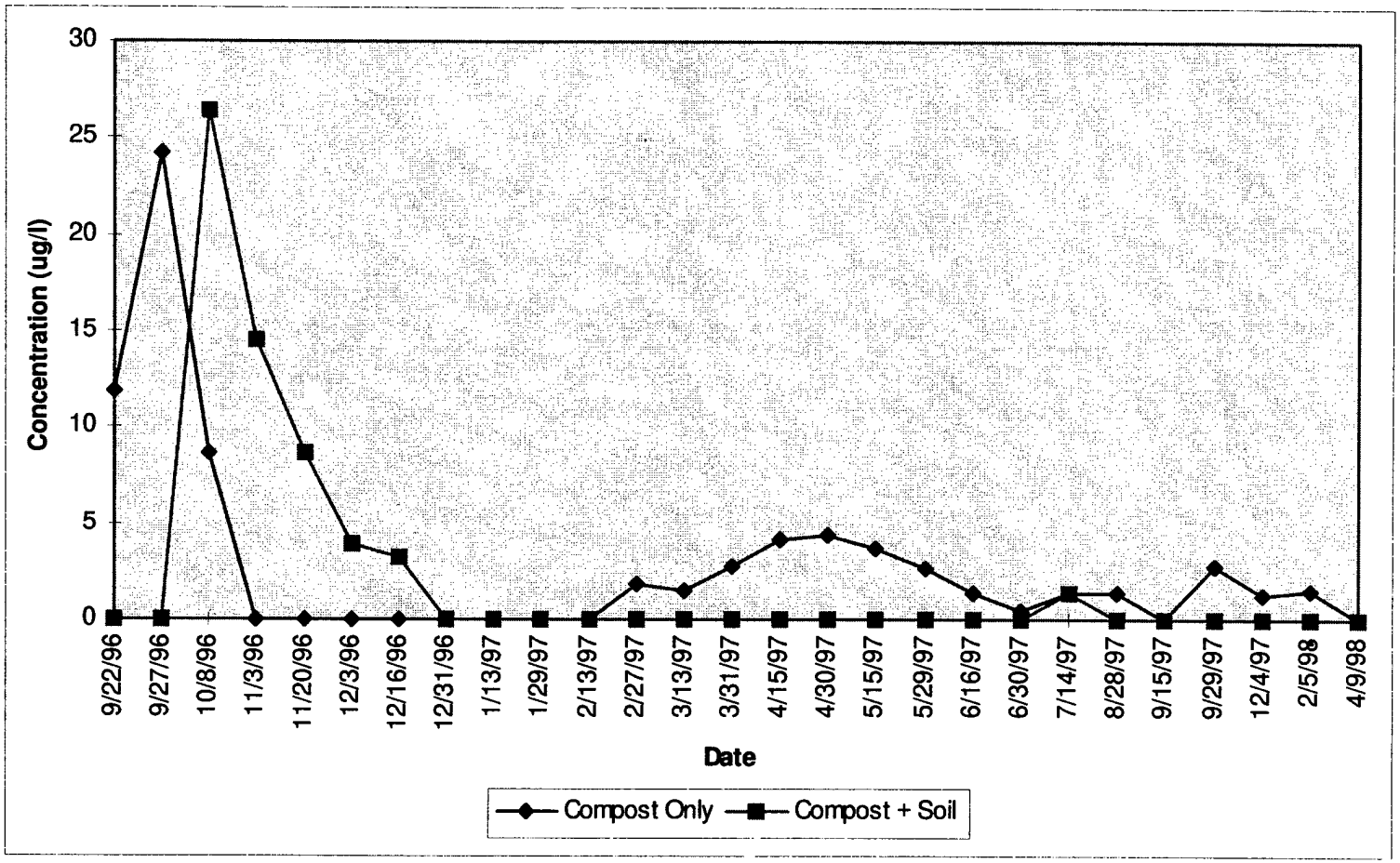


Figure 4-5

Average RDX Concentrations in Leachate

Table 4-5

HMX in Leachate

Date	HMX (mg/L)							
	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	SNC	ND	ND	ND	SNC	SNC	ND	ND
9/27/96	ND	ND	ND	ND	ND	ND	ND	ND
10/8/96	ND	ND	ND	SNC	SNC	31.5	ND	31.5
11/3/96	ND	ND	ND	17.6	22.4	14.8	ND	18.3
11/20/96	ND	ND	ND	14.0	18.1	17.0	ND	16.4
12/3/96	ND	ND	ND	12.6**	10.9**	12.9	ND	12.1
12/16/96	ND	ND	ND	11.6**	10.5**	12.8**	ND	11.6
12/31/96	ND	ND	ND	8.42	7.72	10.4	ND	8.85
1/13/97	ND	ND	ND	7.21**	7.24**	8.11**	ND	7.52
1/29/97	ND	ND	ND	3.99	4.22	4.45	ND	4.22
2/13/97	ND	ND	ND	3.82	4.55	4.41	ND	4.26
2/27/97	ND	ND	ND	2.34	3.55	2.89	ND	2.93
3/13/97	ND	ND	ND	2.06	3.29	2.78	ND	2.71
3/31/97	ND	ND	ND	ND	ND	ND	ND	ND
4/15/97	2.28**	ND	ND	ND	ND	ND	0.922*	ND
4/30/97	1.21**	ND	ND	ND	ND	ND	0.566*	ND
5/15/97	1.46	1.22	1.32	ND	ND	ND	1.33	ND
5/29/97	1.28**	0.689**	0.55**	ND	ND	ND	0.840	ND
6/16/97	1.42	1.22**	1.42**	ND	ND	ND	1.35	ND
6/30/97	1.16	ND	0.844	ND	ND	ND	0.835*	ND
7/14/97	1.27**	ND	0.901**	ND	ND	ND	0.895	ND
8/28/97	ND	ND	2.12**	ND	ND	ND	0.876*	ND
9/15/97	ND	ND	ND	ND	ND	ND	ND	ND
9/29/97	ND	ND	ND	ND	ND	ND	ND	ND
12/4/97	ND	ND	ND	ND	ND	ND	ND	ND
2/5/98	ND	ND	ND	ND	ND	ND	ND	ND
4/9/98	ND	ND	ND	ND	ND	ND	ND	ND
6/29/98	ND	ND	ND	ND	ND	ND	ND	ND
7/31/98	ND	ND	ND	ND	ND	ND	ND	ND

SNC = Sample Not Collected
ND = Not Detected (below detection limits)
*One or more samples were below detection limit and average based on one-half the detection limit.
**On one or more samples, associated quality control sample was out of limits.

Table 4-6

RDX in Leachate

Date	RDX (mg/L)							
	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	SNC	13.9	9.82	ND	SNC	SNC	11.9	ND
9/27/96	8.52	56.3	7.72	ND	ND	ND	24.2	ND
10/8/96	8.39	ND	17.4	SNC	SNC	26.4	8.66*	26.4
11/3/96	ND	ND	ND	13.3	18.9	11.3	ND	14.5
11/20/96	ND	ND	ND	7.83	10.3	7.74**	ND	8.62
12/3/96	ND	ND	ND	2.52	5.68**	3.52**	ND	3.91
12/16/96	ND	ND	ND	2.15**	4.96**	2.42**	ND	3.18
12/31/96	ND	ND	ND	ND	ND	ND	ND	ND
1/13/97	ND	ND	ND	ND	ND	ND	ND	ND
1/29/97	ND	ND	ND	ND	ND	ND	ND	ND
2/13/97	ND	ND	ND	ND	ND	ND	ND	ND
2/27/97	3.71	0.976	0.918	ND	ND	ND	1.87	ND
3/13/97	1.02	2.15	1.27	ND	ND	ND	1.48	ND
3/31/97	5.98	0.686	1.54	ND	ND	ND	2.74	ND
4/15/97	5.89	2.73	3.84	ND	ND	ND	4.15	ND
4/30/97	5.75**	4.43**	2.84**	ND	ND	ND	4.34	ND
5/15/97	4.12	4.05	3.01	ND	ND	ND	3.73	ND
5/29/97	4.19**	2.78**	0.881**	ND	ND	ND	2.62	ND
6/16/97	1.62	1.20	1.32	ND	ND	ND	1.38	ND
6/30/97	0.824	ND	ND	ND	ND	ND	0.475*	ND
7/14/97	1.72**	0.811**	1.56**	3.55**	ND	ND	1.36	1.40*
8/28/97	2.05**	0.674**	1.26**	ND	ND	ND	1.33	ND
9/15/97	ND	SNC	ND	SNC	ND	ND	ND	ND
9/29/97	0.64	5.05	2.74	ND	ND	ND	2.81	ND
12/4/97	2.47	ND	0.98	ND	ND	ND	1.25*	ND
2/5/98	3.06	0.75	0.70	ND	ND	ND	1.50	ND
4/9/98	ND	ND	ND	ND	ND	ND	1.50	ND
6/29/98	ND	ND	ND	ND	ND	ND	1.50	ND
7/31/98	ND	ND	ND	ND	ND	ND	ND	ND

SNC = Sample Not Collected
ND = Not Detected (below detection limits)
*One or more samples were below detection limit and average based on one-half the detection limit.
**On one or more samples, associated quality control sample was out of limits.

on readings made when an associated quality control sample was out of limits. A review of the data revealed that the instrument calibration always drifted downward indicating that the actual concentrations were higher than the measured values.

One of the most interesting aspects of this study is the amount and timing of HMX found in the leachate. HMX was detected in the leachate from the bins containing the compost + soil mixture three weeks after the weathering study began. The highest concentration was found in leachate collected October 10, 1996. After this time, levels declined steadily until the end of March 1997 when they fell below detection limits (Figure 4-5). The peak concentration of 31 ug/l was associated with a small amount of leachate, 0.13 liters. This yields an average loss of 4 ug of HMX per bin. In terms of the amount of HMX lost from the bins (i.e., concentration multiplied by leachate volume), HMX removal from the bins reached a peak on November 3, 1996, when an average of 233 ug of HMX were removed per bin.

In contrast to the bins containing the compost + soil mixture, the HMX removal from the bins containing compost only was delayed for seven months. The first appearance of HMX in the leachate from the bins containing compost only was on April 15, 1997. The concentrations of HMX from the bins filled with treated compost were also much lower than the peak concentrations in leachate from the bins containing the compost + soil mixture. The total amount of HMX removed from the bins containing the compost + soil mixture was also much greater. Each bin containing the compost + soil mixture lost an average of 938 ug of HMX while the bins containing compost only lost 185 ug of HMX in leachate.

The most likely explanation for the higher amounts of HMX leached from the compost + soil mixture is that the mixing of compost with a much larger volume of soil reduced the number of binding sites relative to the amount of explosive that was bound to organic matter. Since the Umatilla soil was practically devoid of organic matter, the HMX was not able to bind with the soil once it began to leach. Due to the heterogeneity of explosive contamination, it is also possible that the compost placed in the bins containing the compost + soil mixture had higher levels of HMX than did the compost placed in the bins containing compost only. The total amount of HMX removed from the bins containing the compost + soil mixture was approximately 1 mg per bin for the entire duration of the study.

RDX was detected in leachate soon after the weathering study was begun. The bins containing compost only produced leachate with detectable levels of RDX in the first sampling period, September 22, 1996. RDX was detected in leachate from the bins containing the compost + soil mixture about two weeks after appearing in the bins containing compost only, and the peak concentrations had a similar lag (Figure 4-6). Unlike HMX, the amount of RDX found in leachate corresponded with the amount of treated compost placed in the bins. More RDX leached from the bins containing compost only than from those containing the compost + soil mixture. The total amount of RDX removed from the bins containing compost only averaged 920 ug per bin while the amount removed from those containing the compost + soil mixture was 324 ug per bin.

The RDX concentrations from the bins containing the compost + soil mixture fell below detection levels after three months and was only detected on one other occasion, July 14, 1997 (Table 4-6). RDX levels in the bins containing compost only dropped to below detection levels one month into the study and then reappeared the next spring and summer. This suggests that the release of RDX from the compost was influenced by temperature due to enhanced microbial activity. Colder ambient temperatures between November 1996 and March 1997 are thought to have decreased microbial activity, resulting in a corresponding decrease in the release of RDX. As with HMX, the total amount of RDX removed from each weathering bin during the entire study was less than 1 mg.

4.5 Nutrients in Leachate

In the first year of the study, leachate from the bins was analyzed for nitrogen, phosphate, total organic carbon, electrical conductivity, and pH. Tables 4-7 and 4-8 list the average values for these analyses of leachate from the bins containing the compost only and compost + soil mixture, respectively. These analyses were suspended after July 14, 1997, because the concentrations were remaining fairly constant and budget constraints shifted the emphasis of analytical work to explosives. The complete analytical data set is provided in Appendix G.

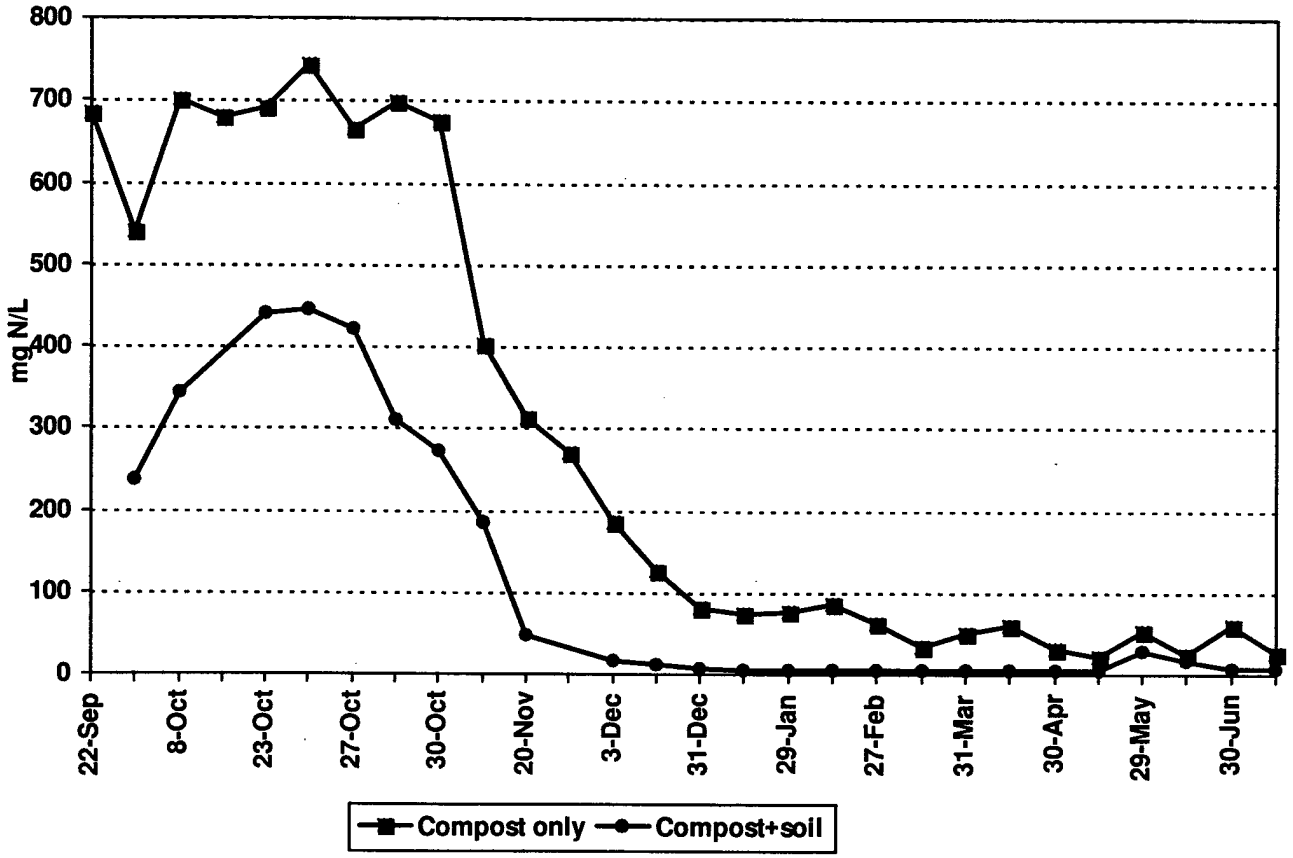


Figure 4-6

Total Nitrogen

Table 4-7

Nutrient and General Analysis of Leachate from Bins Containing Compost Only

Date	Leachate Volume (Liters)	NH_4-N (mg/L)	NO_3-N (mg/L)	TKN (mg/L)	PO_4-P (mg/L)	TOC (mg/L)	EC (µmhos/cm)	pH
9/22/96	4.1	16.1	448	219	49.6	3,663	27,200	8.31
9/27/96	5.4	17.0	365	158	63.1	3,620	23,385	8.10
10/8/96	1.4	48.8	61.5	591	68.8	3,913	24,900	8.12
10/19/96	1.5	58.5	ND	620	66.6	4,235	25,733	7.65
10/23/96	1.0	72.2	ND	618	70.8	4,023	25,767	7.67
10/24/96	0.1	81.5	ND	661	72.4	4,278	27,200	7.88
10/27/96	0.6	71.6	ND	593	73.4	SNC	25,167	7.73
10/28/96	0.4	73.8	ND	625	74.5	SNC	24,567	7.90
10/30/96	12.3	72.1	ND	602	84.1	3,651	23,267	7.55
10/31/96	10.3	SNC	SNC	SNC	SNC	SNC	18,177	7.40
11/3/96	17.4	38.5	ND	364	85.3	2,256	13,930	7.41
11/7/96	4.0	SNC	SNC	SNC	SNC	SNC	13,403	7.67
11/10/96	14.5	SNC	SNC	SNC	SNC	SNC	10,943	7.78
11/17/96	3.2	SNC	SNC	SNC	SNC	SNC	10,333	7.66
11/20/96	4.0	37.5	ND	275	114	1,668	8,673	7.63
11/24/96	5.7	26.6	ND	244	102	1,645	7,447	7.95
12/3/96	9.9	23.2	ND	162	109	1,050	4,767	7.56
12/16/96	41.0	12.4	ND	113	98.3	707	3,180	7.64
12/31/96	56.5	9.0	ND	72.4	70.8	474	1,660	7.52
1/13/97	11.0	7.0	ND	66.8	54.1	427	1,747	7.67
1/29/97	69.1	8.2	6.2	62.1	32.9	319	1,473	7.57
2/13/97	21.4	9.5	5.3	70.6	32.0	382	2,140	8.26
2/27/97	20.7	5.6	11.4	44.1	27.7	301	1,976	8.10
3/13/97	62.4	3.9	0.4	27.7	25.2	162	1,343	7.80
3/31/97	8.9	5.9	5.5	38.3	25.0	230	2,183	8.11
4/15/97	4.9	4.0	15.7	40.5	18.3	344	2,338	8.18
4/30/97	12.4	1.5	4.7	25.1	16.5	249	1,711	7.78
5/15/97	11.9	1.6	1.1	19.3	19.7	230	1,560	8.13
5/29/97	8.4	2.1	2.8	48.2	18.4	508	2,783	7.67
6/16/97	54.7	1.4	0.1	23.2	27.4	218	1,839	7.53
6/30/97	20.8	8.0	0.8	40.8	27.1	210	1,958	7.76
7/14/97	8.6	2.1	ND	24.5	18.1	246	1,948	8.00

SNC = Sample Not Collected

ND = Not Detected (below detection limits)

Table 4-8

Nutrient and General Analysis of Leachate from Bins Containing Compost + Soil

Date	Leachate Volume (Liters)	NH_4-N (mg/L)	NO_3-N (mg/L)	TKN (mg/L)	PO_4-P (mg/L)	TOC (mg C/L)	EC (µmhos/cm)	pH
9/22/96	0.005	SNC	SNC	SNC	SNC	SNC	SNC	SNC
9/27/96	1.11	0.53	217	20.1	1.91	180	2,256	7.35
10/8/96	0.13	0.26	337	4.67	1.67	182	3,940	7.49
10/19/96	SNC	SNC	SNC	SNC	SNC	SNC	SNC	SNC
10/23/96	0.83	0.57	434	6.02	1.84	174	4,763	7.15
10/24/96	0.11	0.99	440	4.74	1.97	213	4,910	7.57
10/27/96	2.2	0.88	409	11.2	1.81	SNC	4,583	7.30
10/28/96	4.7	0.87	302	5.69	3.96	SNC	3,620	7.04
10/30/96	6.4	1.22	260	11.8	2.51	SNC	3,240	7.19
10/31/96	0.9	SNC	SNC	SNC	SNC	SNC	3,410	7.13
11/3/96	12.8	1.22	173	10.7	2.43	205	2,490	6.94
11/7/96	3.9	SNC	SNC	SNC	SNC	SNC	1,846	7.10
11/10/96	13.2	SNC	SNC	SNC	SNC	SNC	1,504	7.35
11/17/96	3.1	SNC	SNC	SNC	SNC	SNC	1,244	7.36
11/20/96	4.0	0.74	39.2	6.75	2.46	118	1,124	7.11
11/24/96	5.6	SNC	SNC	SNC	SNC	SNC	994	7.62
12/3/96	6.9	0.59	10.8	4.77	1.99	38.2	775	7.28
12/16/96	15.7	0.83	5.73	4.16	2.64	88.2	692	7.57
12/31/96	24.6	0.84	1.39	4.05	1.25	63.0	618	7.27
1/13/97	10.9	0.48	0.24	4.12	0.71	37.1	598	7.80
1/29/97	29.5	1.20	ND	4.45	0.56	29.1	610	7.52
2/13/97	14.7	1.24	ND	4.64	0.63	30.8	665	7.94
2/27/97	15.9	1.13	ND	4.32	0.56	29.4	668	7.96
3/13/97	17.0	1.23	ND	4.24	0.38	30.4	748	7.86
3/31/97	18.0	0.83	0.43	4.12	0.31	29.0	856	7.83
4/15/97	13.5	0.64	0.61	3.61	0.38	27.8	973	7.86
4/30/97	9.3	0.26	1.24	3.31	0.18	39.7	1,066	7.96
5/15/97	8.9	0.47	1.29	3.34	0.29	79.7	1,128	7.99
5/29/97	10.7	2.68	19.9	5.80	0.11	26.3	1,183	7.75
6/16/97	46.4	1.81	10.5	4.42	0.07	21.8	925	7.73
6/30/97	45.5	0.95	2.32	3.96	0.11	23.3	816	7.47
7/14/97	17.4	1.90	0.80	4.33	ND	29.1	990	7.72

SNC = Sample Not Collected

ND = Not Detected (below detection limits)

4.5.1 Nitrogen

Figures 4-6 through 4-9 show the change over time in the concentrations of various forms of nitrogen in the leachate from the bins containing either compost only or the compost + soil mixture. To clearly define the removal of nitrogen from the weathering process, several different analyses were run for nitrogen. Total nitrogen, shown in Figure 4-6, is the sum of nitrate nitrogen, ammonium nitrogen, and organic nitrogen. Nitrate nitrogen is shown in Figure 4-7. Kjeldahl nitrogen, which includes the organic nitrogen and ammonium nitrogen, is shown in Figure 4-8 and ammonium nitrogen is shown in Figure 4-9.

Nitrogen was released immediately after the compost was placed in the bins containing compost only. The concentration of total nitrogen in leachate from the compost only was nearly constant at 700 mg/L for about six weeks (September 15 to October 30). Initially, nitrate was the primary form of nitrogen found in the compost only leachate (Figure 4-7). From October 8, 1996, onward, the total nitrogen lost from the bins containing compost only was primarily in the organic form (Figure 4-8). Some ammonia nitrogen was also released from compost only bins (Figure 4-9), however, organic nitrogen was the primary form of nitrogen leached. By the end of December 1996, 15 weeks into the study, the concentration of nitrogen in the compost only leachate reached a constant level less than 100 mg/L. This indicated that all of the excess organic nitrogen had been leached.

The forms of nitrogen leached from the bins containing the compost + soil mixture were considerably different from those associated with the compost only, probably due to microbial activity in the Umatilla soil. A comparison of the total nitrogen (Figure 4-6) and nitrate nitrogen (Figure 4-7) reveals that essentially all of the nitrogen found in leachate from the bins containing the compost + soil mixture was in the nitrate form. A small amount of organic nitrogen was found in the first sampling event (Figure 4-8). However, after the first sampling event, organic nitrogen was first converted to ammonium nitrogen and then to nitrate nitrogen. Ammonium nitrogen present in the compost would have been held by the Umatilla soil and converted to nitrate nitrogen by microbes before being leached. By early December 1996, ten weeks into the study, very little nitrogen was being leached from bins containing the compost + soil mixture, indicating that microbial activity had slowed to the point that organic nitrogen

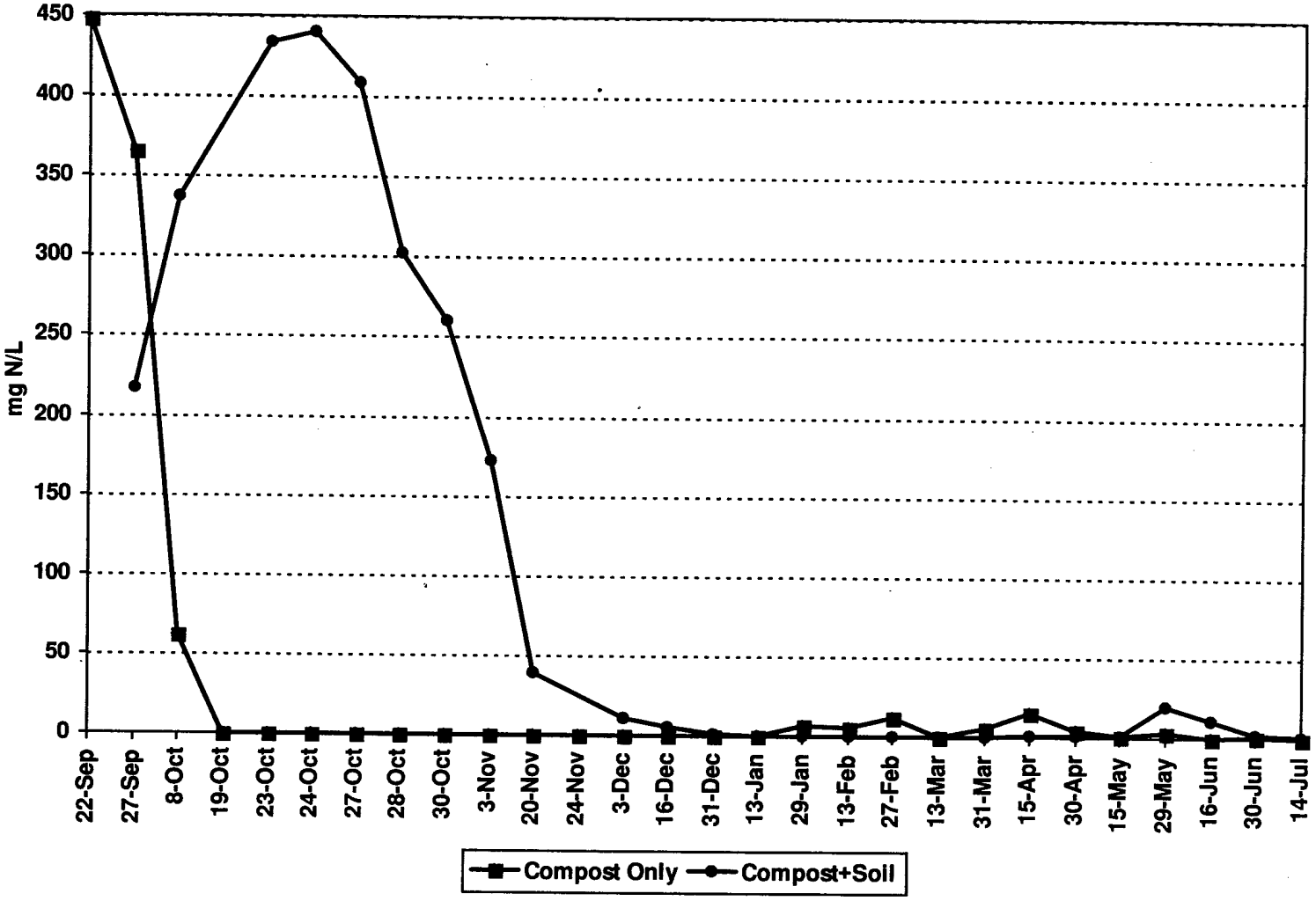


Figure 4-7

Nitrate Nitrogen (NO_3-N) in Leachate

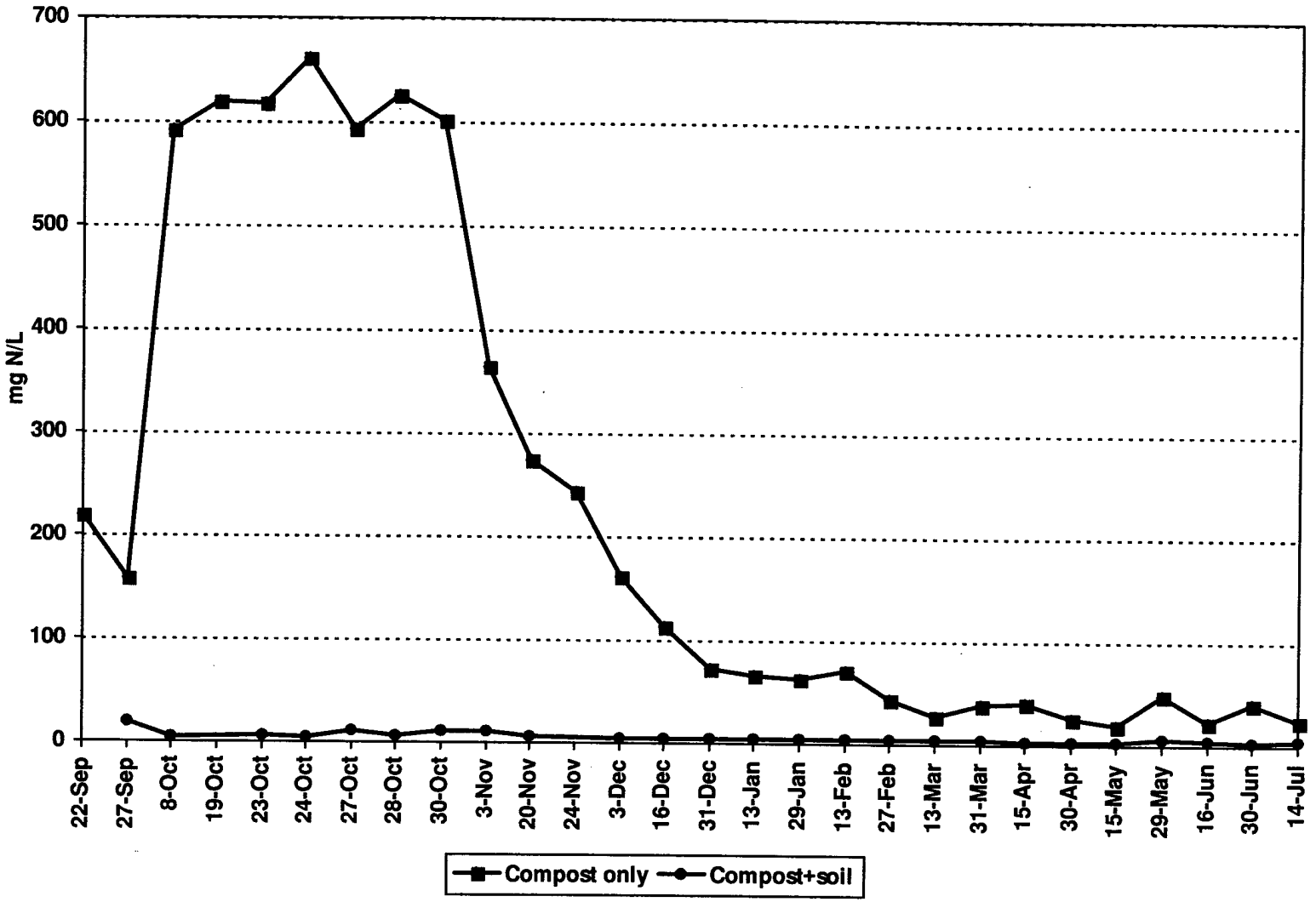


Figure 4-8

Total Kjeldahl Nitrogen (TKN) in Leachate

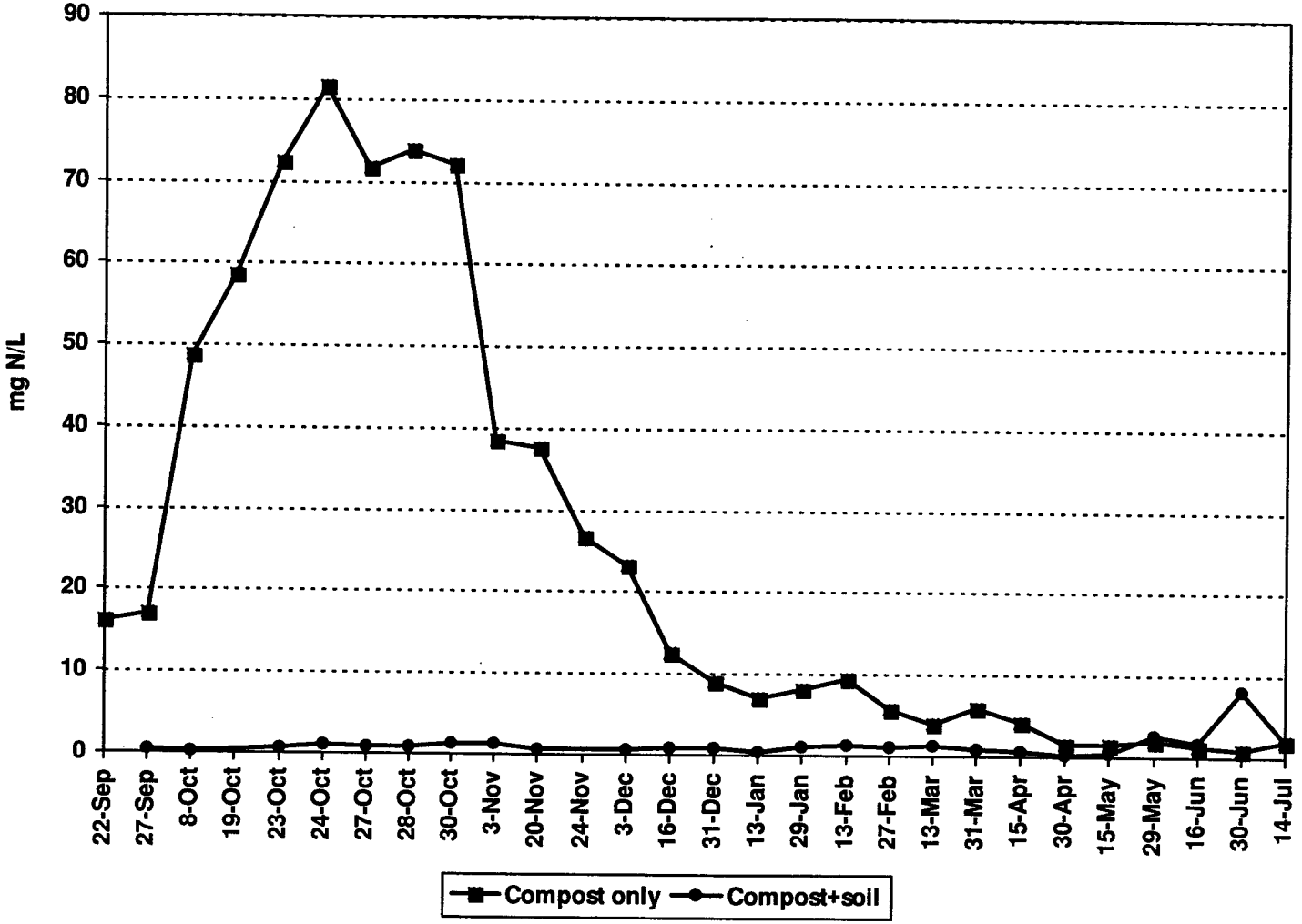


Figure 4-9

Ammonia-Nitrogen in Leachate

was no longer being converted to nitrate nitrogen. The small amount of nitrate nitrogen measured the next spring (May 1997 [Figure 4-7]) indicated that most of the organic nitrogen had been mineralized the previous autumn.

4.5.2 Phosphate

Figure 4-10 shows the change over time in phosphate concentration of leachate from the bins containing either compost only or the compost + soil mixture. Organic phosphate in compost is undoubtedly mineralized like organic nitrogen when organic matter decomposes. Inorganic phosphate, however, is not as soluble and will remain bound to soil provided that there is enough soil on which to bind. For this reason, practically no phosphate leached from the bins containing the compost + soil mixture. Phosphate released from the compost in the surface six inches was held by the Umatilla soil below. In the bins containing compost only, the phosphate that was mineralized was subject to leaching because there was not enough soil to bind up the phosphate. The leaching process was probably slower for phosphate than nitrogen since soils have an ability to fix or retain phosphate. Alkaline conditions, as seen in both the compost only and the compost + soil mixture (Tables 4-7 and 4-8), favor the precipitation of water-insoluble forms of phosphate, dicalcium, and tricalcium phosphate. Temperature also enhances the fixation of phosphate.[Ref. 2] This may be the reason the concentration of phosphate in leachate increased during the winter months (Figure 4-10). By the end of January 1997, twenty weeks into the study, phosphate levels had stabilized, indicating that the remaining phosphate was in stable organic combination with carbon compounds.

4.5.3 Total Organic Carbon

The change in the concentration of total organic carbon in leachate is shown in Figure 4-11. Comparison of the two lines in this graph with the two lines in Figure 4-8 illustrates how the release of organic carbon coincided with the release of organic nitrogen, the main form of nitrogen reflected in the Kjeldahl nitrogen measurements. Like nitrogen and phosphate, organic carbon losses stabilized by the end of December 1996, indicating that the carbon and two nutrients were bound in stable organic compounds.

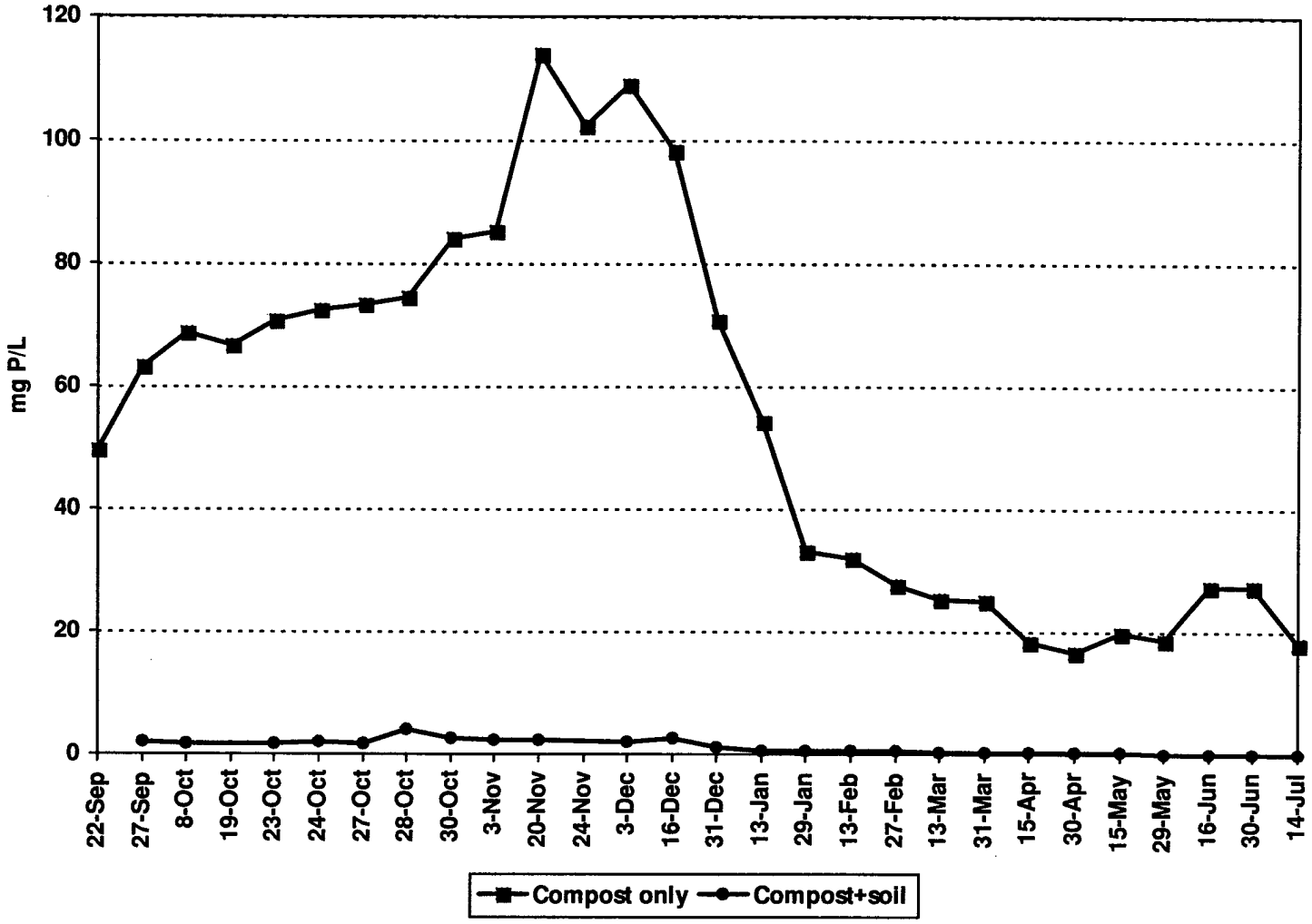


Figure 4-10

Phosphate (PO_4) in Leachate

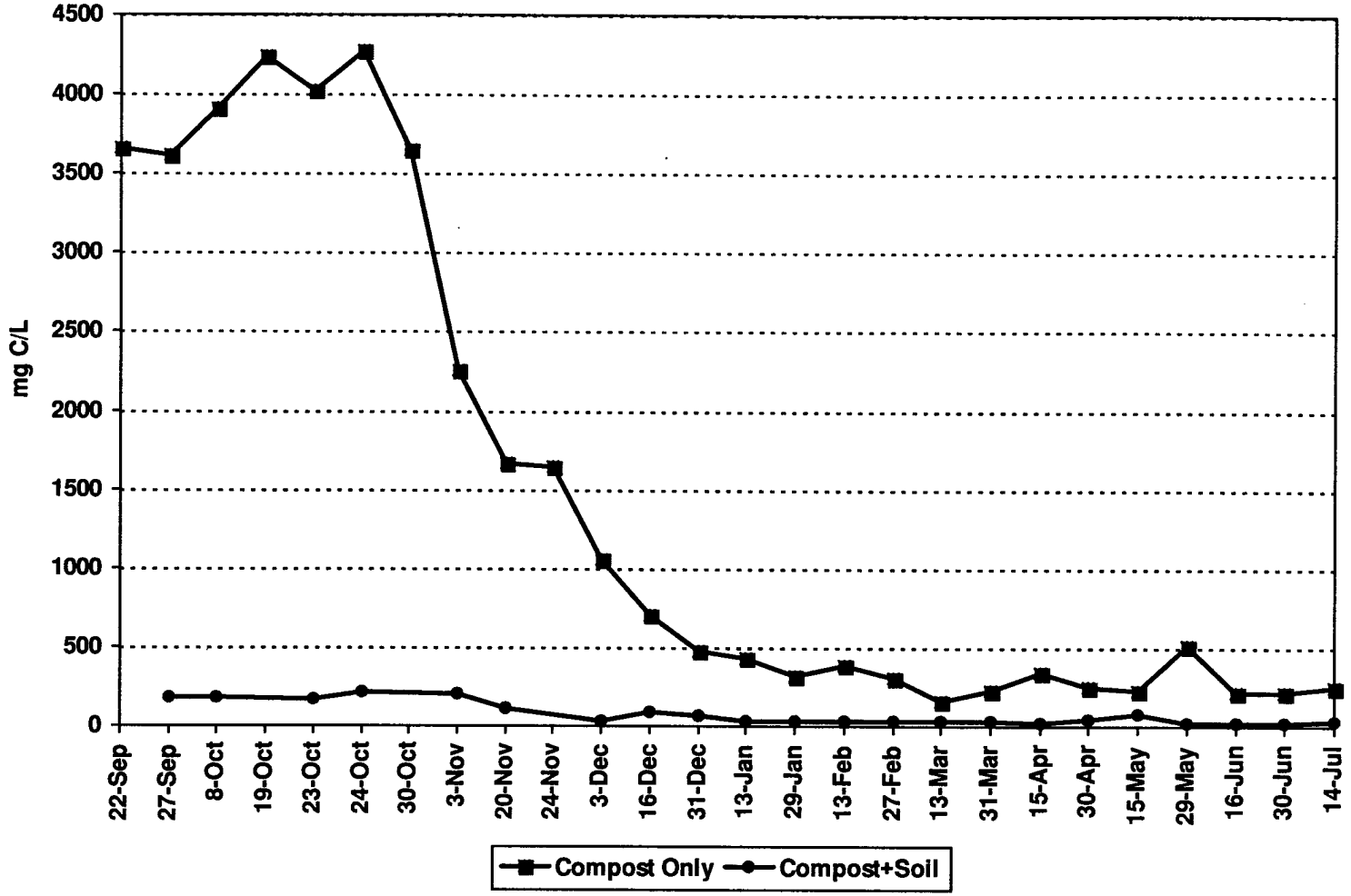


Figure 4-11

Total Organic Carbon (TOC) in Leachate

4.5.4 Electrical Conductivity

Electrical conductivity is a measure of the ion content or salt content. Figure 4-12 shows the change in conductivity of the leachate from the two groups of weathering bins. Like the release of nitrogen, phosphate, and carbon, the high electrical conductivity in the leachate from the bin containing compost only is associated with decomposition of organic matter and mineralization of the organic nitrogen and phosphate. The leachate from the compost + soil mixture had a similar change in electrical conductivity, as did the compost only leachate, but the magnitude was smaller due to the dilution of the compost with clean soil. The presence of these salts is the primary reason the compost is not suitable for growing plants without being leached of salt or diluted with soil.

4.5.5 pH

The change in pH of the leachate from the bins containing either compost only or the compost + soil mixture is shown in Figure 4-13. The higher pH from the compost only leachate indicates that the compost was alkaline. As the compost stabilized over time, it tended to become neutral. The fact that both the compost only and the compost + soil mixture leachates were slightly alkaline throughout a nine-month period of measurement indicates that the Umatilla soil is also slightly alkaline.

4.6 Changes in Compost Composition

The initial level of explosives, metals, and nutrients in the treated compost is shown in Table 4-1. Cores were removed from all six bins after one and two years of weathering. These samples were analyzed only for the explosive analytes shown in Table 3-1. At the end of one year, two cores were taken from each bin. One core sample was left intact as a full depth core sample and the second core was divided into three segments by depth; the top 15 cm, the middle 15 cm, and bottom 15 cm. If explosives or explosive by-products were detected in the full depth core sample, then the samples from the second core were analyzed to identify the depth at which the explosives or explosive by-products were present. Except for Bin No. 2 containing compost only, no explosive analytes were found in the full depth samples. Bin No 2

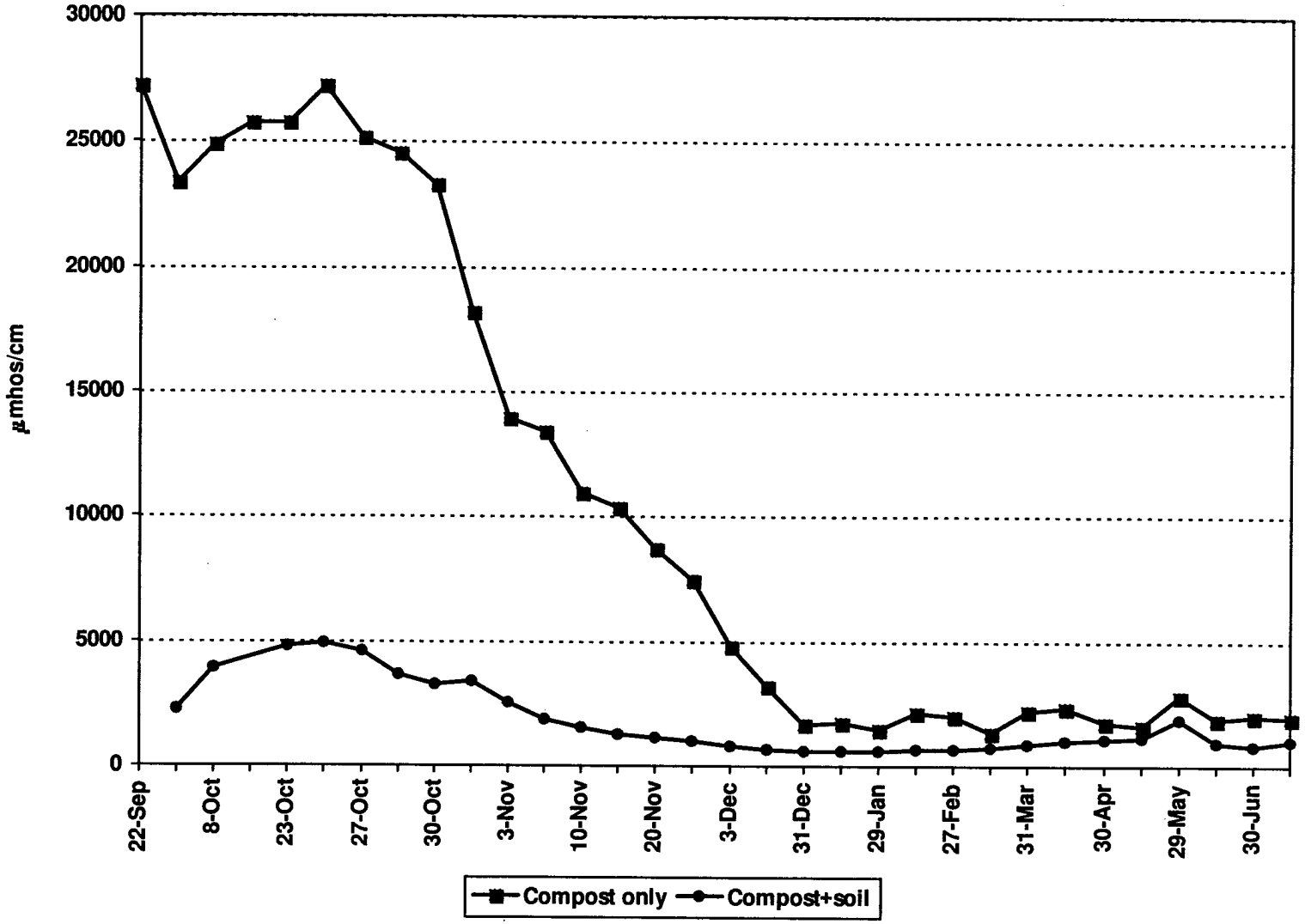


Figure 4-12

Electrical Conductivity in Leachate

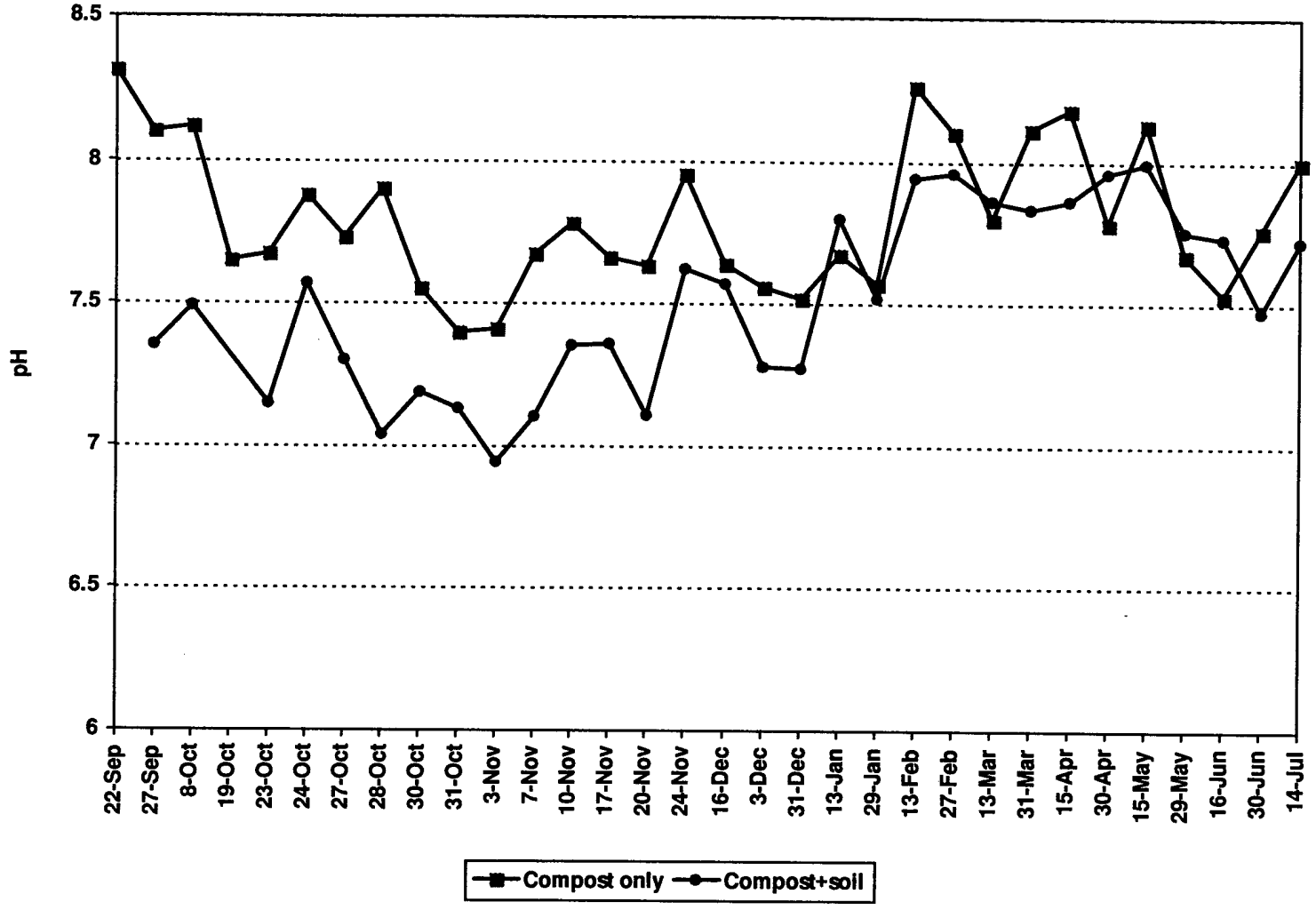


Figure 4-13

pH in Leachate

was found to have TNB (121 ug/kg). Since the full depth sample from bin No. 2 was found to contain a detectable level of TNB, the three depths of the core bin's second core sample were analyzed to determine if the contaminant was stratified due to leaching. The TNB was detected in the two top 15-cm layers (top 30 cm), but not in the bottom layer, indicating that TNB was not moving downward.

SECTION 5.0
CONCLUSIONS

5.1 Background

The biological and chemical processes which were observed in the soil in the compost + soil mixture bins are analogous to a situation where the stack of treated compost is laying on soil. Under most conditions, ammonium and organic nitrogen compounds produced in the compost would be retained in the soil near the soil/compost interface since these compounds tend to be chemically attracted to soil. In order for this nitrogen to become mobile, it normally has to be converted to other nitrogen compounds. For example, be microbially converted to water-soluble nitrates or anaerobically converted to nitrogen or nitrous oxide gases. The form of nitrogen produced is often dependent on the soil's moisture conditions. Likewise, phosphate and other compounds would be expected to leach through the compost, but be retained in the soil beneath the compost.

Although some leaching of RDX and HMX was observed during this project, these results do not necessarily mean these explosives will leach at other sites. For example, the average rainfall at UMADA is approximately 10 inches per year and the evaporation rate typically exceeds the rate of precipitation.[Ref. 4] In contrast to UMADA, Alabama receives an average of 54 inches of rain per year and the annual rate of rainfall exceeds the annual rate of evaporation. Consequently, the opportunities for leaching are considerably lower at UMADA than at TVA's reservation in Alabama and any potential loss of contaminates would be less likely at a site like UMADA.

5.2 Study Results

The immature compost delivered to TVA had very low levels of explosives. TNB, TNT, and RDX had average concentrations, respectively, of 245, 64, and 20 ug/Kg (ppb). The only other explosive analyte detected was the TNT breakdown product, 2-amino-4,6-dinitrotoluene, at a level of 8.2 ug/Kg.

After being weathered for one year, the only explosive analyte detected was TNB and it was found in the top two thirds of treated compost in Bin No. 2. The other bins had no detectable levels of explosives.

From analyses of leachate, the only explosives that were prevalent for more than one sampling event were HMX and RDX. The concentration of HMX and RDX peaked at levels of 31.5 and 26.4 ug/L, respectively. The total amount of these explosives removed from each bin by leaching was around 1.0 mg.

Release of RDX was thought to be influenced by temperature as the concentration in leachate decreased to below detection levels the first winter then became detectable the following spring.

HMX was released from the bins containing the compost + soil mixture almost immediately after the study was begun. Seven months after the study began (April 1997), HMX was detected in the leachates coming from the bins containing compost only. The concentrations of HMX were also much lower in the compost only leachate than in the compost + soil leachate. Also, a much smaller amount of HMX was removed from the compost only bins. The relative losses of HMX from the compost only and compost + soil bins were surprising in view of the fact that the bins containing compost only had around one hundred times more compost than the bins containing the compost + soil mixture.

The leaching of nutrients, organic carbon, and salts occurred as expected. The patterns of leaching of nutrients, organic carbon, and salts (as evidenced by electrical conductivity) were all similar and corresponded with the decomposition of organic matter. Leaching rates became stable after 15 to 20 weeks. Nitrogen removed from the bins containing compost only was primarily in organic form, whereas nitrogen removed from the bins containing the compost + soil mixture was primarily in the form of nitrate. Phosphate removal was slower than nitrogen removal due to its tendency to bind to soil.

5.3 Summary

The conclusions that can be derived from this study are as follows:

1. TNT, which was by far the major explosive contaminant in the Umatilla soil (90% of all explosives), was effectively treated in the windrow composting process as neither it nor its degradation products were detectable in the compost leachate. The treatment criteria for TNT at UMADA was 30 ppm.

2. Though HMX typically accounts for less than 2% of the explosives in Umatilla explosives-contaminated soil, it leached in higher quantities than any other explosive. The total amount of HMX leached was small. There was no treatment criteria set for HMX during composting operations at UMADA.

3. RDX, which accounted for about 8% of the explosives in Umatilla soil, was also leached from the compost, but in smaller amounts than HMX. The treatment criteria for RDX was 30 ppm during composting operations at UMADA.

4. The release of RDX from the compost was temperature-dependent. Low winter temperatures caused a reduction in the loss of RDX. This suggests that the release of RDX was affected by microbial activity.

5. Nutrients, organic carbon, and salts were leached from the compost. Levels in leachate became stable after 15 to 20 weeks of weathering.

6. Organic nitrogen was the primary form of nitrogen leached from the pure compost.

7. The dilution of compost with soil resulted in nitrification of the nitrogen being leached.

8. Mixing soil with compost minimized or reduced the rate of leaching of nutrients, carbon, salt, and explosives with HMX being the exception.

SECTION 6.0
REFERENCES

1. USAEC Report No. SFIM-AEC-ET-CR-98043. "*Results of a Study Investigating the Plant Uptake of Explosive Residues from Explosives-Contaminated Soil Obtained from the Umatilla Army Depot Activity.*" November 1998 (in preparation).

2. USAEC Circular 200-1-18. "*Windrow Composting of Explosives-Contaminated Soil.*" March 1994.

3. Tisdale, S. L. and W. L. Nelson. 1975. "*Soil Fertility and Fertilizers,*" ISBN 0-02-420860-4, Macmillan Publishing Co., Inc., 866 Third Avenue, New York, NY 10022.

4. "*Climatic Atlas of the United States.*" 1974. U S. Department of Commerce, June 1968, National Oceanic and Atmospheric Administration.

5. Spain, Jim C. 1995. "*Biodegradation of Nitroaromatic Compounds,*" Environmental Science Research, Volume 49.

APPENDIX A

METHODS AND PROCEDURES

Appendix A-1

Chain of Custody

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : SP-0001

Title: Sample Chain of Custody

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	11/26/96
Concurred: Eugene A. Zarate	Laboratory Section Leader	11/26/96
Concurred:		
Concurred:		
Approved: Joseph J. Hoagland	Manager	11/27/96

Revision	R0	R1	R2			
Control Date	29-Sep-89	10-Jan-96	29-Nov-96			

Copy No: ___ has been issued to holder on _____

"Sample Chain of Custody"

1.0 PURPOSE

This procedure provides instructions for sample custody from collection to final disposition.

2.0 SCOPE

This procedure applies to all samples collected under a sampling plan which requires documentation of sample custody.

3.0 SUMMARY

Requirements for documentation of sample collection and sample custody are specified.

4.0 REFERENCES

4.1 U. S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition, Most Recent Update (September 1994)

4.2 "Preparation Aids for the Development of Category II Quality Assurance Project Plans," EPA/600/8-91/004, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Developent, U.S. Environmental Protection Agency, Cincinnati, OH 45268

4.3 "Preparation Aids for the Development of Category III Quality Assurance Project Plans," EPA/600/8-91/005, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Enviromental Protection Agency, Cincinnati, OH 45268

4.4 "Sample Receipt, Log-in, and Data Handling", GLP-0016, Tennessee Valley Authority, Analytical Laboratory of Environmental Applications, Muscle Shoals, AL.

5.0 RESPONSIBILITIES

5.1 The laboratory team leader shall ensure that this procedure is followed.

5.2 The sampler shall follow this procedure to ensure sample integrity in the field.

5.3 The person transporting the samples shall follow the procedure to ensure sample integrity in transit.

5.4 The person receiving the samples shall follow this procedure to ensure sample integrity upon receipt and immediately following.

5.5 Laboratory analysts shall follow this procedure during sample analysis.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sample containers shall be cleaned to specifications of the sampling plan, or in their absence, to good commercial practice.

6.1.2 Sample containers shall have preservative added before sampling as required by the sampling plan.

6.2 Limitations and Actions

6.2.1 If the sampling organization has its own sampling procedure, sample custody procedure, labels, or custody forms, they may be substituted for the contents of this procedure as permitted by the sampling plan.

6.2.2 The number of persons handling samples from the time of sampling to receipt by the laboratory should be held to a minimum.

6.2.3 Sample containers shall be labeled by attaching tie-on tags, adhesive labels, or by writing on sample containers with indelible markers. Sample containers shall be labeled with sufficient information that they may be traced to sample collection logs, field sheets, or custody records. Choice of adhesive labels or indelible ink should take into consideration that samples may come into contact with melted ice or condensed moisture during shipment or storage.

6.2.4 Individual samples shall be sealed or sample shipping containers shall be sealed with a tamper-proof seal when they will be relinquished by TVA to a common carrier or if the sampling plan requires it. If the samples will remain in the custody of TVA employees from the time of sampling through transport to the laboratory or under lock and key (as in a locked vehicle or storage container) during this time, use of seals is not required. However, even if seals are not required, their use is strongly urged on shipping containers if the sample is to change hands several times in transport.

6.3 Requirements

6.3.1 Apparatus/Equipment

This procedure specifies no additional apparatus or equipment in addition to any sampling plan.

6.3.2 Materials

6.3.2.1 Sample containers specified in the sampling plan shall be utilized.

6.3.2.2 Labels - Samples labels shall have an adhesive which does not readily release when containers become damp.

6.3.2.3 Custody Forms - Sample chain of custody forms shall be used to record custody of samples after sampling from relinquishment by the sampling organization through transport to receipt by the laboratory. The following information shall be supplied on the custody form:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Requested analysis
g. Sampling location
h. Comments
i. Signature of sample collector.

In addition the form shall contain an area so that each relinquishment and receipt of samples may be documented.

Example custody forms are attached as appendices 10.1 and 10.2. Other forms specific to a given project may be developed as long as they contain the minimum information specified above.

Note: If sample collection time and location are already recorded on a field sheet or sampling log, that information need not be repeated on this form provided a copy of the sampling information is transmitted to the laboratory with the custody sheet.

6.3.2.4 Tamper-evident seals - These seals shall be individually numbered or otherwise marked so that they could not be removed and replaced without it being detected. Two styles have been useful for samples or sample containers.

6.3.2.4.1 Adhesive seals advertised as meeting forensic science requirements, such as Kapak brand seals.

6.3.2.4.2 Padlock-style plastic seals for hasps.

6.3.2.5 Field Logbooks or Field Sheets - Sampling activities may be documented in field logbooks or field sheets designed for that purpose. When these are used, they shall contain:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Reference to the sampling procedure
g. Sampling location
h. Comments
i. Signature of sample collector.

7.0 PROCEDURE

7.1 Field Operations

7.1.1 Prior to sampling, label sample containers with an adhesive label or with indelible marker. (Note: If the sampling conditions require it, labels may be affixed after sampling and cleaning the outside of the container.)

"Sample Chain of Custody"

7.1.2 Document sample information in a field log, field sheet, or the custody sheet if the first two are not provided.

7.1.3 Seal the sample container with an adhesive seal if the sampling plan requires it.

7.1.4 Complete a "Sample Chain of Custody" form.

7.1.4.1 If field logs or field sheets contain collection time and location, these items may be omitted from the form. In that case, draw a diagonal line in that column and attach a copy of the field logs or sheet so that the laboratory may have pertinent sampling information.

7.1.4.2 If a numbered seal is to be used on the shipping container, note that number in the comments section of the custody form.

7.1.4.3 If the shipping container is to be sealed, sign and date the "relinquished" area of the form.

7.1.5 Place the original copy of the paperwork in a plastic bag inside the shipping container. Retain one copy for field files. Transmit a third copy by separate courier, mail or fax to the laboratory.

7.1.6 Place the samples in a shipping container. As required by the sampling plan, place ice (or commercial substitute) and a temperature test bottle in the container as well. Seal the shipping container if the sampling plan requires it. See also 6.2.4.

7.1.7 Deliver the container to be transported to the laboratory.

7.2 Laboratory Receipt (Reference also GLP-0016)

7.2.1 Inspect the seals. Open the shipping container. Inspect the sample custody form to ensure that it is correctly completed. Sign as receiver. Compare the shipping container contents to the information on the form.

7.2.2 If the "relinquished" blank is not completed and the person delivering the samples is present, have that person sign the "relinquished by." Otherwise write "Not completed", date and initial. If a person signs "relinquished by," provide that person a copy of the paperwork.

7.2.2 As required by the sampling plan, measure the temperature of any samples or temperature blanks and record that information on the custody sheet.

7.2.3 Communicate any errors, broken seals, missing seals, broken samples, differing identification numbers, extra samples, missing samples or misidentification to field personnel. Document all discussions by memorandum or database sample comment file. Document all problems and their resolution by memorandum or database sample comment file. If seals show signs of tampering, bring this to the attention of the group leader or team leader.

7.2.4 Refer to GLP-0016 for further sample receipt and log-in instructions.

7.2.6 Following logging, store the samples in a locked, refrigerated storage area as required by the sampling plan or project plan.

7.3 Laboratory Custody

7.3.1 Samples in locked storage areas, being prepared, being processed, or in autosampler trays are considered to be in the custody of the laboratory. When sampling plans require it, laboratory work areas shall be locked when unattended.

7.4 Sample Disposal

7.4.1 When customers request it, samples shall be returned to them following analysis.

7.4.2 Otherwise, dispose of samples after the time period specified in the sampling plan or project plan. If these do not specify a date, samples should be kept no longer than three months after all analyses are complete.

7.4.3 If the sampling plan requires it, document sample disposal in the workorder file, or custody records.

8.0 SAFETY

8.1 Wear rubber gloves and protective eyewear when handling samples unless it is known that the samples are innocuous.

8.2 Avoid contact with samples. Be aware of broken containers, corrosives, irritants, biohazards, flammability, pyrophoricity, reactivity, radioactivity

and toxicity. Inspect labels and shipping information for warnings. When hazards are known, label samples with hazard information if that is not already provided by the customer.

8.3 In case of skin contact, wash thoroughly with soap and water.

8.4 In case of eye contact, hold the eyes open and wash for at least 15 minutes in an eyewash. Call for help.

8.5 Flammable liquids must be refrigerated only in explosion-proof refrigerators to avoid the risk of explosion caused by sparks in the electrical contacts of the compressor.

8.6 In handling samples, be aware of spills on outside of containers. Clean the exterior of containers as needed.

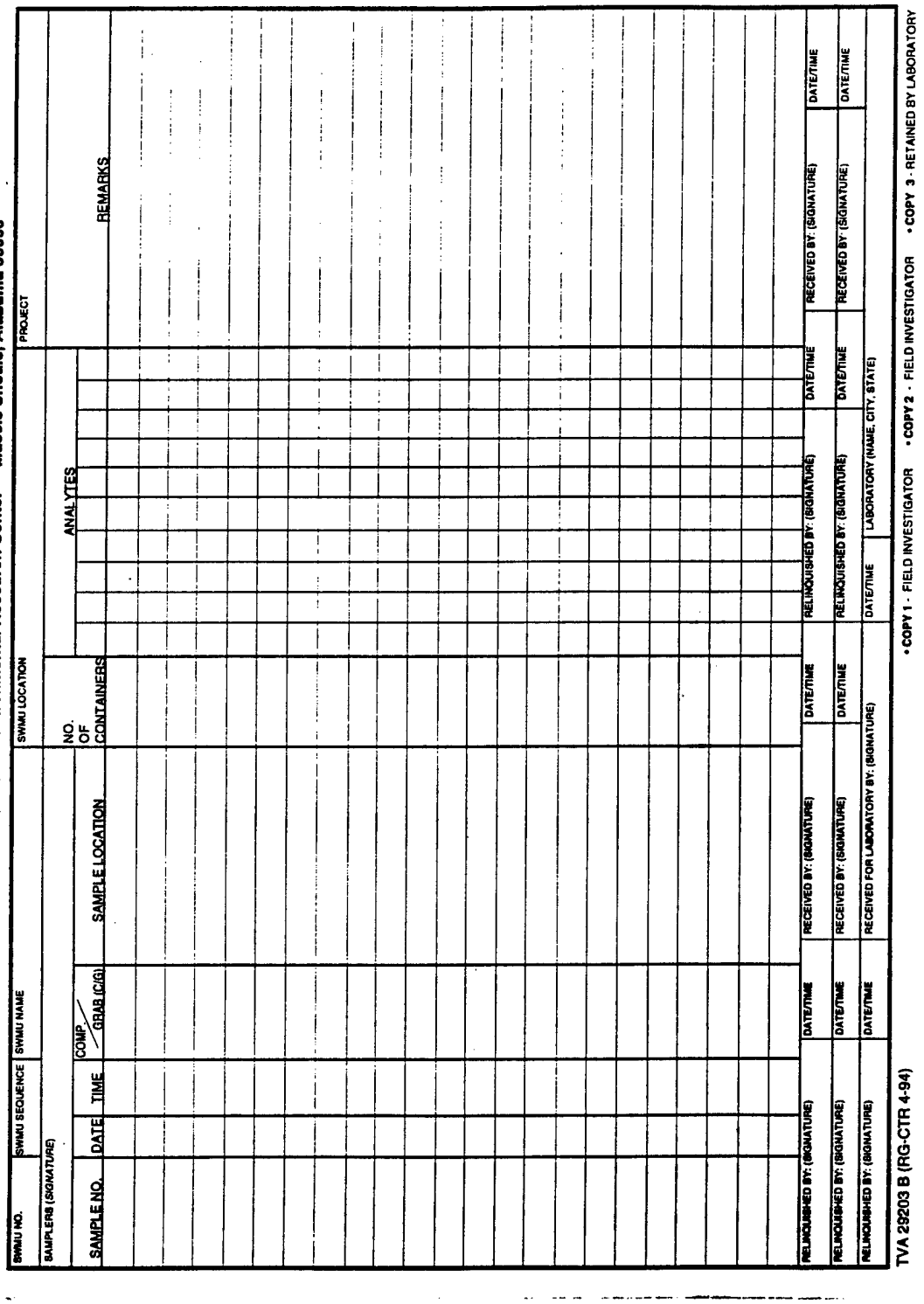
9.0 NOTES

None

"Sample Chain of Custody"

10.0 ATTACHMENTS AND APPENDICES

10.1 Chain of Custody Record - TVA 29203 B (RC-CTR 4-94)



CHAIN OF CUSTODY RECORD

Environmental Site Remediation • TVA Environmental Research Center • Muscle Shoals, Alabama 35660

SWMU NO. | SWMU SEQUENCE | SWMU NAME | SWMU LOCATION | PROJECT

SAMPLERS (SIGNATURE)

SAMPLE NO.	DATE	TIME	COMP / GRAB (C/G)	SAMPLE LOCATION	NO. OF CONTAINERS	ANALYTES	REMARKS

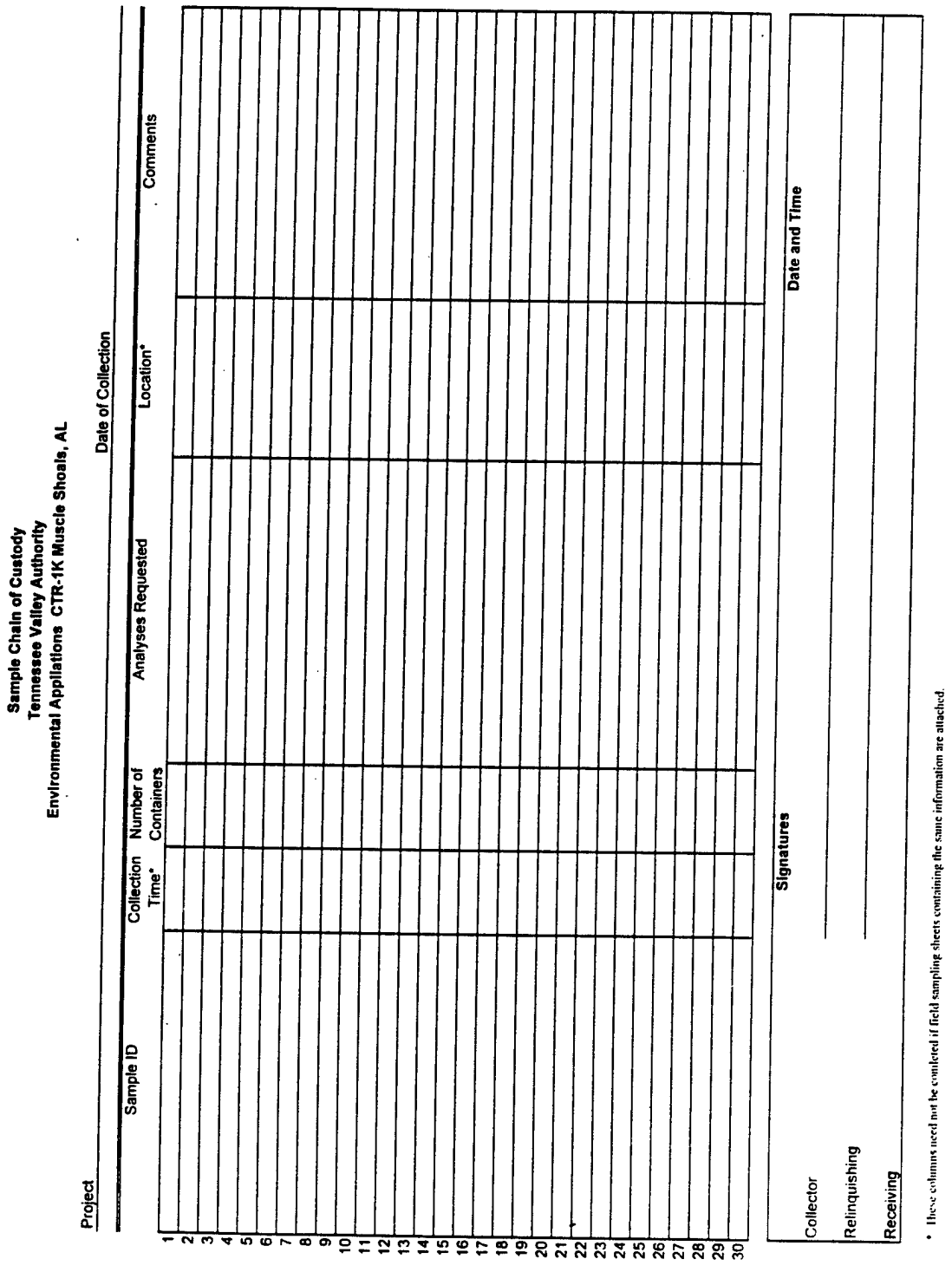
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED FOR LABORATORY BY: (SIGNATURE)	DATE/TIME	LABORATORY (NAME, CITY, STATE)			

TVA 29203 B (RG-CTR 4-94)

• COPY 1 - FIELD INVESTIGATOR • COPY 2 - FIELD INVESTIGATOR • COPY 3 - RETAINED BY LABORATORY

"Sample Chain of Custody"

10.2 Sample custody form - General



Sample Chain of Custody
Tennessee Valley Authority
Environmental Applications CTR-1K Muscle Shoals, AL

Project _____ Date of Collection _____

	Sample ID	Collection Time*	Number of Containers	Analyses Requested	Location*	Comments
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

Signatures	Date and Time
Collector	
Relinquishing	
Receiving	

* These columns need not be completed if field sampling sheets containing the same information are attached.

END OF PROCEDURE

Appendix A-2

Moisture Analysis: Method ASTM E 871

Designation: E 871 – 82 (Reapproved 1992)

Standard Method for Moisture Analysis of Particulate Wood Fuels[1]

This standard is issued under the fixed designation E 871; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the determination of total weight basis moisture in the analysis sample of particulate wood fuel. The particulate wood fuel may be sanderdust, sawdust, pellets, green tree chips, hogged fuel, or other type particulate wood fuel having a maximum particle volume of 16.39 cm^3 (1 $in.^3$). It is used for calculating other analytical results to a dry basis. Moisture, when determined as herein described, may be used to indicate yields on processes, to provide the basis for purchasing and selling, or to establish burning characteristics.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

3. Summary of Method

3.1 Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications.

4. Significance and Use

4.1 The test procedures described in this method can be used to determine the total weight basis moisture of any particulate wood fuel meeting the requirements specified in this method.

5. Apparatus

5.1 *Drying Oven*—For determining the moisture of wood, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation of 103 ± 1°C shall be used.

5.2 *Open Containers*, nonporous glass, metal, or ceramic and of a configuration so as to accommodate the test sample. The minimum volume shall be 32.18 cm^3 (2 $in.^3$).

5.3 *Desiccator*, of sufficient size to contain the open container.

6. Procedure

6.1 *Sampling:*

6.1.1 *Place of Sampling*—Take the sample where the wood is being loaded into or unloaded from means of transportation or when discharged from storage bins or conveyors.

NOTE—Samples collected from the surface of piles are, in general, unreliable because of the exposure to the environment. If necessary, collect nine increments from a foot or more below the surface at nine points covering the pile.

6.1.2 *Collection of Gross Sample:*

6.1.2.1 Collect increments regularly, systematically, and with such frequency that the entire quantity of wood sampled will be represented proportionally in the gross sample.

6.1.2.2 The quantity of the sample shall be large enough to be representative but not less than 10 kg (22 lb).

6.1.2.3 Place the samples in an airtight container immediately after collection. Maintain the samples in the airtight container whenever possible to prevent gains or losses in moisture from the atmosphere.

6.1.3 Sample reduction may be done by two methods, a coning and dividing process, or by using a riffle. The operations of mixing, coning, and quartering are described in Practice D 346.

6.1.3.1 Accomplish coning and dividing reduction by placing the gross sample on a sheet of rubber or oil cloth. Thoroughly mix it by raising first one corner of the cloth and then the other. After mixing cone and quarter sample, continue the operations until the sample is reduced sufficiently so that one quarter weighs about 50 g (0.11 lb). This shall constitute a laboratory sample.

6.1.3.2 Accomplish riffle reduction using a standard coal riffle. Riffle the gross sample repeatedly until one half of the riffle sample equals about 50 g (0.11 lb), which will constitute a laboratory sample. Riffles and procedures are described in Method D 2013.

6.2 Dry sample container for 30 min at 103 ± 1°C in the oven, then cool in desiccator to room temperature. Weigh to the nearest 0.02 g and record as container weight, W_c. Place a minimum of 50 g of sample in the container, weigh the sample and container to the nearest 0.01 g, and record as initial weight, W_i.

6.3 Place the sample and container in the oven for 16 h at 103 ± 1°C.

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[1] This method is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

Current edition approved May 28, 1982. Published December 1982.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

6.4 Remove the sample and the container from the oven and cool in the desiccator to room temperature. Remove the sample and container from the desiccator, weigh immediately to the nearest 0.01 g, and record the weight.

6.5 Return the sample and container to the oven at 103 ± 1°C for 2 h. Repeat 6.4.

6.6 Continue 6.4 until the total weight change between weighings varies less than 0.2 % and record as the final weight, W_f.

7. Calculation

7.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(W_i - W_f)/(W_i - W_c)] \times 100$$

where:

W_c = container weight, g,
W_i = initial weight, g, and
W_f = final weight, g.

8. Precision and Bias

8.1 The following criteria should be used for judging the acceptability of results:

8.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.5 %.

8.2.1 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 1 %.

Appendix A-3

Nitrate + Nitrite Nitrogen: Method AP-0058

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0058

Title: NO_3-N by Flow Injection Analysis

Signature	Title	Date
Prepared by: Sammie Smith Sammie Smith	Analytical Chemist	9/23/97
Concurred: Eugene A. Zarate Eugene A. Zarate	Laboratory Section Leader	9/23/97
Concurred: William J. Rogers William J. Rogers	QA Officer	9/22/97
Concurred:		
Approved: Joseph J. Hoagland Joseph J. Hoagland	Manager	9/23/97

Revision	R0					
Control Date	23-Sep-97					

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1.0 PURPOSE

This procedure provides a method for the determination of nitrate and nitrite in drinking, ground, and surface water, and domestic and industrial wastes.

2.0 SCOPE

2.1 This method covers the determination of nitrate and nitrite in drinking, ground, and surface waters, and domestic and industrial wastes.

2.2 The method is based on reactions that are specific for the nitrate and nitrite (NO_3^- and NO_2^-) ions.

2.3 The applicable range is 0.2 to 20.0 mg N/L.

3.0 SUMMARY

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone can be determined by removing the cadmium column. Nitrate may be determined by difference.

4.0 REFERENCES

4.1 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Nitrate-Nitrite, Method 353.2 (Colorimetric, Automated, Cadmium Reduction)."

4.2 *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*. Book 5. Chapter A1. U.S Department of the Interior, U.S. Geological Survey.

4.3 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-107-04-1-A, "Nitrate/Nitrite, Nitrite in Surface Water, Wastewater."

4.4 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 Samples may be preserved by addition of a maximum of 2 mL of concentrated H_2SO_4 per liter (preferred - 1 mL of 1N H_2SO_4 per 100 mL) and stored at 4°C. Acid preserved samples have a holding time of 28 days.

6.2 Limitations and Actions

6.2.1 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Residual chlorine can interfere by oxidizing the cadmium column.

6.2.2.2 Low results may be obtained for samples that contain high concentrations of iron, copper of other metals. In this method, EDTA is added to the buffer to reduce this interference.

6.2.2.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference may be eliminated by extracting such samples with an organic solvent prior to analysis.

6.2.2.4 Sample color and turbidity may interfere. Turbidity can be removed by filtration through a 0.45 um pore diameter membrane filter prior to analysis. Sample color may be corrected by running the samples through the manifold without color formation (Sulfanilamide color reagent, reagent 3). The nitrate concentration is determined by subtracting the value obtained without color formation from the value obtained with color formation.

6.3 Apparatus/Equipment

6.3.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimeter detector

6.3.3.5 Data system

6.3.4 Special Apparatus

6.3.4.1 Cadmium Granules Column

6.3.4.1.1 Cadmium Preparation: Place **10-20 g of coarse cadmium granules** (0.3 - 1.5 mm diameter, Lachat Part # 50231) in a 250 mL beaker. Wash with **50 mL of acetone**, then **water**, then two **50 mL portions of 1 N hydrochloric acid** (reagent 4). Rinse several times with water. **Cadmium is toxic and carcinogenic. Wear gloves.**

6.3.4.1.2 Copperization: Add a **100 mL** portion of **2% copper sulfate solution** (reagent 5) to the cadmium prepared above. Swirl for about 5 minutes, then decant the liquid and repeat with a fresh **2% copper sulfate solution** (reagent 5). Continue this process until the blue aqueous **copper** color persists. Decant and wash with at least **five portions of ammonium chloride buffer solution** (reagent 2) to remove colloidal copper. The cadmium should be black or dark gray. The copperized granules may be **stored** in a **stoppered bottle under ammonium chloride buffer** (reagent 2).

6.3.4.1.3 Packing the Column

6.3.4.1.3.1 The empty cadmium column is available as Lachat Part # 50230. Wear gloves and do all cadmium transfers over a special tray or beaker dedicated to this purpose. Clamp the empty column upright so that both hands are free. Unscrew one of the colored fittings from an end of the column. Pull out and save the foam plug. The column and threads are glass so be careful not to break or chip them. Fasten this fitting higher than the open end of the column and completely fill the column, attached fittings, and tubing with ammonium chloride buffer (reagent 2).

6.3.4.1.3.2 Scoop up the prepared copperized cadmium granules with a spatula and pour them into the top of the filled column so that they sink down to the bottom of the column. Continue pouring the cadmium in and tapping the column with a screwdriver handle to dislodge any air bubbles and to prevent gaps in the cadmium filling. When the cadmium granules reach to about 5 mm from the open end of the column, push in the foam plug and screw on the top fitting. Rinse the outside of the column with water.

6.3.4.1.3.3 If air remains in the column or is introduced accidentally, connect the column into the manifold at the two state switching valve, pump ammonium chloride buffer (reagent 2) through the column with the pump on maximum, and tap firmly with a screwdriver handle, working up the column until all air is removed.

6.3.4.1.4 Cadmium Granules Column Instillation To Manifold

6.3.4.1.4.1 Before inserting the column, pump all reagents into the manifold.

6.3.4.1.4.2 Turn the pump off and immediately connect both column tubes to the two state switching valve used to place the column in line with the manifold. Do not let air enter the column.

6.3.4.1.4.3 Return the pump to normal speed. The direction of reagent flow through the column is not relevant.

6.3.4.2 Cadmium Wire Column

6.3.4.2.1 Join **two glass tubes, 122 cm x 1.5 mm each**, and bend into a "**U**" shape about **4 cm** apart. Secure the tubes on a **122 cm x 10 cm board** to prevent breaking. Let the open ends of the tubes **extend over the board about 5 cm** to make connections.

6.3.4.2.2 Cut **two 127 cm lengths of 0.050 inch diameter cadmium alloy wire** (95% cadmium, 5% silver).

6.3.4.2.3 Cadmium Wire Preparation: Wash wire with **acetone** to remove oil and grease, then **water**, then with **1 N hydrochloric acid** (reagent 4) to remove oxides. Rinse several times with **water**. **CAUTION: Collect and store all waste cadmium. Cadmium is toxic and carcinogenic. Wear gloves.**

6.3.4.2.4 Place the two lengths of cadmium wire into the two legs of the column using pliers. Push only about **5 to 6 mm** of wire at a time into the tube to avoid bending and kinking the wire. Push each wire down to the bend in the column as far as it will go. Connect the column to the **two state switching valve** on the manifold using short lengths of Tygon tubing and available fittings. Care should be taken to **minimize any dead volume.**

6.3.4.2.5 Copperization: Pump **2% copper sulfate solution** (reagent 5) through the column until the wire has a metallic appearance. Pump **ammonium chloride solution** (reagent 2) through the column for three to four minutes to remove colloidal copper. **Store** the column filled with **ammonium chloride solution** (reagent 2).

6.3.4.2.6 Cadmium Wire Column Instillation To Manifold

6.3.4.2.6.1 Before inserting the column, pump all reagents into manifold.

6.3.4.2.6.2 Turn the pump off and immediately connect both column tubes to the two state switching valve used to place the column in-line with the manifold.

6.3.4.2.6.3 Set the pump to normal speed.

6.3.4.2.6.4 The direction of reagent flow through the column is not relevant.

6.4 Reagents and Standards

6.4.1 Preparation of Reagents

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation, degas all solutions except the standards with helium. Bubble helium through a degassing tube (Lachat Part 50100) through the solution for at least one minute.

Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. 15 N Sodium Hydroxide**

Add **150 g NaOH pellets** very slowly to **250 mL or g of water** or add **300 g 50% NaOH solution** very slowly to **100 mL or g of water**. **CAUTION**: The solution will get very hot! Swirl until dissolved. Cool and store in a plastic bottle.

6.4.1.2 **Reagent 2. Ammonium Chloride buffer, pH 8.5**

By Volume: In a **1 L** volumetric flask, dissolve **85.0 g ammonium chloride** (NH_4Cl) and **1.0 g disodium ethylenediamine tetraacetic acid dihydrate** ($Na_2EDTA \cdot 2H_2O$) in about **800 mL water**. Dilute to the mark and shake or stir to mix. Adjust the pH to **8.5** with **15 N sodium hydroxide solution** (reagent 1).

By weight: To a tared **1L** container, add **85.0 g ammonium chloride** (NH_4Cl), **1.0 g disodium ethylenediamine tetraacetic acid dihydrate** ($Na_2EDTA \cdot 2H_2O$) and **938 g water**. Shake or stir until dissolved. Then adjust the pH to **8.5** with **15 N sodium hydroxide solution** (reagent 1).

6.4.1.3 **Reagent 3. Sulfanilamide color reagent**

By Volume: To a **1 L** volumetric flask add about **600 mL water**. Then add **100 mL of 85% phosphoric acid** (H_3PO_4), **40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake to wet, and stir with a stir bar for 30 minutes to dissolve. Dilute to the mark, invert or stir to mix. Store in a dark bottle.

By weight: To a tared, dark **1 L** container add **876 g water, 170 g 85% phosphoric acid** (H_3PO_4), **40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake to wet, and stir with stir bar for 30 minutes until dissolved. Store in a dark bottle.

6.4.1.4 **Reagent 4. 1 N Hydrochloric Acid (HCl)**

By Volume: In a **100 mL** container, add **8 mL concentrated HCl** to **92 mL water**. Stir or shake to mix.

By weight: To a **100 mL** container, add **92 g water** then add **9.6 g concentrated HCl**. Stir or shake to mix.

6.4.1.5 **Reagent 5. 2% Copper Sulfate Solution**

By Volume: In a **1 L** volumetric flask, dissolve **20 g copper sulfate pentahydrate** ($CuSO_4 \cdot 5H_2O$) in about **800 mL water**. Dilute to mark with **water**. Invert to mix thoroughly.

By Weight: To a **1 L** container, add **20 g copper sulfate pentahydrate** ($CuSO_4 \cdot 5H_2O$) to **991 g water**. Stir or shake to dissolve.

6.4.2 Preparation of Standards

Note: Following are standards preparations for running 3 channels simultaneous for PO_4-P, NH_3-N and NO_2-N + NO_3-N. Also included is the preparation of a NO_2-N standard which is used to assess the cadmium reduction column's efficiency.

6.4.2.1 **Standard 1. Stock Orthophosphate Standard - 1000 mg P/L as PO_4^{3-}**

Dry **primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) for one hour at 105°C. In a **1 L** volumetric flask dissolve **4.396 g primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Stock Ammonia Standard - 1000 mg N/L as NH_3**

Dry **ammonium chloride** (NH_4Cl) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.3 **Standard 3. Stock Nitrate Standard - 1000 mg N/L as NO_3^-**

In a **1 L** volumetric flask dissolve **7.220 g potassium nitrate** (KNO_3) in about **600 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.4 **Standard 4. Stock Nitrite Standard - 1000 mg N/L as NO_2^-**

In a **1 L** volumetric flask dissolve **4.93 g sodium nitrate** ($NaNO_2$) in about **800 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.5 **Standard 5. Working Standard - 50 mg/L PO_4-P, NH_3-N and NO_3-N**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** from each of the **Stock Orthophosphate Standard** (standard 1), the **Stock Ammonia Standard** (standard 2), and the **Stock Nitrate Standard** (standard 3). Dilute to mark with **water** and mix.

6.4.2.6 **Standard 6. Working Nitrite Standard - 20 mg N/L as NO_2^-**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **20 mL Stock Nitrate Standard** (standard 4). Dilute to mark with **water** and mix.

6.4.2.7 **Standard 7. Working Quality Control Standard - 32.61 mg P/L as PO_4^{3-}, 31.06 mg N/L as NH_4, and 27.11 mg N/L as NO_3^-.**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the E M Science **1000 mg/L Phosphate Standard Solution** (326.1 mg P/L), **20 mL** of the E M Science **1000 mg/L Ammonia Standard Solution** (776.5 mg N/L), and **60 mL** of the E M Science **1000 mg/L Nitrate Standard Solution** (225.9 mg N/L). Dilute to mark with **water** and mix.

Note: 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.8 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

	Calibration Standards Concentration mg/L	Prepared From	
		Concentration mg/L	Aliquot mL
1	20.00	50	200
2	10.00	50	100
3	4.00	50	40
4	2.50	50	25
5	1.00	10	50
6	0.10	1	50
7	0.02	0.10	100
8	0.00	Water	0

For standards for samples that have 1 mL of 1 N H_2SO_4 added per 100 mL, add **5 mL** of **1N H_2SO_4** to each standard after building to volume.

Note: If other acid concentrations are used to preserve samples, match for standards.

6.4.2.9 **Cadmium Reduction Column Efficiency Check Standard - 2.00 mg N/L as NO_2^-**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the **Working Nitrite Standard** (standard 6). Dilute to mark with **water,** add **5 mL** of **1N H_2SO_4** and mix.

6.4.2.10 **Laboratory Control Standard - 1.63 mg P/L as PO_4^{3-}, 1.55 mg N/L as NH_3, and 1.36 mg N/L as NO_3^-.**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 7). Dilute to mark with **water,** add **10 mL** of **1N H_2SO_4** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, a cadmium reduction column efficiency check standard, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above four QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2 Prepare reagents and standards as described in section 6.4.

7.1.3 Set up manifold as shown in section 9.3.

7.1.4 Enter data system parameters as in section 9.1 or 9.2.

7.1.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.1.6 Load standard and sample trays.

7.1.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.9 If samples require color correction, inject the samples with color development, then inject the samples with water replacing the color reagent (reagent 3).

7.1.10 At end of run, turn the two state switching valve to isolate the cadmium reduction column. Remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.11 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual, page 43, Task 11 - Creating a Custom Report)

7.2.3 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

7.2.4 Samples that require color correction: From the value obtained with color developer added, subtract the value obtained without color developer. When a large number of samples are analyzed, use a spreadsheet to calculate the color correction.

7.2.5 Report results in mg NO_3-N/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these

reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating or inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters - Cadmium Granules Reduction Column

Method Filename:	PANHANOA.MET
Method Description:	Ortho P (a) = 4.0 to 0.02 mg P/L
	NH_3-N (a) = 20.0 to 0.1 mg N/L
	NO_2-N/NO_3-N (a) = 20.0 to 0.2 mg N/L

Analyte Data:

Analyte Name:	Nitrate (NO_3)-N
Concentration Units:	mg NO_3-N/L
Chemistry:	Direct
Inject to Peak Start (s):	22.0
Peak Base Width (s):	29.000
% Width Tolerance:	100.000
Threshold:	4100.000
Autodilution Trigger:	Off
QuickChem Method:	10-107-04-1-A

Calibration Data:

Levels: (mg NO_3-N/L)	1: 20.000	2: 10.000	3: 4.000
	5: 1.000	6: 0.100	8: 0.000
Calibration Rep Handling:	Average		
Calibration Fit Type:	1st Order Poly		
Force through Zero:	No		
Weighing Method:	None		

Concentration Scaling: None

Sampler Timing:

Method Cycle Period: 50.0

Min. Probe in Wash Period: 9.0

Probe in Sample Period: 25.0

Valve Timing:

Method Cycle Period: 50.0

Sample Reaches 1st Valve: 18.0

Valve: On

Load Time: 0.0

Load period 20.0

Inject Period: 30.0

Sample Loop: Microloop

9.2 Data System Parameters - Cadmium Wire Reduction Column

Method Filename: PANHANOW.MET

Method Description: Ortho P (a) = 4.0 to 0.02 mg P/L

NH_3-N (a) = 20.0 to 0.1 mg N/L

NO_2-N/NO_3-N (a) = 20.0 to 0.2 mg N/L

Analyte Data:

Analyte Name: Nitrate (NO_3)-N

Concentration Units: mg NO_3-N/L

Chemistry: Direct

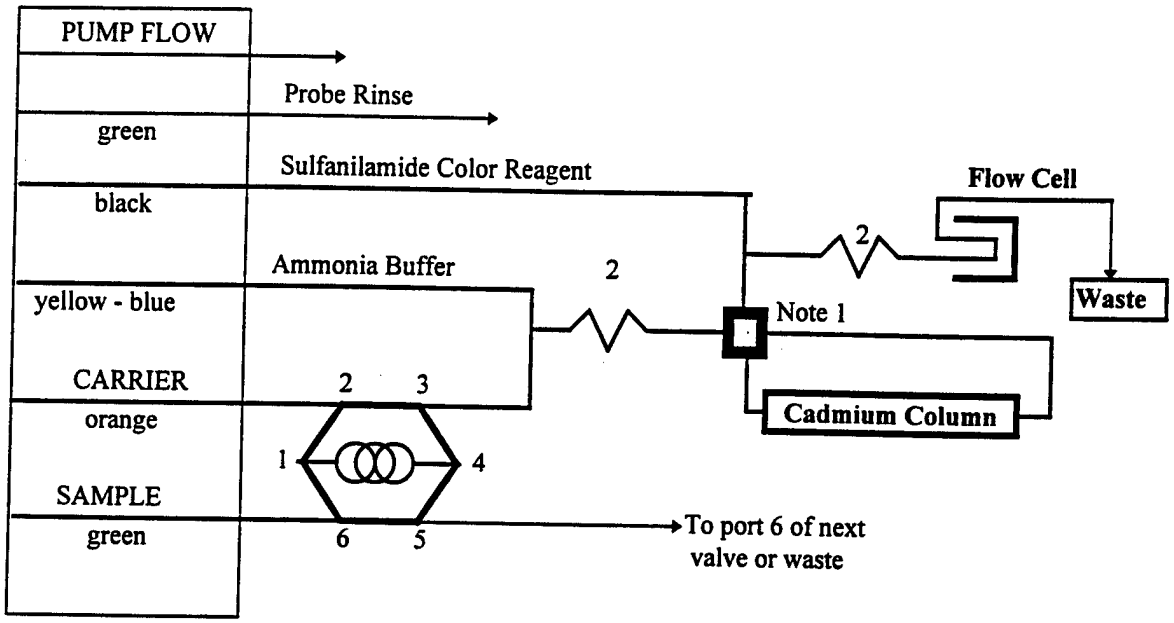
Inject to Peak Start (s): 50.5

Peak Base Width (s): 29.000

% Width Tolerance: 100.000

Threshold:	4100.000		
Autodilution Trigger:	Off		
QuickChem Method:	10-107-04-1-A		
Calibration Data:			
Levels: (mg NO_3-N/L)	1: 20.000	2: 10.000	3: 4.000
	5: 1.000	6: 0.100	8: 0.000
Calibration Rep Handling:	Average		
Calibration Fit Type:	1st Order Poly		
Force through Zero:	No		
Weighing Method:	None		
Concentration Scaling:	None		
Sampler Timing:			
Method Cycle Period:	70.0		
Min. Probe in Wash Period:	9.0		
Probe in Sample Period:	30.0		
Valve Timing:			
Method Cycle Period:	70.0		
Sample Reaches 1st Valve:	18.0		
Valve:	On		
Load Time:	0.0		
Load period	25.0		
Inject Period:	45.0		
Sample Loop:	Microloop		

9.3 Nitrate Manifold Diagram



Sample Loop = Microloop Interference Filter = 520 nm

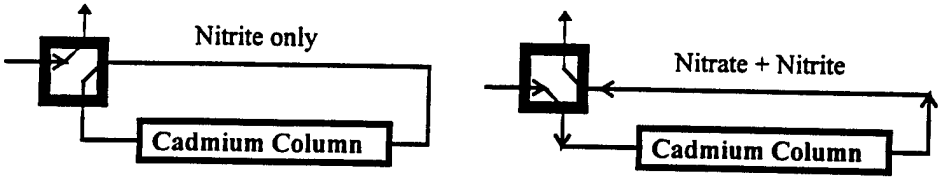
Carrier is DI Water

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm**.

2 is **70 cm** of tubing on a **4.5 cm** coil support.

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

Note 1: This is a 2 state switching valve used to place the cadmium column in-line with the manifold.



10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-4

Ammonia Nitrogen: Method AP-0059

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0059

Title: NH_4-N by Flow Injection Analysis

Signature	Title	Date
Prepared by: Sammie Smith Sammie Smith	Analytical Chemist	9/24/97
Concurred: Eugene A. Zarate Eugene A. Zarate	Laboratory Section Leader	9/24/97
Concurred: William J. Rogers William J. Rogers	QA Officer	9/24/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	9/24/97

Revision	R0					
Control Date	24-Sep-97					

Copy No: ___ has been issued to holder on _____

1.0 PURPOSE

This procedure provides a method for the determination of ammonia in drinking and surface waters.

2.0 SCOPE

2.1 This method covers the determination of ammonia in drinking and surface waters.

2.2 The method is based on reactions that are specific for the ammonium ion.

2.3 The applicable range is 0.1 to 20.0 mg N/L as NH3.

3.0 SUMMARY

This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

4.0 REFERENCES

4.1 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Ammonia, Method 350.1 (Colorimetric, Automated Phenate)."

4.2 U.S. Environmental Protection Agency, 40 CFR Part 36 Table 1B, footnote 6, 1994.

4.3 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-107-06-1-A, "Determination Of Ammonia By Flow Injection Analysis, Colorimetry."

4.4 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the Analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 Samples may be preserved by addition of a maximum of 2 mL of concentrated H_2SO_4 per liter (preferred - 1 mL of 1N H_2SO_4 per 100 mL) and stored at 4°C. Acid preserved samples have a holding time of 28 days.

6.2 Limitations and Actions

6.2.1 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

6.2.2.2 Color, turbidity and certain organic species may interfere. Turbidity can be removed by filtration through a 0.45 um pore diameter membrane filter prior to analysis. Sample color may be corrected for by running the samples through the

manifold without color formation (omit Sodium Phenolate, reagent 1). The ammonium concentration is determined by subtracting the value obtained without color formation from the value obtained with color formation.

6.3 Apparatus/Equipment

6.3.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimetric detector

6.3.3.5 Data system

6.3.4 Special Apparatus

6.3.4.1 Heating Unit

6.4 Reagents and Standards

6.4.1 Preparation of Reagents -

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation, degas all solutions except the standards, Sodium Phenolate (Reagent 1) and Sodium Hypochlorite (Reagent 2) with helium. Bubble helium through a degassing tube (Lachat Part 50100) through the solution for at least one minute.

Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. Sodium Phenolate**

CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed in the body through the skin.

By Volume: In a **1 L** volumetric flask, dissolve **88 mL** of **88% liquefied phenol** or **83 g crystaline phenol** (C_6H_5OH) in approximately **600 mL water**. While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool, dilute to the mark, and mix. Do not degas this reagent.

By weight: To a tared **1 L** container, add **888 g water**. Add **94.2 g** of **88 liquefied phenol** or **83 g crystalline phenol** (C_6H_5OH). While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool and invert to mix. Do not degas this reagent.

6.4.1.2 **Reagent 2. Sodium Hypochlorite**

By Volume: In a **500 mL** volumetric flask, dilute **250 mL Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] to mark with **water**. Invert to mix.

By weight: To a tared **500 mL** container, add **250 g Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] and **250 g water**. Invert to mix.

6.4.1.3 **Reagent 3. Buffer**

By Volume: In a **1 L** volumetric flask, dissolve **50.0 g disodium ethylenediamine tetraacetate dihydrate** ($Na_2EDTA \cdot 2H_2O$) and **5.5 g sodium hydroxide** (NaOH) in about **900 mL water**. Dilute to the mark and invert or stir to mix.

By weight: To a tared **1 L** container, add **50.0 g disodium ethylenediamine tetraacetate dihydrate** ($Na_2EDTA \cdot 2H_2O$) and **5.5 g sodium hydroxide** (NaOH). Add **968 g water**. Invert or stir to mix.

6.4.1.4 **Reagent 4. Sodium Nitroprusside**

By Volume: In a **1 L** volumetric flask, dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferrricyanide [$Na_2Fe(CN)5NO \cdot 2H2O$]) dilute to the mark with **water**. Stir or shake to mix.

By weight: To a tared **1 L** flask, dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferrricyanide [$Na_2Fe(CN)_5NO \cdot 2H_2O$]) and **1000 g water**. Stir or shake to mix.

6.4.2 Preparation of Standards

Note: Following are standards preparations for running 3 channels simultaneously for PO_4-P, NH_3-N and NO_2-N + NO_3-N. Also included is the preparation of a NO_2-N standard which is used to assess the cadmium reduction column's efficiency.

6.4.2.1 **Standard 1. Stock Orthophosphate Standard - 1000 mg P/L as PO_4**

Dry **primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) for one hour at 105°C. In a **1 L** volumetric flask dissolve **4.396 g primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Stock Ammonia Standard - 1000 mg N/L as NH_3**

Dry **ammonium chloride** (NH_4Cl) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in about **800 mL water.** Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.3 **Standard 3. Stock Nitrate Standard - 1000 mg N/L as NO_3^-**

In a **1 L** volumetric flask dissolve **7.220 g potassium nitrate** (KNO_3) in about **600 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.4 **Standard 4. Stock Nitrite Standard - 1000 mg N/L as NO_2^-**

In a **1 L** volumetric flask dissolve **4.93 g sodium nitrate** ($NaNO_2$) in about **800 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.5 **Standard 5. Working Standard - 50 mg/L PO_4-P, NH_3-N and NO_3-N**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** from each of the **Stock Orthophosphate Standard** (standard 1), the **Stock Ammonia Standard** (standard 2), and the **Stock Nitrate Standard** (standard 3). Dilute to mark with **water** and mix.

6.4.2.6 **Standard 6. Working Nitrite Standard - 20 mg N/L as NO_2^-**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **20 mL Stock Nitrate Standard** (standard 4). Dilute to mark with **water** and mix.

6.4.2.7 **Standard 7. Working Quality Control Standard - 32.61 mg P/L as PO_4^{3-}, 31.06 mg N/L as NH_4, and 27.11 mg N/L as NO_3^-.**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the E M Science **1000 mg/L Phosphate Standard Solution** (326.1 mg P/L), **20 mL** of the E M Science **1000 mg/L Ammonia Standard Solution** (776.5 mg N/L), and **60 mL** of the E M Science **1000 mg/L Nitrate Standard Solution** (225.9 mg N/L). Dilute to mark with **water** and mix.

Note: 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.8 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

	Calibration Standards Concentration mg/L	Prepared From	
		Concentration mg/L	Aliquot mL
1	20.00	50	200
2	10.00	50	100
3	4.00	50	40
4	2.50	50	25
5	1.00	10	50
6	0.10	1	50
7	0.02	0.10	100
8	0.00	Water	0

For standards for samples that have 1 mL of 1 N H_2SO_4 added per 100 mL, add **5 mL** of **1N H_2SO_4** to each standard after building to volume.

Note: If other acid concentrations are used to preserve samples, match for standards.

6.4.2.9 **Cadmium Reduction Column Efficiency Check Standard - 2.00 mg N/L as NO_2^-**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the **Working Nitrite Standard** (standard 6). Dilute to mark with **water,** add **5 mL** of **1N H_2SO_4** and mix.

6.4.2.10 **Laboratory Control Standard - 1.63 mg P/L as PO_4, 1.55 mg N/L as NH_3, and 1.36 mg N/L as NO_3^-.**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 7). Dilute to mark with **water,** add **10 mL** of **1N H_2SO_4** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above three QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.11 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2 Prepare reagents and standards as described in section 6.4.

7.1.3 Set up manifold as shown in section 9.2.

7.1.4 Enter data system parameters as in section 9.1.

7.1.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Allow 15 minutes for heating unit to warm up to 60°C. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.1.6 Load standard and sample trays.

7.1.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.9 If samples require color correction, inject the samples with color development, then inject the samples with water replacing the color reagent (reagent 1).

7.1.10 At end of run, remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.11 To prevent baseline drifts, peaks that are too wide, or other problems with NH3-N precision, clean the NH_3-N manifold by placing the manifold reagent lines in 1M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of water). Pump for about 5 minutes.

7.1.12 Remove all reagent lines from the hydrochloric acid and place them in water. Pump until the HCl is thoroughly washed out (about 5 minutes).

7.1.13 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual*, page 43, "Task 11 - Creating a Custom Report")

7.2.3 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

7.2.4 Samples that require color correction: From the value obtained with color developer added, subtract the value obtained without color developer. When a large number of samples are analyzed, use a spreadsheet to calculate the color correction.

7.2.5 Report results in mg NH_3-N/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating or inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters

Method Filename:	PANHANOW.MET
Method Description:	Ortho P (a) = 4.0 to 0.02 mg P/L
	NH_3-N (a) = 20.0 to 0.1 mg N/L
	NO_2-N/NO_3-N (a) = 20.0 to 0.2 mg N/L

Analyte Data:

Analyte Name:	Ammonia (NH_3)-N
Concentration Units:	mg NH_3-N/L
Chemistry:	Direct
Inject to Peak Start (s):	28.0
Peak Base Width (s):	21.000
% Width Tolerance:	100.000
Threshold:	8000.000
Autodilution Trigger:	Off
QuickChem Method:	10-107-06-1-A

Calibration Data:

Levels: (mg NH_3-N/L)	1: 20.000	2: 10.000	3: 4.000
	5: 1.000	6: 0.100	8: 0.000
Calibration Rep Handling:	Average		
Calibration Fit Type:	1st Order Poly		
Force through Zero:	No		
Weighing Method:	None		
Concentration Scaling:	None		

Sampler Timing:

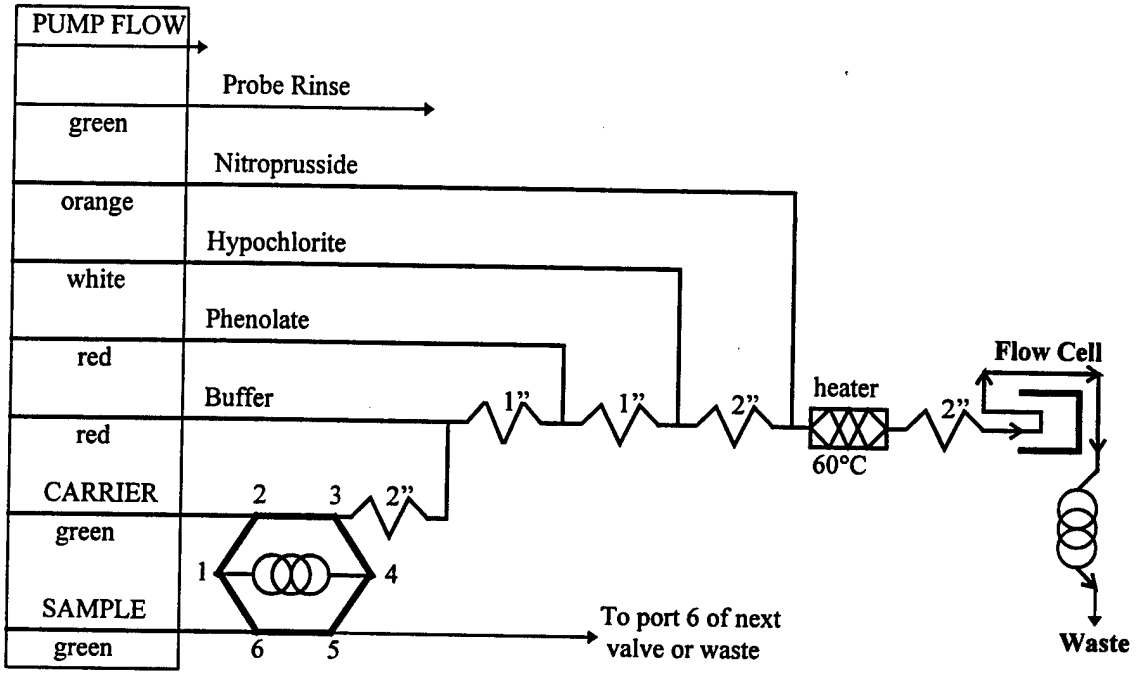
Method Cycle Period:	70.0
Min. Probe in Wash Period:	9.0
Probe in Sample Period:	30.0

Valve Timing:

Method Cycle Period:	70.0
Sample Reaches 1st Valve:	18.0
Valve:	On
Load Time:	0.0
Load period	25.0
Inject Period:	45.0

Sample Loop: 13 cm x 0.5 mm i.d.

9.2 Ammonia Manifold Diagram



Sample Loop = 13 cm x 0.5 mm i.d.

Interference Filter = 630 nm

Carrier is DI Water

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm**. The sample loop uses **0.5 mm (0.022") i.d.** tubing.

1 is **70 cm** of tubing on a **4.5 cm** coil support.

Apparatus: The 60°C includes 650 cm of tubing wrapped around the heater block at the specified temperature.

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-5

Total Kjeldahl Nitrogen: Method AP-0064

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0064

Title: TKN by Flow Injection Analysis (Lachat QuickChem 8000)

Signature	Title	Date
Prepared by: Sammie C. Smith Sammie Smith	Chemist	10/15/97
Concurred: Eugene A. Zarate Eugene A. Zarate	Laboratory Section Leader	10/15/97
Concurred: William J. Rogers William J. Rogers	QA Officer	10/15/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	10/15/97

Revision	R0					
Control Date	17-Oct-97					

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1.0 PURPOSE

This procedure provides a method for the determination of total Kjeldahl nitrogen (TKN) in water and wastewater.

2.0 SCOPE

2.1 This method covers the determination of total Kjeldahl nitrogen in water and wastewater.

2.2 The colorimetric method is based on reactions that are specific for the ammonia ion. The digestion converts organic forms of nitrogen to the ammonium form. Nitrate is not converted to ammonium during digestion.

2.3 The applicable range is 0.1 to 20 mg N/L.

2.4 Samples containing particulates should be filtered or homogenized.

3.0 SUMMARY

3.1 The sample is heated in the presence of sulfuric acid, H_2SO_4, for two and one half hours. The residue is cooled, diluted with water and analyzed for ammonia. This digested sample may also be used for total phosphorus determination.

3.2 Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of the digestion described.

3.3 Organic nitrogen is obtained by subtracting the free-ammonia concentration from the Kjeldahl nitrogen concentration.

3.4 Approximately 0.3 mL of the digested sample is injected onto the chemistry manifold where its pH is controlled by raising it to a known, basic pH by neutralization and with a concentrated buffer. This in-line neutralization converts the ammonium cation to ammonia, and also prevents undue influence of the sulfuric acid matrix on the pH-sensitive color reaction which follows.

3.5 The ammonia thus produced is heated with salicylate and hypochlorite to produce blue color which is proportional to the ammonia concentration. The color is intensified by adding sodium nitroprusside. The presence of potassium tartrate in the buffer prevents precipitation of calcium and magnesium.

4.0 REFERENCES

4.1 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Kjeldahl, Total, Method 351.2 (Colorimetric, Semi-Automatic Block Digestor, AAII) "

4.2 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Ammonia, Method 350.1 (Colorimetric, Automated Phenate)."

4.3 ASTM , Water(I), Volume 11.01, Method D3590-89, "Test Methods for Kjeldahl Nitrogen in water", p. 447.

4.4 Code of Federal Regulations 40, Chapter 1, Part 136, Appendix B.

4.5 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-107-06-2-D, "Determination Of Total Kjeldahl Nitrogen By Flow Injection Analysis, Colorimetry (Block Digestor Method)."

4.6 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the Analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 Samples may be preserved by addition of a maximum of 2 mL of concentrated H_2SO_4 per liter (preferred - 1 mL of 1N H_2SO_4 per 100 mL) and stored at 4°C. Acid preserved samples have a holding time of 28 days.

6.2 Limitations and Actions

6.2.1 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted with reagent 7 to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Samples must not consume more than 10% of the sulfuric acid during digestion (one mL of sulfuric acid should remain after digestion). The buffer will accommodate a range of 4.5-5.0% (v/v) H_2SO_4 in the digested sample with no change in signal intensity.

6.2.2.2 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed.

6.2.2.3 Digests must be free of turbidity. Some boiling stones have been shown to crumble upon vigorous vortexing.

6.3. Apparatus/Equipment

6.3.1 Balance – analytical. capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimetric detector

6.3.3.5 Data system

6.3.3.6 10 nm band pass, 80 uL, glass flow cell

6.3.3.7 660 nm interference filter

6.3.3.8 Helium degassing tube

6.3.4 Special Apparatus

6.3.4.1 Heating Unit

6.3.4.2 75 mL digestion tubes with cold fingers

6.3.4.3 Digestion tube rack

6.3.4.4 Cold finger rack assembly

6.3.4.5 Block Digestor

6.3.4.6 5 mL dispenser

6.3.4.7 10 mL dispenser

6.3.4.8 Vortex mixer

6.3.4.9 Countdown timer

6.4 Reagents and Standards

6.4.1 Preparation of Reagents -

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation. degas all solutions with helium except the standards. Mercuric Sulfate Solution (Reagent 1) and Digestion Solution (Reagent 2). Bubble helium through a degassing tube (Lachat Part 50100) into the solution for at least one minute.

Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. Mercuric Sulfate Solution**

By Volume: To a **100 ml** volumetric flask add **40.0 mL water** and **10 mL concentrated sulfuric acid (H_2SO_4)**. Then add **8.0 g red mercuric oxide (HgO)**. Stir until dissolved, dilute to the mark and invert to mix. Warming the solution while stirring may be required to dissolve the mercuric oxide.

6.4.1.2 **Reagent 2 Digestion Solution**

By Volume: To a **1 L** volumetric flask. add **133.0 g potassium sulfate** (K_2SO_4) and **200 mL concentrated sulfuric acid** (H_2SO_4) to approximately **700 mL water**. Add **25.0 mL Reagent 1**. Dilute to the mark with water and invert to mix.

6.4.1.3 **Reagent 3. Buffer**

Note: To reduce the possibility of the potassium tartrate being contaminated, it is recommended that the tartrate buffer is boiled for 10 minutes. To verify that the tartrate buffer is pure enough, compare the reagent baseline to the DI water baseline. The baseline, with all reagents flowing should not be greater than 0.15V different from just the DI water pumping in all lines.

By Volume: In a **1L** container add **900 mL water, 50 g potassium tartrate** (or potassium sodium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$), **50 g sodium hydroxide** (NaOH), and **26.8 g sodium phosphate dibasic heptahydrate** ($Na_2HPO_4 \cdot 7H_2O$). Mix until dissolved. Boil for 10 minutes. Cool to room temperature and transfer to a **1L** volumetric flask. Dilute to the mark and invert to mix.

6.4.1.4 **Reagent 4. Sodium Hydroxide (0.8 M)**

By Volume: In a **1 L** volumetric flask dissolve **32 g sodium hydroxide** (NaOH) in about **800 mL of water**. Dilute to the mark and stir to mix.

By Weight: In a **1 L** container dissolve **32 g sodium hydroxide** (NaOH) in **985 g of water** and mix.

6.4.1.5 **Reagent 5. Salicylate Nitroprusside**

By Volume: In a **1 L** volumetric flask dissolve **150.0 g sodium salicylate** [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] in about **800 mL water**. Dilute to the mark and mix. Store in a dark bottle.

By Weight: To a tared **1 L** dark container, add **150.0 g sodium salicylate** [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] and **908 g water**. Mix and store in a dark bottle.

6.4.1.6 **Reagent 6. Hypochlorite Solution**

By Volume: In a **250 mL** volumetric flask, dilute **15.0 mL Regular Clorox Bleach** (5.25% sodium hypochlorite. The Clorox Company, Oakland CA) to the mark with water. Invert to mix.

By Weight: To a tared **250 mL** container, add **16 g of Regular Clorox Bleach** (5.25% sodium hypochlorite, The Clorox Company , Oakland CA) and **234 g water**. Shake to mix.

6.4.1.7 **Reagent 7. Diluent**

Note: Diluent is used for the **carrier** and for off line dilutions.

By Volume: In a **1 L** volumetric flask add about **700 mL water**, then add **48 mL concentrated sulfuric acid** (H_2SO_4), (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **31.7 g potassium sulfate** (K_2SO_4). Dilute to the mark with water and mix.

By Weight: In a tared **1 L** container, add **940 g water** then **88.3 g concentrated sulfuric acid** (H_2SO_4), (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **31.7 g potassium sulfate** (K_2SO_4) and mix.

6.4.2 Preparation of Standards

Note: Working standards are prepared per instructions below and then processed through the digestion procedure along with the samples.

6.4.2.1 **Standard 1. Stock Standard 1000 mg N/L**

Dry **ammonium chloride** (NH_4Cl) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in about **800 mL water.** Dilute to mark with **water** and mix.. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Working Standard - 50 mg N/L**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** of the **1000 mg N/L** stock standard (standard 1), dilute to mark with **water** and mix.

6.4.2.3 **Standard 3. Working Quality Control Standard - 31.06 mg N/L**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **20 mL** of the E M Science **1000 mg N/L Ammonia Standard Solution** (776.5 mg N/L), dilute to mark with **water** and mix.

Note: 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.4 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

	Calibration Standards Concentration mg/L	Prepared From	
		Concentration mg/L	Aliquot mL
1	20.00	50	200
2	10.00	50	100
3	4.00	50	40
4	2.50	50	25
5	1.00	10	50
6	0.10	1	50
7	0.02	0.10	100
8	0.00	Water	0

6.4.2.5 **Laboratory Control Standard - 1.55 mg N/L**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 3). Dilute to mark with **water** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above three QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 Digestion Procedure

7.1.1.1 Both standards and samples are carried through this procedure.

7.1.1.2 Using a digestion tube rack to hold the digestion tubes, place **20.0 mL of sample** or standard in the digestion tubes. Use an acid resistant repipet device to add **5 mL of the digestion** solution (Reagent 2). Mix.

7.1.1.3 Add **2-4 Hengar granules** to each tube. Hengar granules are effective for smooth boiling.

7.1.1.4 Verify that boiling stones have been placed in each tube. Place tubes in the preheated block digestor for **one hour** at **160°C**. Water from the samples should have boiled off before increasing the temperature in step 7.1.1.5.

7.1.1.5 After the water has boiled off, place the **cold fingers** on the tubes. Continue to digest for **1.5 additional hours** with the controller set to **380°C**. This time includes the ramp time for the temperature to come up to 380°C. The typical ramp time is 50 - 60 minutes. 380°C must be maintained for 30 minutes.

7.1.1.6 Before removing samples, gather the necessary supplies to dilute the samples with water. Remove the samples from the digestion block and place on a rack stand. Allow tubes to cool for a minimum of **8 minutes**.

7.1.1.7 With the water dispenser calibrated for 10 mL, add **10 mL of water** to each tube.

7.1.1.8 Place the tubes on a block digestor that is heated to **105°C**. Let the tubes stay on the digestor three to five minutes, but no more than five minutes to avoid loss of volume. Remove the tubes to a tube rack stand.

7.1.1.9 Using a vortex mixer and a countdown timer, mix the samples two at a time for one minute. Do not let the unmixed samples remain unheated for more than three minutes. If there are a large number of samples, it will be necessary to return the tubes with unmixed samples back to the 105°C block digestor to keep the samples warm until mixed but for no more than three minutes at a time. Alternate placing the unmixed samples on and off of the heating block as needed until all samples are mixed. Caution must be given in not allowing the samples to get too cool, which will prevent the potassium sulfate and ammonium sulfate crystals from going into solution.

7.1.1.10 Hold the tubes up to a light source and swirl to see if there are any undissolved crystals in the solution (not to be confused with very fine boiling stone residue). If crystals are present, reheat and remix.

7.1.1.11 After all of the samples have been mixed, use the water dispenser to add an addition **10 mL of water** to each tube. The total final volume should be 21 mL. Mix well using the vortex mixer.

7.1.1.12 Allow the samples to cool to room temperature and analyze.

7.1.2 Analysis Procedure

7.1.2.1 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2.2 Prepare reagents and standards as described in section 6.4

7.1.2.3 Set up manifold as shown in section 9.2

7.1.2.4 Enter data system parameters as in section 9.1

7.1.2.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Allow 15 minutes for heating unit to warm up to 60°C. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. Add the buffer line first, pump for about 5 minutes or at least until the air bubbles introduced during the transfer passes through the flow cell. Then place all other transmission lines in the proper reagents.

7.1.2.6 Load standard and sample trays.

7.1.2.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.2.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.2.9 After the standards are injected and the system has automatically prepared a calibration curve, the system will inject the samples from the sample tray.

7.1.2.10 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted with reagent 7 to bring the analyte concentration within range.

7.1.2.11 At the end of the run, remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.2.12 To prevent baseline drifts, peaks that are too wide, or other problems with precision, clean the manifold by placing the manifold reagent lines in 1 M hydrochloric acid (1 volume of concentrated HCl added to 11 volumes of water). Pump for about five minutes.

7.1.2.13 Remove all reagent lines from the hydrochloric acid and place them in water. Pump until the HCl is thoroughly washed out (about 5 minutes).

7.1.2.14 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Orion FIA Software Installation and Tutorial Manual,* page 43, "Task 11 - Creating a Custom Report")

7.2.3 Report on those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted with reagent 7 and reanalyzed.

7.2.4 Report results in mg N/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating of inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters

Method Filename:	TN_D.MET
Method Description:	TKN (d) = 20.0 to 0.1 mg N/L

Analyte Data:

Analyte Name:	Total N
Concentration Units:	mg N/L
Chemistry:	Direct
Inject to Peak Start (s):	42.0
Peak Base Width (s):	39.000
% Width Tolerance:	100.000
Threshold:	8000.000
Autodilution Trigger:	Off
QuickChem Method:	10-107-06-2-D

Calibration Data:

Levels: (mg N/L)	1: 20.000	2: 10.000	3. 4.000
	4: 1.000	5: 0.100	6. 0.000

Calibration Rep Handling: Average

Calibration Fit Type: 1st Order Poly

Force Through Zero: No

Weighing Method: None

Concentration Scaling: None

Sampler Timing:

Method Cycle Period (s): 55.0

Min. Probe in Wash Prd. (s): 9.0

Probe in Sample Period (s): 25.0

Valve Timing:

Method Cycle Period (s): 55.0

Sample Reaches 1st Valve (s): 19.0

Valve: On

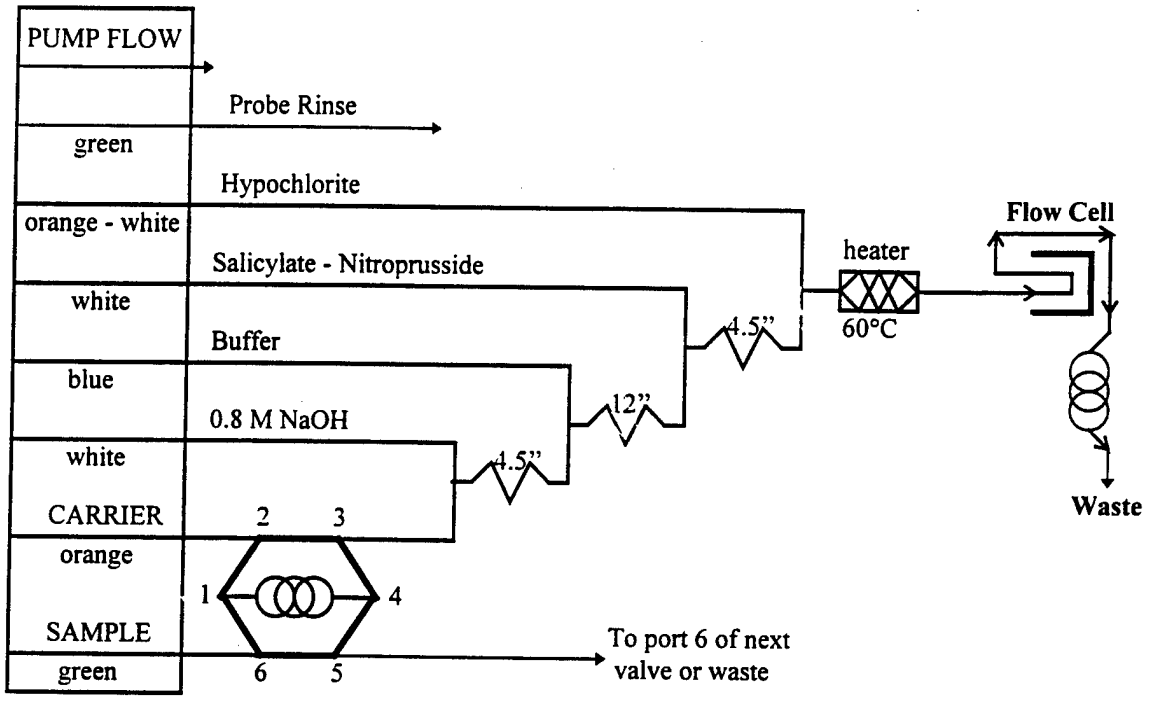
Load Time (s): 0.0

Load period (s): 20.0

Inject Period (s): 35.0

Sample Loop: 50 cm

9.2 Total Kjeldahl Nitrogen Manifold Diagram



Sample Loop = 50 cm

Interference Filter = 660 nm

Carrier is Diluent (reagent 7)

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm**.

4.5 is **70 cm** of tubing on a **4.5 cm** coil support.

12 is **255 cm** of tubing on a **12 cm** coil support.

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  includes 650 cm of tubing wrapped around the heater block at 60°C.

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-6

Orthophosphate (PO_4 phosphate): Method AP-0060

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0060

Title: PO_4-P by Flow Injection Analysis

Signature	Title	Date
Prepared by: Sammie Smith	Analytical Chemist	9/23/97
Concurred: Eugene A. Zarate	Laboratory Section Leader	9/24/97
Concurred: William J. Rogers	QA Officer	9/23/97
Concurred:		
Approved: Joseph D. Hoagland	Manager	9/23/97

Revision	R0					
Control Date	23-Sep-97					

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1.0 PURPOSE

This procedure provides a method for the determination of orthophosphate in drinking, ground, and surface waters, and domestic and industrial wastes.

2.0 SCOPE

2.1 This method covers the determination of orthophosphate in drinking, ground, and surface waters, and domestic and industrial wastes.

2.2 This method is based on reactions that are specific for the orthophosphate (PO_4^{3-}) ion.

2.3 The applicable range is 0.02 to 4.00 mg P/L.

3.0 SUMMARY

3.1 Only orthophosphate forms a blue color in this test. Polyphosphates and organic phosphorus compounds are not recovered. The sulfuric acid in the molybdate reagent does not have enough time with polyphosphates to hydrolyze them.

3.2 The orthophosphate reacts with ammonium molybdate and potassium tartrate under acidic conditions to form an antimony-phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

4.0 REFERENCES

4.1 U.S. Environmental Protection Agency, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA-600/R-93/100, August 1993, "Phosphorus, All Forms, Method 365.1 (Colorimetric, Automated, Ascorbic Acid)."

4.2 *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments.* Book 5. Chapter A1. U.S. Department of the Interior, U.S. Geological Survey, Method I-2601-78.

4.3 *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, p. 4 - 116, Method 4500-P F (1992).

4.4 *Guideline and Format for EMSL-Cincinnati Methods*. EPA-600/8-83-020, August 1983.

4.5 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-115-01-1-A, "Determination Of Orthophosphate In Waters By Flow Injection Analysis Colorimetry."

4.6 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the Analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned (use phosphate-free detergents), acid rinsed with 1:1 HCl, then rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 The USEPA recommends that samples be stored at 4° C with a maximum holding time of 48 hours, and that samples for dissolved phosphorus be filtered immediately upon collection.

6.1.3 If samples of high (pH > 8) are suspected add 1 drop of phenolphthalein indicator to a 50 mL aliquot of sample. If a red color develops, add 11 N sulfuric acid (310 mL concentrated H_2SO_4 /L) drop-wise to just discharge the color. Acid samples (pH < 4) must be neutralized with 1 N NaOH (40 g NaOH/L).

6.2 Limitations and Actions

6.2.1 If the analyte concentration is not within the analytical range of the calibration curve, the sample must be diluted to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Silica forms a pale blue complex which also absorbs at 880 nm. This interference is generally insignificant as a silicate concentration of approximately 30 mg SiO_2/L would be required to produce a 0.005 mg P/L positive error in orthophosphate.

6.2.2.2 Concentrations of ferric iron greater than 50 mg/L will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates.

6.2.2.3 For dissolved orthophosphate, sample turbidity must be removed by filtration prior to analysis. Sample color that absorbs at 880 nm will also interfere. When in doubt about background absorbance, the background concentration should be determined.

6.3 Apparatus/Equipment

6.3.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimetric detector

6.3.3.5 Data system

6.3.4 Special Apparatus

6.3.4.1 Heating Unit

6.4 Reagents and Standards

6.4.1 Preparation of Reagents

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation, degas the carrier solution and other reagents as noted with helium. Bubble Helium through a degassing tube (Lachat Part 50100) through the solution for at least one minute. Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. Stock Ammonium Molybdate Solution**

By Volume: In a **1 L** volumetric flask dissolve **40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in approximately **800 mL water**. Dilute to mark with **water** and stir for **two hours**. Store in plastic and refrigerate.

By Weight: To a tared **1 L** container add **40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ and **983 g water**. Stir for **two hours**. Store in plastic and refrigerate.

6.4.1.2 **Reagent 2. Stock Antimony Potassium Tartrate Solution**

By Volume: In a **1 L** volumetric flask dissolve **3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$) in approximately **800 mL of water**. Dilute to mark with **water** and mix. Store in a dark bottle and refrigerate.

By Weight: To a **1 L dark** tared container add **3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$) and **995 g water**. Mix. Store in a dark bottle and refrigerate.

6.4.1.3 **Reagent 3. Molybdate Color Reagent**

By Volume: To a **1 L** volumetric flask add about **500 mL water**, then add **35.0 mL concentrated sulfuric acid** (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **72.0 mL Stock Antimony Potassium Tartrate Solution** (Reagent 2) and **213 mL Stock Ammonium Molybdate Solution** (Reagent 1). Dilute to the mark with **water** and mix. Degas with helium and refrigerate.

By Weight: To a tared **1 L** container add **680 g water**, then **64.4 g concentrated sulfuric acid** (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **72.0 g Stock Antimony Potassium Tartrate Solution** (Reagent 2) and **213 g Stock Ammonium Molybdate Solution** (Reagent 1). Mix and degas with helium. Refrigerate.

6.4.1.4 **Reagent 4. Ascorbic Acid Reducing Solution, 0.33 M**

By Volume: In a **1 L** volumetric flask dissolve **60.0 g granular ascorbic acid** in about **700 mL water.** Dilute to the mark with **water**, mix and degas. After degassing add **1.0 g dodecyl sodium sulfate** ($CH_3(CH_2)_{11}OSO_3Na$). Refrigerate. Discard if solution becomes yellow.

By Weight: To a tared **1 L** container add **60.0 g granular ascorbic acid** and **975 g water**. Stir until dissolved then degas. After degassing add **1.0 g dodecyl sodium sulfate** ($CH_3(CH_2)_{11}OSO_3Na$). Refrigerate. Discard if solution becomes yellow.

6.4.1.5 **Reagent 5. Sodium Hydroxide - EDTA Rinse**

Dissolve **65 g sodium hydroxide** (NaOH) and **6 g tetrasodium ethylenediamine tetraacetic acid** (Na_4EDTA) in **1.0 L** or **1.0 kg water**.

6.4.2 Preparation of Standards

Note: Following are standards preparations for running 3 channels simultaneous for PO_4-P, NH_3-N and NO_2-N + NO_3-N. Also included is the preparation of a NO_2-N standard which is used to assess the cadmium reduction column's efficiency.

6.4.2.1 **Standard 1. Stock Orthophosphate Standard - 1000 mg P/L as PO_4^{3-}**

Dry **primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) for one hour at 105°C. In a **1 L** volumetric flask dissolve **4.396 g primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Stock Ammonia Standard - 1000 mg N/L as NH_3**

Dry **ammonium chloride** (NH_4Cl) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in about **800 mL water**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.3 **Standard 3. Stock Nitrate Standard - 1000 mg N/L as NO_3^-**

In a **1 L** volumetric flask dissolve **7.220 g potassium nitrate** (KNO_3) in about **600 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.4 **Standard 4. Stock Nitrite Standard - 1000 mg N/L as NO_2^-**

In a **1 L** volumetric flask dissolve **4.93 g sodium nitrate** ($NaNO_2$) in about **800 mL water**. Add **2 mL chloroform**. Dilute to mark with **water** and mix. Refrigerate. This solution is stable for six months.

6.4.2.5 **Standard 5. Working Standard - 50 mg/L PO_4-P, NH_3-N and NO_3-N**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** from each of the **Stock Orthophosphate Standard** (standard 1), the **Stock Ammonia Standard** (standard 2), and the **Stock Nitrate Standard** (standard 3). Dilute to mark with **water** and mix.

6.4.2.6 **Standard 6. Working Nitrite Standard - 20 mg N/L as NO_2^-**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **20 mL Stock Nitrate Standard** (standard 4). Dilute to mark with **water** and mix.

6.4.2.7 **Standard 7. Working Quality Control Standard - 32.61 mg P/L as PO_4^{3-}, 31.06 mg N/L as NH_4, and 27.11 mg N/L as NO_3^-.**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the E M Science **1000 mg/L Phosphate Standard Solution** (326.1 mg P/L), **20 mL** of the E M Science **1000 mg/L Ammonia Standard Solution** (776.5 mg N/L), and **60 mL** of the E M Science **1000 mg/L Nitrate Standard Solution** (225.9 mg N/L). Dilute to mark with **water** and mix.

Note: 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.8 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

	Calibration Standards Concentration mg/L	Prepared From	
		Concentration mg/L	Aliquot mL
1	20.00	50	200
2	10.00	50	100
3	4.00	50	40
4	2.50	50	25
5	1.00	10	50
6	0.10	1	50
7	0.02	0.10	100
8	0.00	Water	0

For standards for samples that have 1 mL of 1 N H_2SO_4 added per 100 mL, add **5 mL** of **1N H_2SO_4** to each standard after building to volume.

Note: If other acid concentrations are used to preserve samples, match for standards.

6.4.2.9 **Cadmium Reduction Column Efficiency Check Standard - 2.00 mg N/L as NO_2^-**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **50 mL** of the **Working Nitrite Standard** (standard 6). Dilute to mark with **water,** add **5 mL** of **1N H_2SO_4** and mix.

6.4.2.10 **Laboratory Control Standard - 1.63 mg P/L as PO_4, 1.55 mg N/L as NH_3, and 1.36 mg N/L as NO_3^-.**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 7). Dilute to mark with **water,** add **10 mL** of **1N H_2SO_4** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above three QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2 Prepare reagents and standards as described in section 6.4.

7.1.3 Set up manifold as shown in section 9.2.

7.1.4 Enter data system parameters as in section 9.1.

7.1.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Allow 15 minutes for heating unit to warm up to 37°C. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.1.6 Load standard and sample trays.

7.1.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.9 If samples require color correction, inject the samples with color development, then inject the samples with water replacing the color reagent (reagent 3).

7.1.10 At end of run, remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.11 Place the color reagent and ascorbic acid transmission lines into the NaOH - EDTA solution (Reagent 5). Pump for about 5 minutes to remove any precipitated reaction products.

7.1.12 Remove the reagent lines from the NaOH - EDTA solution and place them in water. Pump for an additional 5 minutes.

7.1.13 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual, page 43, Task 11 - Creating a Custom Report)

7.2.3 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

7.2.4 Samples that require color correction: From the value obtained with color developer added, subtract the value obtained without color developer. When a large number of samples are analyzed, use a spreadsheet to calculate the color correction.

7.2.5 Report results in mg PO_4-P/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating or inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters

Method Filename:	PANHANOW.MET
Method Description:	Ortho P (a) = 4.0 to 0.02 mg P/L
	NH_3-N (a) = 20.0 to 0.1 mg N/L
	NO_2-N/NO_3-N (a) = 20.0 to 0.2 mg N/L

Analyte Data:

Analyte Name:	Orthophosphate (PO_4)-P
Concentration Units:	mg PO_4-P/L
Chemistry:	Direct
Inject to Peak Start (s):	10.0
Peak Base Width (s):	23.000
% Width Tolerance:	100.000
Threshold:	5000.000
Autodilution Trigger:	Off
QuickChem Method:	10-115-01-1-A

Calibration Data:

Levels: (mg NO_3-N/L)	3: 4.000	4: 2.500	5: 1.000
	6: 0.100	7: 0.020	8: 0.000
Calibration Rep Handling:	Average		
Calibration Fit Type:	1st Order Poly		
Force through Zero:	No		
Weighing Method:	None		
Concentration Scaling:	None		

Sampler Timing:

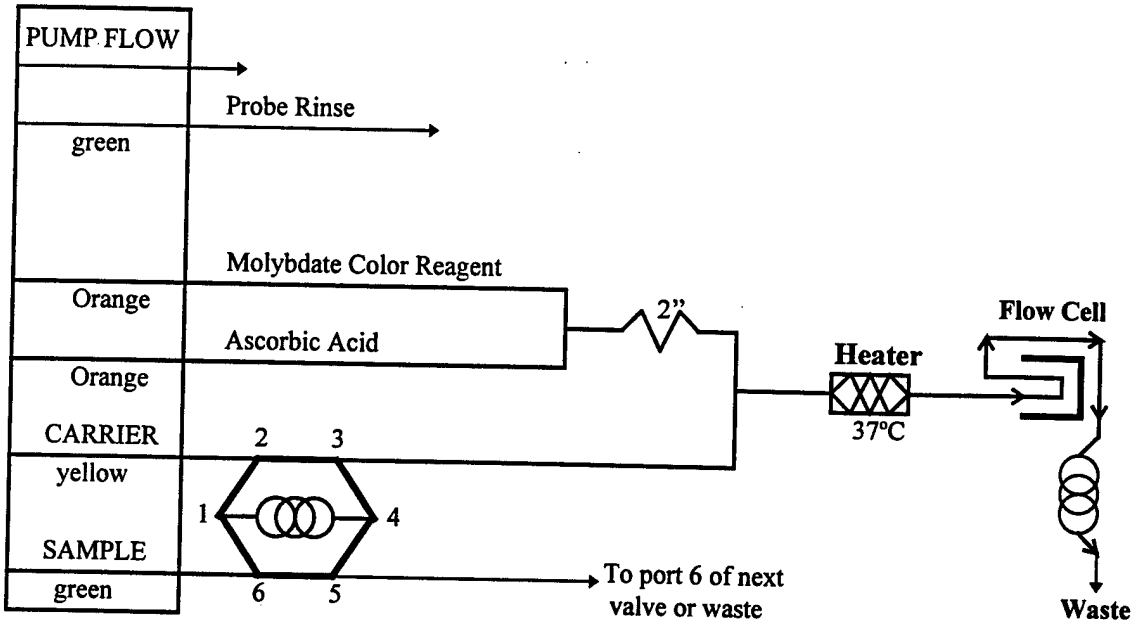
Method Cycle Period:	70.0
Min. Probe in Wash Period:	9.0
Probe in Sample Period:	30.0

Valve Timing:

Method Cycle Period:	70.0
Sample Reaches 1st Valve:	18.0
Valve:	On
Load Time:	0.0
Load period	25.0
Inject Period:	45.0

Sample Loop: 75.5 cm

9.2 Orthophosphate Manifold Diagram



Sample Loop = 75.5 cm

Interference Filter = 880 nm

Carrier is DI Water

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm.**

2 is **135 cm** of tubing on a **7 cm** coil support.

Apparatus: The 

includes 175 cm of tubing wrapped around the heater block at 37°C. An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-7

Total P: Method ASA 24-3.3

ASA 24-2.3 Method (Digestion)
as used for Total P Analysis

A. Reagents

1. Perchloric acid ($HClO_4$), 60% (Warning: Perchloric acid can react violently or explosively with hot organic matter.)
2. Nitric acid (HNO_3), concentrated reagent grade

B. Procedure

1. Mix 2.0 g of finely ground soil (0.5 mm) to a 250-ml volumetric or Erlenmeyer flask. (If the sample is high in organic matter, add 20 ml of HNO_3 and heat to oxidize the sample before adding the perchloric acid.) Add 30 ml of 60% perchloric acid. Digest the mixture at a temperature a few degrees below the boiling point on a hot plate in a hood until the dark color due to organic matter disappears. Then continue heating at the boiling temperature 20 min longer. At this stage, heavy white fumes of perchloric acid appear, and the insoluble material becomes like white sand. If necessary, add 1 or 2 ml of perchloric acid to move down any black particles that stick to the sides of the flask. The total digestion with perchloric acid usually requires about 40 minutes. Cool the mixture. Add distilled water to obtain a volume of 250 ml, and mix the contents. Allow time for the solid material to settle before taking an aliquot for further analysis.

2. Submit the digested sample for analysis by ICP for Total P.

C. References

1. "Method (Digestion)," Section 24-2.3 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix A-8

Inorganic P: Method ASA 24-3.3.3

ASA 24-3.3
Inorganic P for Organic P Calculation

A. Reagents

1. Sulfuric acid (H_2SO_4), 1*N*

B. Procedure

1. Place a 1-g sample of unignited soil in a 100-ml polypropylene centrifuge tube. Add 50 ml of 1*N* sulfuric acid and place the tube on a shaker for 16 hours.

2. Centrifuge the sample for 15 minutes. If the extract is not clear, filtration may be needed using acid-resistant filter paper.

3. Submit the sample for orthophosphate analysis. This value will be Inorganic P.

4. Calculate:

Organic P = Total P - Inorganic P

C. References

1. "Ignition Method," Section 24-3.3 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix A-9

pH: Method 150 Series

pH - Method 150.1 or 150.2

1.0 Procedure

For liquid samples, perform pH measurements by either Method 150.1 or 150.2 as appropriate.

2.0 Recordkeeping

Retain all worksheets, notes, and machine printouts as quality assurance records.

3.0 Quality Control Samples

Periodically, reanalyze calibration buffers. When possible, perform calibration with two buffers and check calibration with a third.

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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Issued 1971
Editorial revision 1978 and 1982

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

8.5 For acid rain samples it is most important that the magnetic stirrer is not used. Instead, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the electrode(s) to equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	–0.29	–0.01
3.5	0.11	–0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	–0.03	–0.002
8.0	0.13	–0.12	–0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293–65, p 178 (1976).
3 Peden, M. E. and Skowron, L. M., Ionic Stability of Precipitation Samples, Atmospheric Environment, Vol. 12, pp. 2343-2349, 1978.

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

pH, Continuous Monitoring (Electrometric)—Method 150.2

1. Scope and Application

1.1 This method is applicable to the continuous pH measurement of drinking, surface, and saline waters, domestic and industrial waste waters.

2. Summary of Method

2.1 The pH of a sample is determined electrometrically using a glass electrode with a reference electrode or a single combination electrode.

3. Sample Handling and Preservation

3.1 The composition of the water or waste contacting the measuring electrode system must be representative of the total flow from the water body.

4. Interferences

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Manually inspect the conditions of the electrodes every 30 days for coating by oily materials or buildup of lime. If oil and grease and/or scale buildup are not present, this time interval may be extended.

4.3.1 Coatings of oil, grease and very fine solids can impair electrode response. These can usually be removed by gentle wiping and detergent washing. The use of flow-through electrode housings which provide higher flow velocity helps to prevent the coating action.

4.3.2 Heavy particulate matter such as lime accumulation can be removed by careful scrubbing or immersion in dilute (1+9) hydrochloric acid. Continuous monitoring under these conditions benefits from ultrasonic or other in-line continuous cleaning methods.

4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. For best results, meters having automatic temperature compensation should be calibrated with solutions within 5°C of the temperature of the stream to be measured. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5. Apparatus

5.1 pH Monitor - A wide variety of instruments are commercially available with various specifications and optional equipment. For unattended use, the monitor should be equipped with automatic or fi

should be attainable in the range of pH 6.0 to 8.0. Accuracy data for continuous monitoring equipment are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water" Standard 1293-78, Method D, p. 226 (1981).

temperature compensation and with a recorder or alarm function.

5.2 Glass electrode - with shielded cable between electrode and monitor unless preamplification is used.

5.3 Reference electrode - a reference electrode with a constant potential and with either a visible electrolyte or viscous gel fill.
NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.4 Temperature sensor - for automatic compensator covering general ambient temperature range.

5.5 Electrode mounting - to hold electrodes; may be flow through (for small flows), pipe mounted or immersion.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is required.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, which have been validated by comparison to NBS standards, is recommended for routine operation. These buffers may be retained for at least six months if kept stoppered.

7. Calibration

7.1 Immersion type electrodes - easily removed from mounting.

7.1.1 The electrode should be calibrated at a minimum of two points that bracket the expected pH of the water/waste and are approximately three pH units or more apart.

7.1.2 Repeat calibration adjustments on successive portions of the two buffer solutions until readings are within ±0.05 pH units of the buffer value. If calibration problems occur, see 4.3.

7.1.3 Because of the wide variety of instruments available, no detailed operating instructions are provided. Instead, the analyst should refer to the particular manufacturer's instructions.

7.1.4 Calibration against two buffers should be carried out at least daily. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data supports a longer period between calibration.

7.2 Immersion type electrodes - not easily removed from mounting.

7.2.1 Collect a grab sample of the flowing material from a point as close to the electrode as possible. Measure the pH of this grab sample as quickly as possible with a laboratory - type pH meter. Adjust the calibration control of the continuous monitor to the reading obtained.

7.2.2 The temperature and condition of the grab sample must remain constant until its pH has been measured by the laboratory pH meter. The temperature of the sample should be measured and the temperature compensator of the laboratory pH meter adjusted.

7.2.3 The laboratory - type pH meter should be calibrated prior to use against two buffers as outlined in 7.1.

7.2.4 The continuous pH monitoring system should be initially calibrated against two buffers as outlined in 7.1 before being placed into service. Recalibration (every 30 days) at two points is recommended if at all possible to ensure the measuring electrode is in working order. If this is not possible, the use of electrode testing features for a broken or malfunctioning electrode should be considered when purchasing the equipment.

7.2.5 The indirect calibration should be carried out at least once a day. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data support a longer period between calibration.

7.2.6 If the electrode can be removed from the system, but with difficulty, it should be directly calibrated as in 7.1 at least once a month.

7.3 Flow-through type electrode - easily removed from its mounting.

7.3.1 Calibrate using buffers as in 7.1. The buffers to be used may be the process stream itself as one buffer, and as a second buffer after adjustment of pH by addition of an acid or base. This will provide the larger volumes necessary to calibrate this type electrode.

7.3.2 Since the velocity of sample flow-through a flow through electrode can produce an offset error in pH reading, the user must have data on hand to show that the offset is known and compensation has been accomplished.

7.4 Flow-through type electrode - not easily removed from its mounting.

7.4.1 Calibrate as in 7.2.

7.4.2 Quality control data must be on hand to show the user is aware of possible sample flow velocity effects.

8. Procedure

8.1 Calibrate the monitor and electrode system as outlined in Section 7.

8.2 Follow the manufacturer's recommendation for operation and installation of the system.

8.3 In wastewaters, the electrode may require periodic cleaning. After manual cleaning, the electrode should be calibrated as in 7.1 or 7.2 before returning to service.

8.4 The electrode must be placed so that the water or waste flowing past the electrode is representative of the system.

9. Calculations

9.1 pH meters read directly in pH units. Reports pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Because of the wide variability of equipment and conditions and the changeable character of the pH of many process waters and wastes, the precision of this method is probably less than that of Method 150.1; however, a precision of 0.1 pH unit

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[1] National Bureau of Standards Special Publication

5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

[1]National Bureau of Standards Special Publication 260.

Appendix A-10

pH: Method ASA 12-2.6

Soil pH
ASA 12-2.6

Procedure:

1. Calibrate the pH meter according to manufacturer's instructions using two buffers to bracket the expected range of measurements. Buffers should be approximately three pH units apart.

2. Where available, check the calibration with a third buffer.

3. Prepare a slurry of soil and water in the ratio requested by the customer. Note: Some customers may request 0.01 *M* $CaCl_2$ rather than water.

Example: Slurry 10.0 g soil and 10.0 ml water.

4. Stir the slurry vigorously with a glass rod and place the electrode into the slurry. Allow the electrode to come to equilibrium and measure the pH.

5. Record information about the calibration buffers (manufacturer, expiration date, known value), the check buffer and its measurement, and sample measurements.

References:

"pH, Method 150.1 (Electrometric)," *Methods for Chemical Analysis of Water and Wastes* - Revised March 1983, U. S. Environmental Protection Agency, Cincinnati, OH, PB84-128677.

"Glass Electrode - Calomel Electrode pH Meter Method," Section 12-2.6 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix A-11

Electrical Conductivity: Method 120 Series

Conductance - Method 120.1 (Specific Conductance, μmhos at 25°C)

1.0 Procedure

Perform conductivity measurements in accordance with Method 120.1 as attached.

2.0 Recordkeeping

Retain all worksheets, notes, and machine printouts as quality assurance records.

3.0 Quality Control Samples

Duplicate samples may be run (one per batch) when sample quantity permits. A quality control sample made from oven-dried (105°C) reagent grade potassium chloride may be used as well.

4.0 References

"2510 Conductivity", *Standard Methods for the Examination of Water and Wastewater*, 18th edition 1992, Edited by Greenberg et. al.

CONDUCTANCE

Method 120.1 (Specific Conductance, umhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline wates, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferable analyzed at 25°C. If not, temprature corrections aremade and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
   3.4 Temperature variations and corrections represent the largest source of potential error.
4. Sample Handling and Preservation
   4.1 Analyses can be performed either in the field or laboratory.
   4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45 micron filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.
5. Apparatus
   5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.
   5.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant. YSI #3403 or equivalent.
   5.4 Thermometer
6. Reagents
   6.1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7456 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C.
7. Cell Calibration
   7.1 The analyst should use the standard potassium chloride solution (6.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

Approved for NPDES
Issued 1971.
Editorial revision, 1982

Conductivity 0.01 m KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8. Procedure
   - 8.1 Follow the direction of the manufacturer for the operation of the instrument.
   - 8.2 Allow samples to come to room temperature (23 to 27°C), if possible.
   - 8.3 Determine the temperature of samples within 0.5°C. If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°.
9. Calculation
   - 9.1 These temperature corrections are based on the standard KCl solution.
     - 9.1.1 If the temperature of the sample is below 25°C, add 2% of the reading per degree.
     - 9.1.2 If the temperature is above 25°C, subtract 2% of the reading per degree.
   - 9.2 Report results as Specific Conductance, μmhos/cm at 25°.
10. Precision and Accuracy
    - 10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Accuracy as Bias, μmhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

- 10.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 μmhos/cm at 25°C, the standard deviation was ±6.

Bibliography

1. The procedure to be used for this determination is found in:
   Annual Book of ASTM Standards Part 31, "Water," Standard D1125-64, p. 120 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 71, Method 205 (1975).
3. Instruction Manual for YSI Model 31 Conductivity Bridge.
4. Peden, M. E., and Skowron. "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol. 12, p. 2343-2344, 1978.

Appendix A-12

Metals: Method 6010B

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Method 6010B - Inductively Coupled Plasma - Atomic Emission Spectroscopy

1.0 Procedure

Perform analysis for metals and certain other elements amenable to ICP analysis in accordance with Method 6010B from SW-846 as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be 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. In one mode of analysis the position used should be as free as possible from spectral interference and should 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 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $\geq$ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences 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 dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4{\cdot}4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO_3 (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g Fe_2O_3 (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous KH_2PO_4 (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g H_2SeO_3 (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: Do not dry. Dissolve 2.964 g NH_4SiF_6, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH_4VO_3 (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

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TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 mg/L
Cu -	200 mg/L	V -	200 mg/L
Fe -	1000 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see "NOTE" to Section 5.4), Mg, Sb, and Tl
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b]	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

[a] Not all elements were analyzed by all laboratories.
[b] RSD = relative standard deviation.
[c] Results for Se are from two laboratories.
[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Accuracy[c] (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

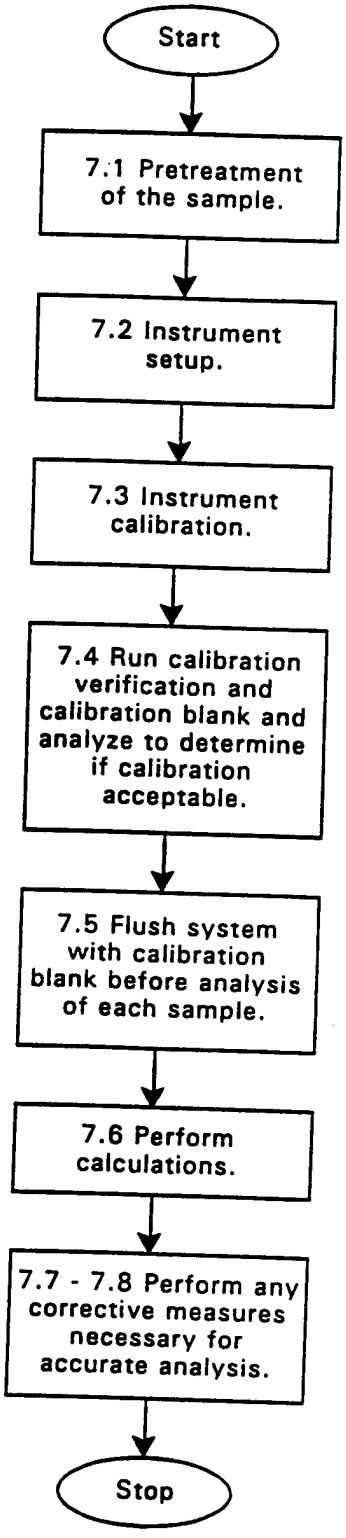
Element	Spiked Coal Fly Ash (NIST-SRM 1633a) Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)	Spiked Electroplating Sludge Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY



Appendix A-13

Metals (Hg): Method 7470A/71A

Method 7470A/7471A Mercury (Manual Cold-Vapor Technique)

1.0 Procedure

For liquid samples for mercury, perform analysis in accordance with Method 7470A as attached. For solid samples for mercury, perform analysis in accordance with Method 7471A as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

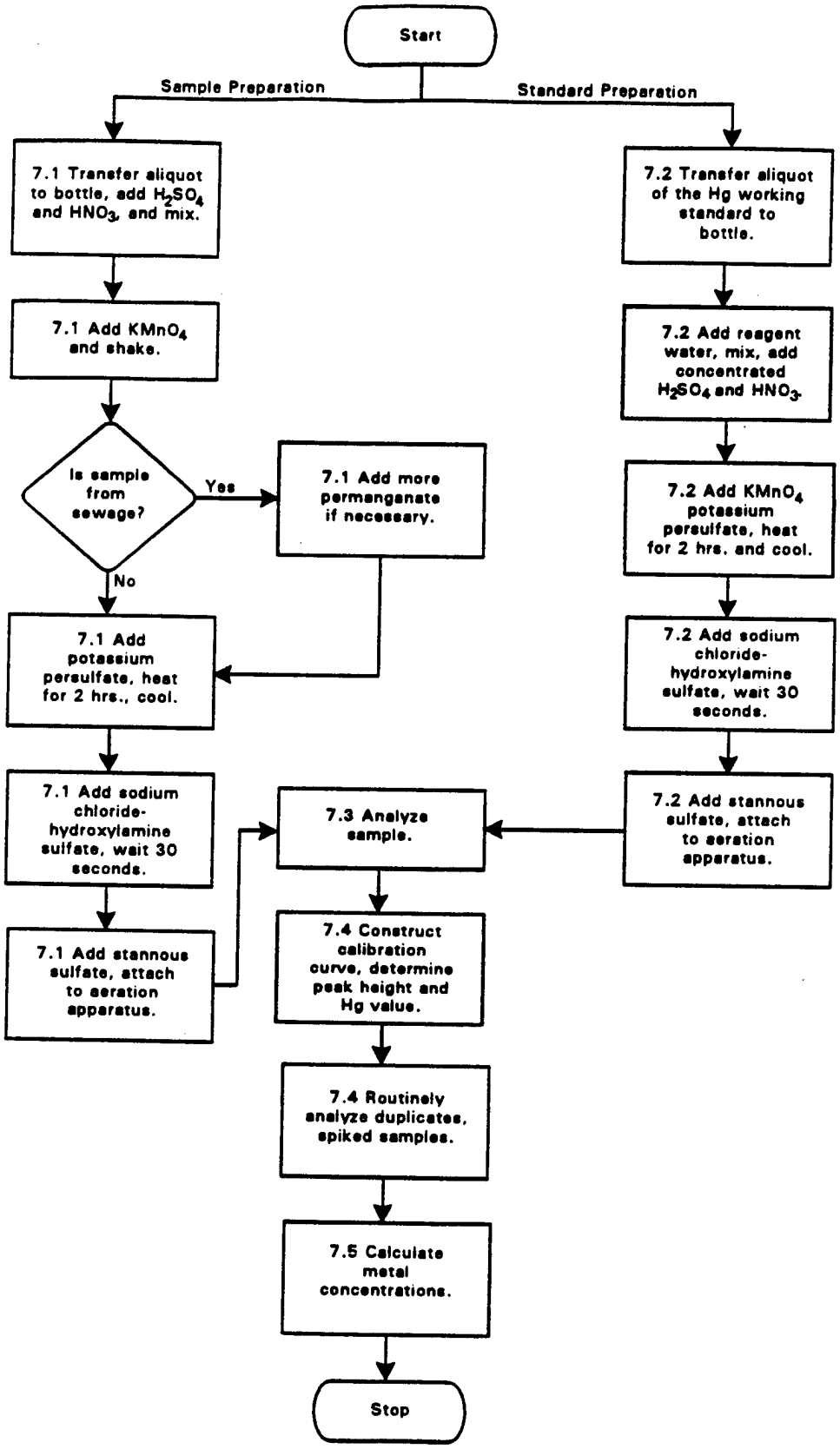
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470A
MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



Revision 1
September 1994

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the

absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into

account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

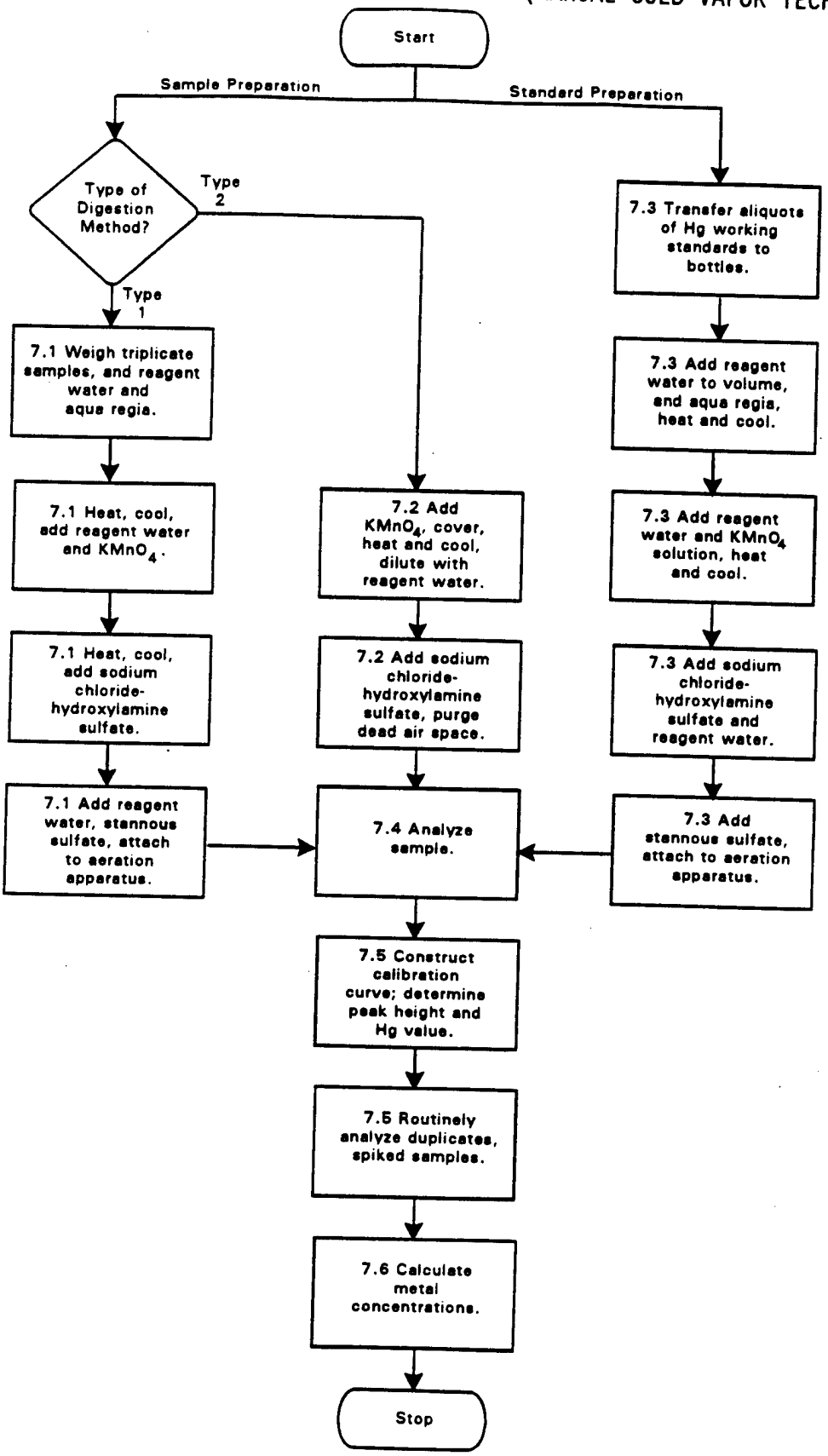
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



Revision 1
September 1994

Appendix A-14

Metals (Se): Method 7740A

Method 7740 - Selenium (Atomic Absorption, Furnace Technique)

1.0 Procedure

Perform analysis for selenium in accordance with Method 7740 as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 250-mL Griffin beaker.

4.2 10-mL volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for the analysis of Se.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

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

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 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.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured uL-aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

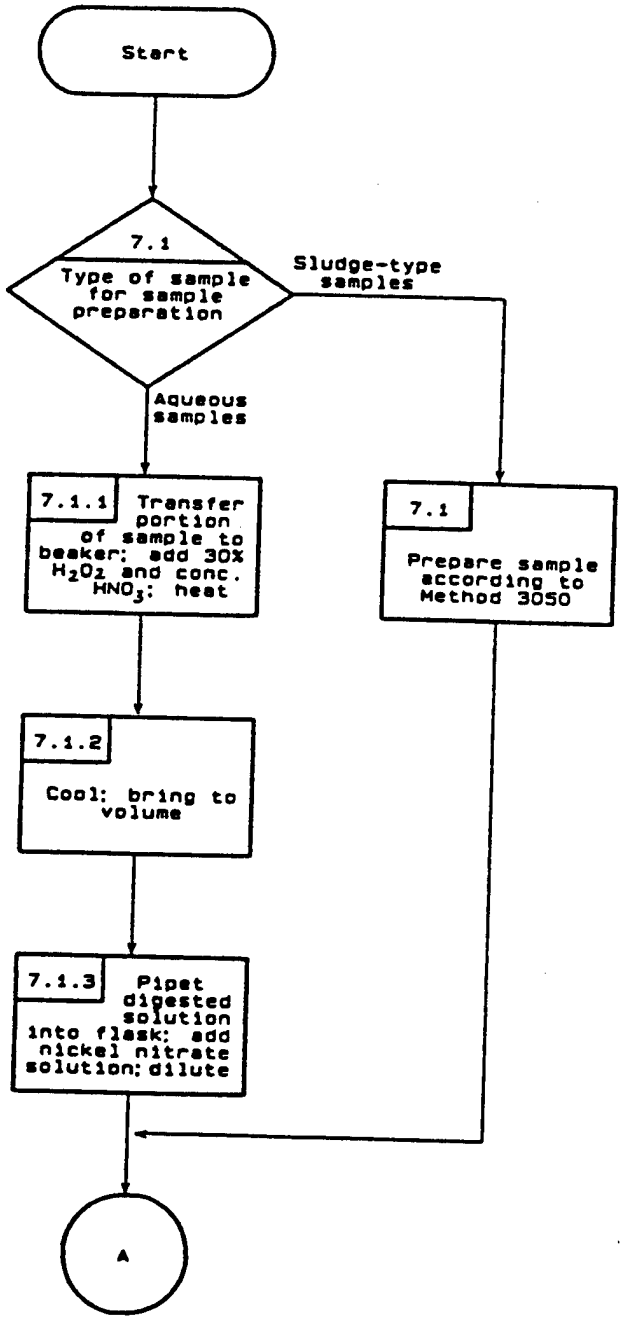
10.0 REFERENCES

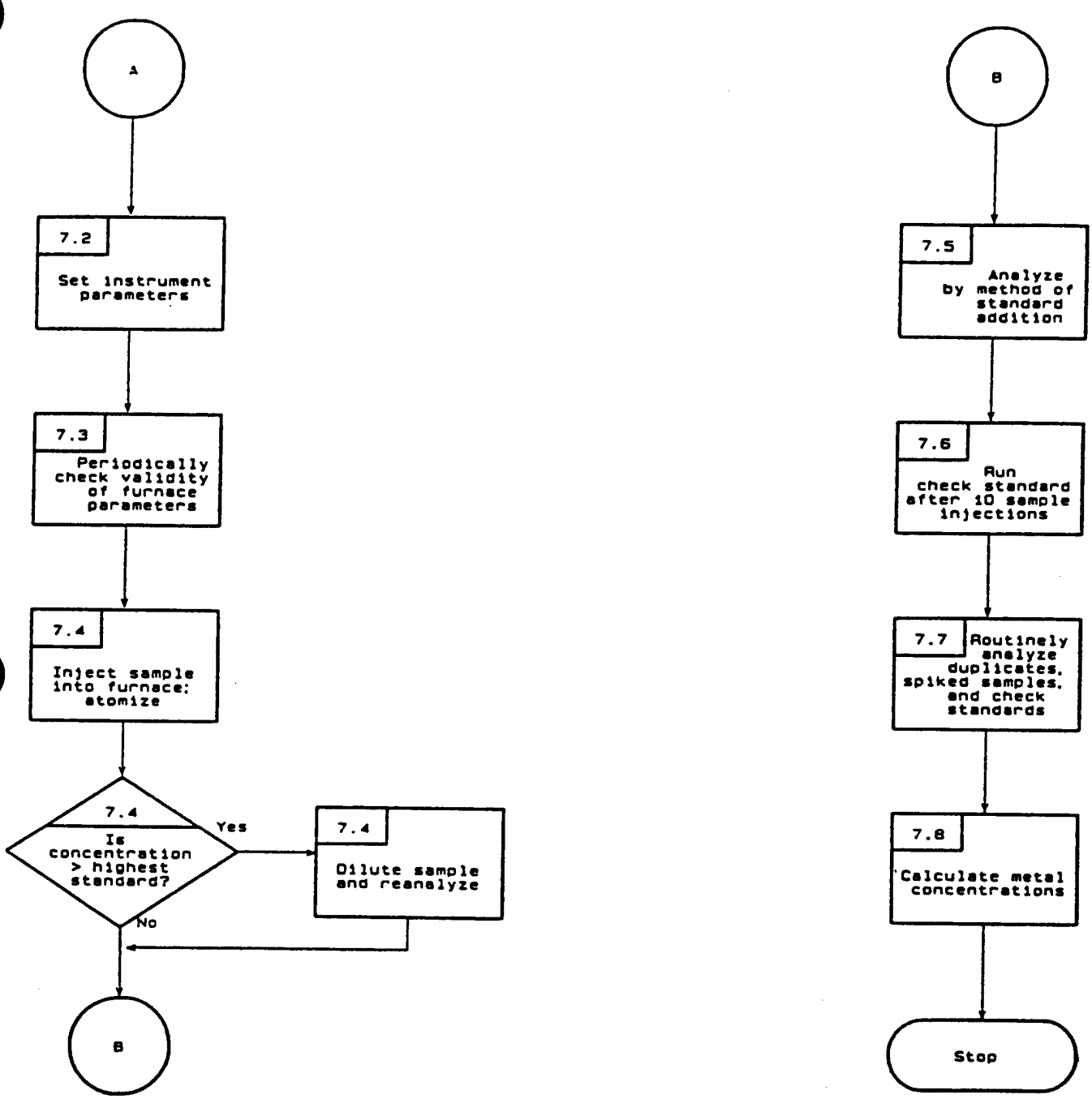
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g


Start
7.1
Type of sample for sample preparation
Sludge-type samples
Aqueous samples
7.1.1 Transfer portion of sample to beaker; add 30% H_2O_2 and conc. HNO_3; heat
7.1
Prepare sample according to Method 3050
7.1.2
Cool; bring to volume
7.1.3 Pipet digested solution into flask; add nickel nitrate solution; dilute
A


A
7.2
Set instrument parameters
7.3
Periodically check validity of furnace parameters
7.4
Inject sample into furnace; atomize
7.4
Is concentration > highest standard?
Yes
No
7.4
Dilute sample and reanalyze
B
B
7.5
Analyze by method of standard addition
7.6
Run check standard after 10 sample injections
7.7
Routinely analyze duplicates, spiked samples, and check standards
7.8
Calculate metal concentrations
Stop

Appendix A-15

Metals (As): Method 7060A

Method 7060A - Arsenic (Atomic Absorption, Furnace Technique)

1.0 Procedure

Perform analysis for arsenic in accordance with Method 7060 as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background

correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a suitable recording device.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the reagent can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 6H_2O$ or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3, 30% H_2O_2, and 5% nickel nitrate solution or other appropriate matrix modifier. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool, transfer to a volumetric flask, and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution or other appropriate matrix modifier, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

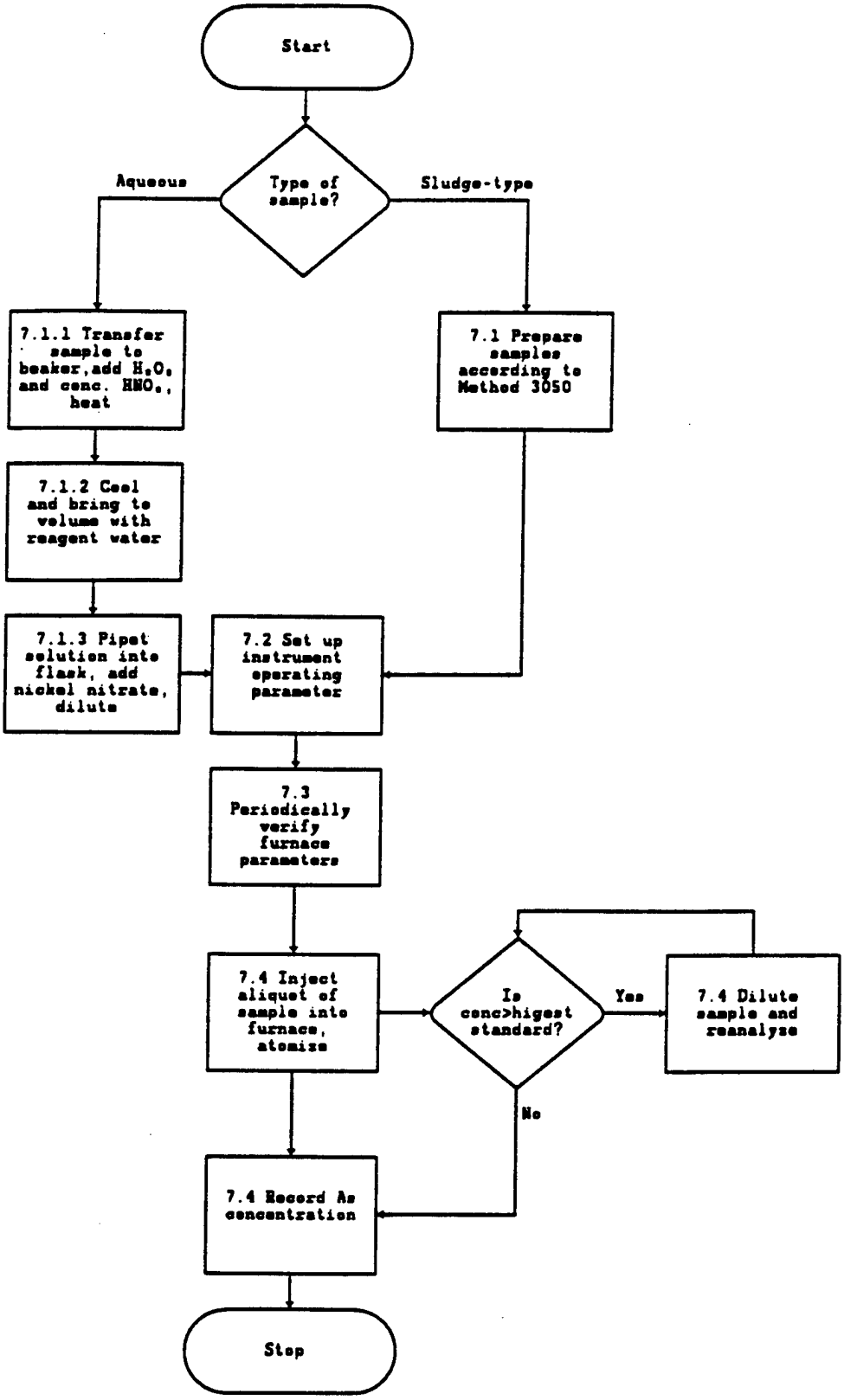
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
Type of sample?
Aqueous
Sludge-type
7.1.1 Transfer sample to beaker, add H_2O_2 and conc. HNO_3, heat
7.1 Prepare samples according to Method 3050
7.1.2 Cool and bring to volume with reagent water
7.1.3 Pipet solution into flask, add nickel nitrate, dilute
7.2 Set up instrument operating parameter
7.3 Periodically verify furnace parameters
7.4 Inject aliquot of sample into furnace, atomize
Is conc>higest standard?
Yes
7.4 Dilute sample and reanalyze
No
7.4 Record As concentration
Stop

Appendix A-16

Metals Digestion: Method 3005A

Method 3005A - Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy

1.0 Procedure

Prepare liquid samples for further analysis by AA or ICP in accordance with Method 3005A as attached.

2.0 Recordkeeping

Retain all worksheets, percent recovery calculations, weights, volumes, preparation information, spiking solution concentrations, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-μm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source 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.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with 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.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

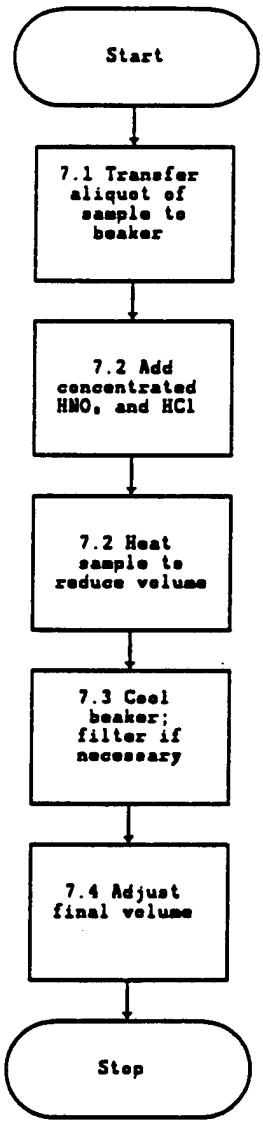
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

Appendix A-17

Metals Digestion: Method 3050B

Although the following procedure lists a post-project approval date, the methods described herein accurately describe the procedures used during the study.

Method 3050B - Acid Digestion of Sediments, Sludges, and Soils

1.0 Procedure

Prepare solid samples for further analysis by AA or ICP in accordance with Method 3050B as attached.

2.0 Recordkeeping

Retain all worksheets, percent recovery calculations, weights, volumes, preparation information, spiking solution concentrations, and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method: method blank, reagent blank, calibration check sample.

For each batch, introduce one quality control sample made from a separate stock than that used to calibrate the machine (a laboratory control sample).

Where possible, for each batch analyze one matrix spike sample.

For each batch, analyze a matrix spike duplicate or a sample duplicate.

METHOD 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C ± 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

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

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source 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 vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 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 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

10.0 REFERENCES

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6. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Environmental Science and Technology, Vol. 26, Page 173, January 1992. Presented Sixth Annual Waste Testing and Quality Assurance Symposium, July 1990.

7. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Sixth Annual Waste Testing and Quality Assurance Symposium, Reprinted in Solid Waste Testing and Quality Assurance: Fourth Volume, ASTM STP 1076, Ed., American Society for Testing and Materials, Philadelphia, 1992.

8. NIST published leachable concentrations. Found in addendum to certificate of analysis for SRMs 2709, 2710, 2711 - August 23, 1993.

9. Kingston, H.M. Haswell, S.J. ed., Microwave Enhanced Chemistry, Professional Reference Book Series, American Chemical Society, Washington, D.C., Chapter 3, 1997.

TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery[a,c]							
	Sample 4435		Sample 4766		Sample HJ		Average	
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704 "River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710 "Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B (µg/g ± SD)

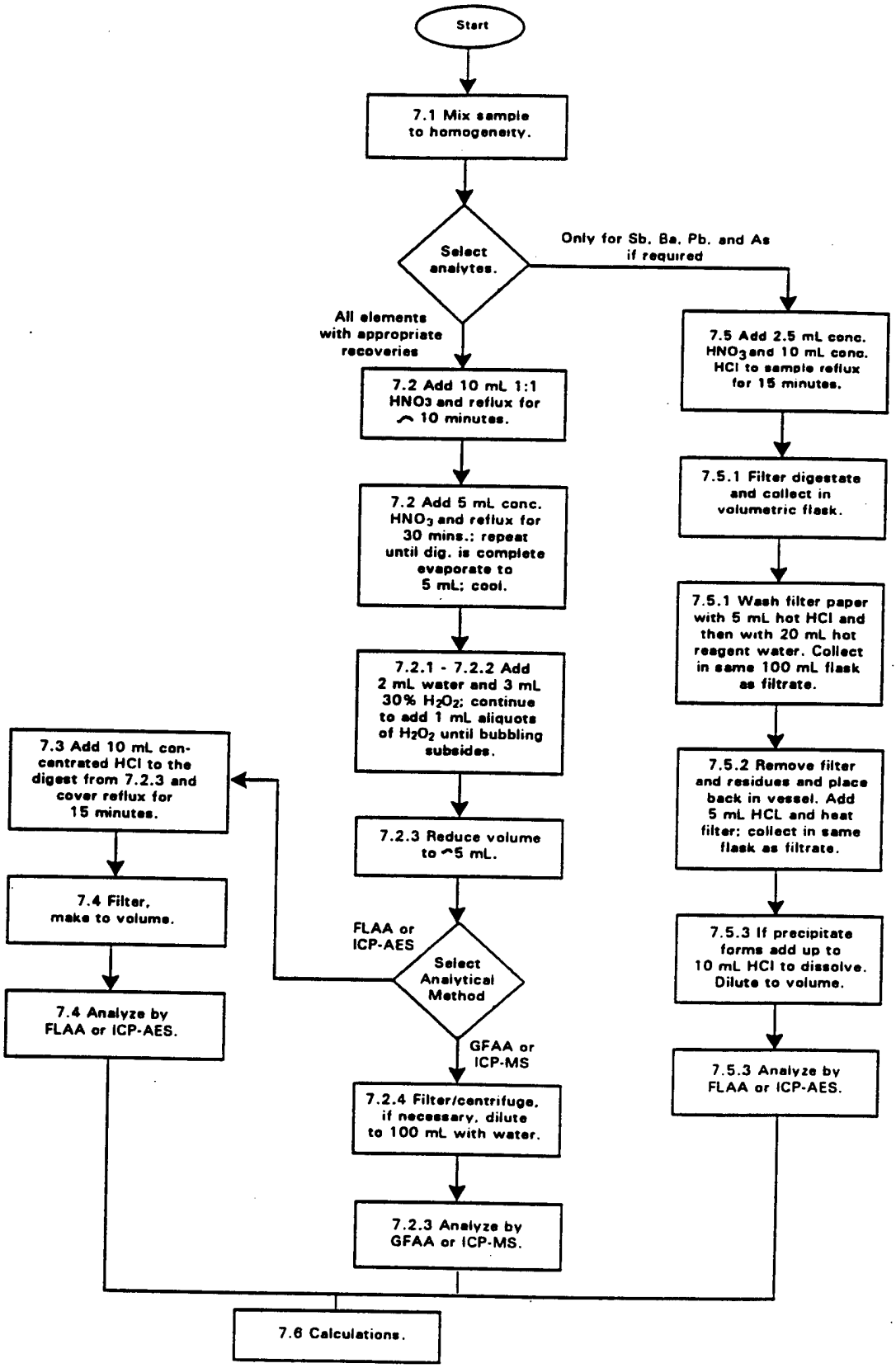
Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*
Ni	7.8 ± 0.29	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

NA - Not Available * Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.

Appendix A-18

Total Organic Carbon (TOC): Method 415 Series

Total Organic Carbon - Method 415.1 with Dohrmann DC-190

1.0 Procedure

Perform Total Organic Carbon (or Non-purgeable Organic Carbon[1]) in accordance with "Organic Cargon, Total", Method 415.1 (Combustion or Oxidation) and in accordance with chapters 6 and 10 of the operating manual for the Dorhmann DC-190 high temperature organic carbon analyzer as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples and notes as quality assurance records.

3.0 Quality Control Samples

For each batch of samples, perform a method blank and a calibration check sample. For each batch introduce one quality control sample made from a separate stock than that used to calibrate the instrument. Where possible, for each batch analyze one matrix spike sample. For each batch analyze a matrix spike duplicate or sample duplicate.

[1] Note: Non-Purgeable Organic Carbon is run when no effort has been made to sample or retain volatiles. This is the analysis of interest for most soil research.

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

Approved for NPDES
Issued 1971
Editorial revision 1974

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

SECTION 6
OPERATION

INTRODUCTION

This section contains instructions for routine operation along with detailed descriptions on how to operate and calibrate the different modes.

6.1 ROUTINE OPERATION

SUMMARY
* Daily Start-Up * Daily Operation * Daily and Long-term Shutdown

DAILY START-UP

Check utility supply.

Enough carrier gas for a day's operation.

Acid reservoir at least 1/3 full.

Replenish IC chamber.

Confirm the IC chamber is half full (gas off).

Fill the IC chamber by using the "Acid to IC chamber" function (press **MAIN 2 5**). Each use of this function will result in 20 pulses and is equivalent to 2 ml of acid.

Turn on gas.

Press **CARRIER** .

For Boat Users :

Connect the 1/8 inch PTFE line from the boat module furnace to the DC-190 dehumidifier (see Figure 4.8).

Check system status.

(Press **MAIN 1** to view the status menu.)

Flow rate = 180 - 220 cc/min.

Dryer temperature = 0 - 10 ^{o}C

Furnace Temperature = Furnace set point (Furnace light is green.) For most applications, the temperature should be 680^{o}C.

Confirm or change set-up number on display (see Section 6.8).

Check set-up.

(See Section 6.2 for help in choosing set-up.)

Modes last used are lit up. Make any changes for the day and print the set-up parameters. System is ready for analysis.

DAILY OPERATION

Press START when ready.

It is good practice to run a check standard at the beginning of the day before analyzing unknowns, especially if any conditions have been changed. Update calibration if needed. See Section 6.3 for notes on operating and calibrating.

DAILY SHUTDOWN

Check the RUN status.

The unit should not be in a RUN mode.

For Boat Users :

Disconnect the 1/8 inch PTFE line which runs from the boat furnace to the dehumidifier.

Shut off the gas.

Press CARRIER .

NOTE: The furnace and the NDIR should be left on unless the unit is going to be relocated or will not be used for a long time. Frequently turning the furnace on/off reduces the life of the heater element. The NDIR requires at least 2 hours for stabilization after power up.

6.2 SELECTING THE ANALYSIS PARAMETERS

Most analysis have three parameters:

1) Analysis mode.
2) Inlet mode.
3) Volume.

NOTE: The ASM and RSM operating modes have other parameters which must be selected. See Sections 6.4 and 6.5 for guidelines in selecting these parameters.

SELECT THE ANALYSIS MODE

Use Table 6.1 to match your application to an analysis mode. The default mode is **NPOC** . To set another mode, press the corresponding button.

Table 6.1
ANALYSIS MODE SELECTION

ANALYSIS MODE	APPLICATION	METHOD
NPOC	Any water sample.	IC purged from sample at sparging station. Inject into TC port. NPOC ---(TC Furnace)---> CO_2
TOC	Any water sample. Method of choice when sample has no volatiles.	TOC = TC - IC Two (2) injections per analysis. DC-190 calculates the difference. See See TC and IC descriptions.
IC	Any sample where dissolved CO_2 or carbonate concentration is of interest.	Sample injected into IC port. IC ---(IC Chamber)---> CO_2
TC	Any water sample.	Sample injected into TC port. TC ---(TC Furnace)---> CO_2
POC	Water sampler where volatile organics or other purgeables are of interest.	Sample is sparged at POC sparge station. LiOH scrubber removes IC from sparged gas. POC Gas --> IC Scrubber --> POC---(TC Furnace)---> CO_2
Boat Option, TC	Solids, sludges, slurries and waters with particulates greater than 0.5 mm.	Sample introduced onto platinum boat. Boat pushed into 183 furnace. Sample ---($800^{0}C$)---> CO_2

SELECT THE INLET MODE

The default inlet mode is **SYRINGE** . To select a different mode, refer to the following Table, then press the button corresponding to the new inlet mode.

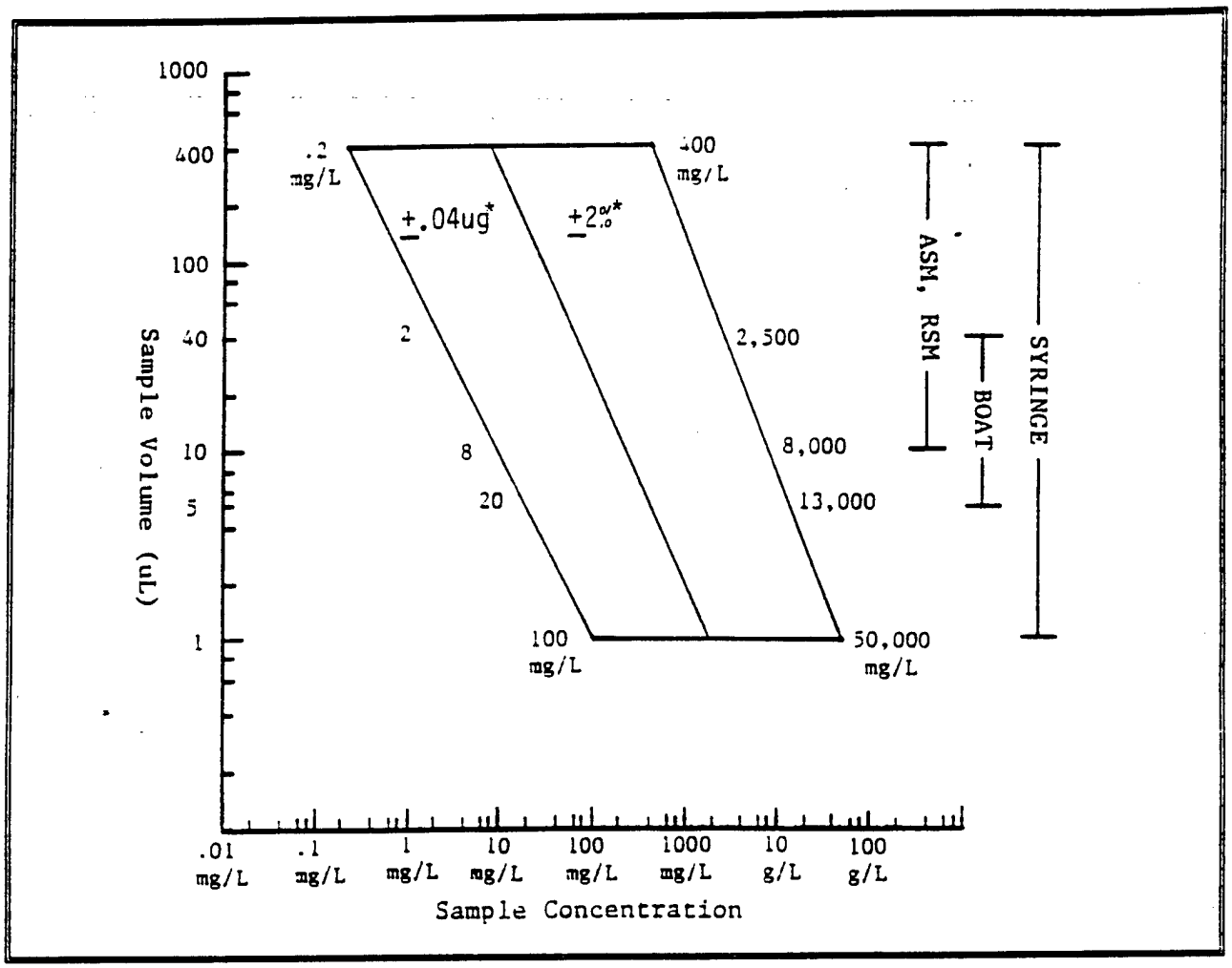
Table 6.2
INLET MODE SELECTION

ANALYSIS MODE	INLET MODE	DEFAULT		POSSIBLE VOLUME (ul)
		Volume (ul)	Range (mgC/L)	
NPOC TOC IC TC	Syringe	50	1 - 2000	1 - 400 20 - 200 *
	ASM	50	1 - 2000	10 - 400
TOC IC TC	RSM	50	1 - 2000	10 - 400
TC NPOC	Boat	40	2 - 4000	5 - 40
POC	N/A	10 mL	.01 - 20	2 - 10 mL

* This is the range for the manual micropipettor which is used with the **SYRINGE** mode.

SELECT VOLUME

The default volume and corresponding concentration range for each inlet mode are shown in the previous table. If the default concentration range is unsuitable, a better sample volume may be selected using Figure 6.1. Enter the new sample volume on the inlet mode menu.



* Expected precision. See Section 1.4.

FIGURE 6.1 Concentration Range vs. Sample Volume

EXAMPLE: Expected sample concentration range = 5 to 5,000 ppm.
From Figure 6.1, 20 ul gives 4 to 6,000 ppm.
(Note the logarithmic scales.)
20 ul is compatible with all inlet modes, except POC.

6.3 MANUAL OPERATION

Use these instructions for syringe or micropipettor operation in NPOC, TOC, IC, TC or POC modes. The following table shows the general operation sequence for syringe injections. Specific notes for each analysis mode follow the table.

GENERAL OPERATION SEQUENCE - ALL MODES

* If it is desired to save the current operating parameters before making any changes, select a new set-up number (see Section 6.7).
* Choose set-up.
* Have the syringe filled and ready. (Have the septum installed as shown in Figure 6.2.)
* Press **START** .
* Inject the sample. (Review the injection technique for the mode selected.)
* At the conclusion of the analysis, the screen will display the final ppm value along with:

  Continue Y/N ?

  (This question must be answered before the system will perform any other action.)
* Press **YES** to make more injections.
* Press **NO** to end the run.
* Press **STOP** to end the run after the current analysis. To terminate the run, immediately press **STOP** five times.

ABOUT SYRINGES

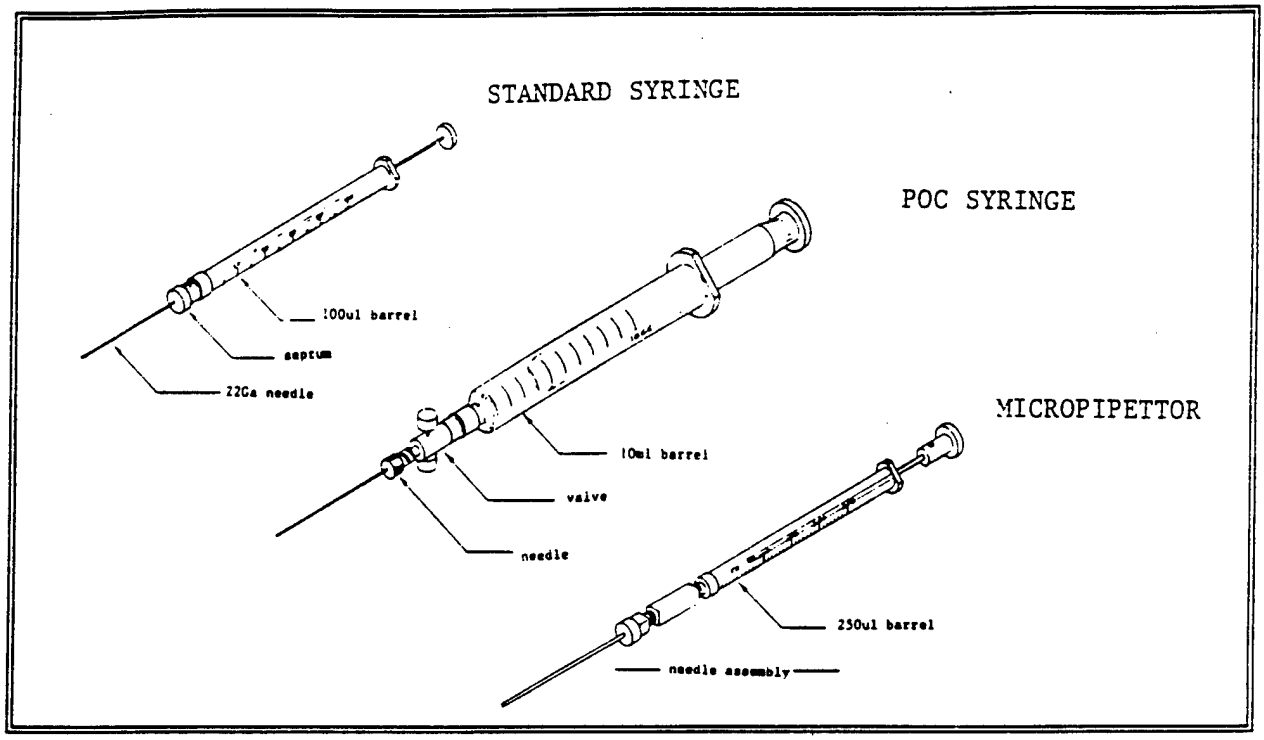


FIGURE 6.2. SYRINGE ASSEMBLIES

Assemble the syringes and micropipettor as shown in Figure 6.2. Always have a grey septum attached to the syringe or pipettor.

It is important for reliable sample introduction to use blunt-point needles such as those supplied with the DC-190. Side-port needles should not be used except on the POC syringe.

The 100 uL syringe (P/N 060-871) provided with the DC-190 has a 22S gauge (0.006 inch I.D.) needle. The 22 gauge (0.016 inch I.D.) replacement needles (P/N 060-872) are provided in the DC-190 operating kit for sample types requiring a larger I.D. needle.

Also available are a micropipettor barrel (250 uL syringe barrel, P/N 060-875) and a micropipettor needle (P/N 888-297). The micropipettor is used for samples containing particulates up to 0.5 mm diameter or samples which are incompatible with (react with or corrode) a stainless steel needle. The micropipettor probe should be used with a 250 uL syringe barrel only.

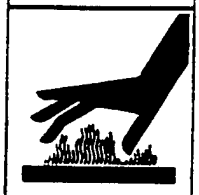
Injection Technique

As soon as the INJECT light comes on, press **OPEN/CLOSE**

Immediately insert the syringe into the injection port that has the illuminated LED.

Make seal during injection by pressing the grey septum against the port.

⚠CAUTION



Hot vapors. Make good seal before injection. See manual sect. 5.

Samples will expand rapidly when injected into the combustion tube. Hot steam may vent from the injection port unless a good seal is made with the syringe septa when injecting.

⚠WARNING

Explosion hazard. Do not inject samples with >10% hydrocarbon content.

The DC-190 has a 100% O_2 atmosphere in the combustion tube. Samples with more than 10% hydrocarbons may explode when injected into this environment

Inject at 50 ul/sec rate.

Withdraw the syringe and immediately press **OPEN/CLOSE** to close the port.

For 1 - 10 ul volumes, wait 5 seconds in between injecting and withdrawing syringe.

Micropipettor Users:

When using a micropipettor, wipe off the outside of the probe after drawing up the sample.

For volumes below 50 uL, the injection rate is crucial to obtaining reproducible results. Make the injection rapidly without jarring the syringe. (**HINT:** After withdrawing the syringe, look at the tip. If it is wet on the outside, inject faster; if it is partially empty, inject slower.)

Wait 10 seconds after injecting before withdrawing the pipettor for all volumes.

Sample Pretreatment

None, unless the samples are inhomogeneous or contain large particulates (> 0.5 mm diameter).

TOC

(This is a combination of the TC and IC modes.)

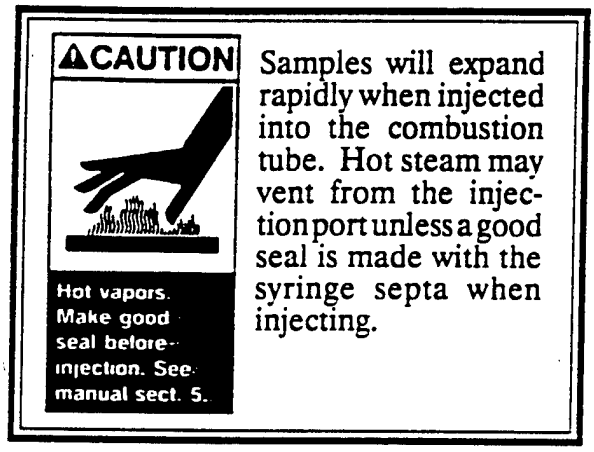
Injection Technique

Use the same technique as for the TC and IC modes.

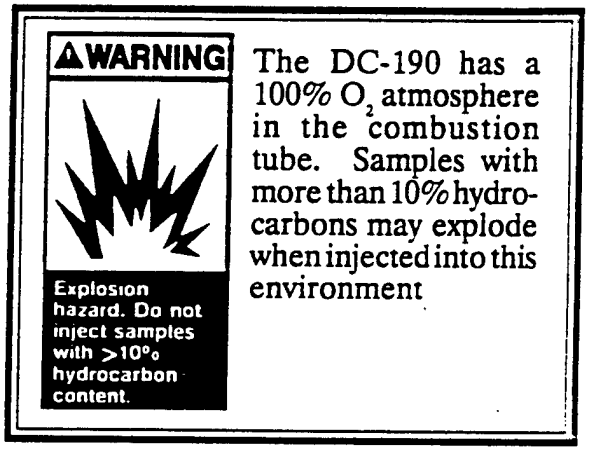
Make two injections per analysis.

The first injection goes in the TC port.

Have the syringe filled and ready for the second injection which is made to the IC port. Look for the prompt from the display.



Samples will expand rapidly when injected into the combustion tube. Hot steam may vent from the injection port unless a good seal is made with the syringe septa when injecting.



The DC-190 has a 100% O_2 atmosphere in the combustion tube. Samples with more than 10% hydrocarbons may explode when injected into this environment

NOTE: When high pH samples are expected, treat combustion tube with 2 injections of 100 ul of pH1 HCl or HNO_3 solution.

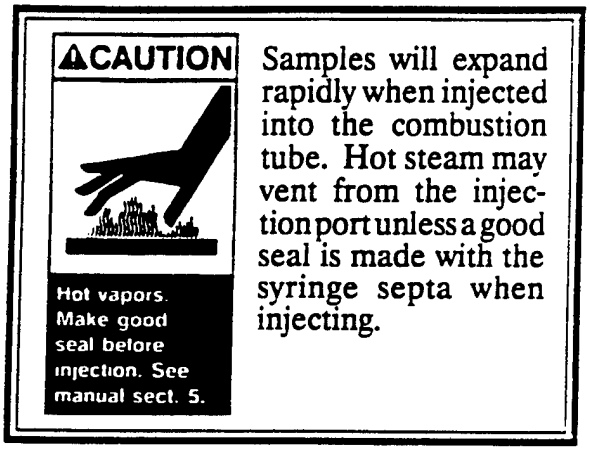
NPOC

(This is the default analysis mode.)

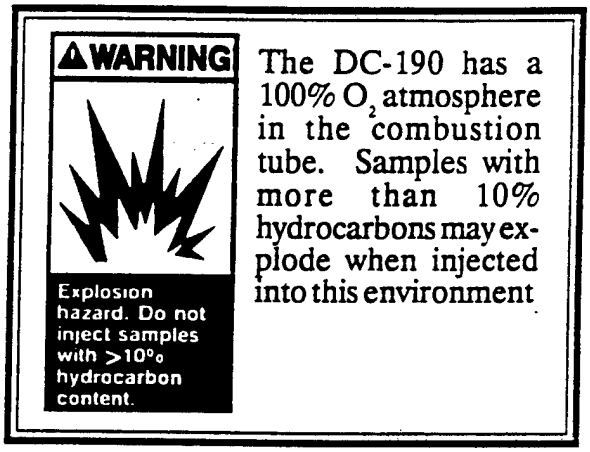
Injection Technique

Use the same technique as for the **TC** and **IC** modes.

Inject into the **TC** port only.



Samples will expand rapidly when injected into the combustion tube. Hot steam may vent from the injection port unless a good seal is made with the syringe septa when injecting.



The DC-190 has a 100% O_2 atmosphere in the combustion tube. Samples with more than 10% hydrocarbons may explode when injected into this environment

Sample Pretreatment

The sample must be sparged prior to injection to remove the IC.

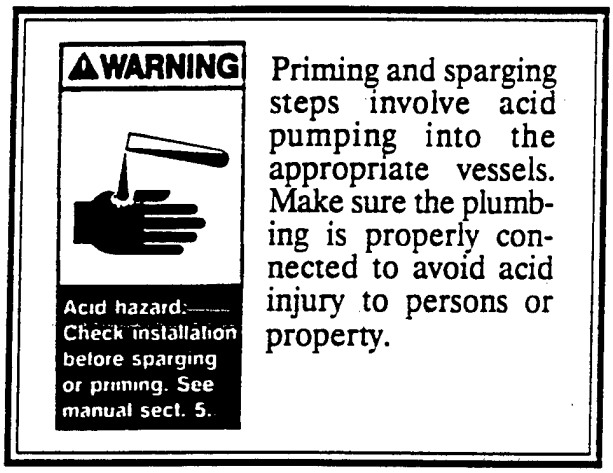
To sparge the sample:

- Pour about 10 mL of sample into a 20 mL vial (P/N 889-726).
- Screw the vial into Sparger A or Sparger B.
- Press **A** or **B**, and then **1** to start sparging.
- The sample will be automatically acidified. Each unit of "Add acid" is equivalent to 100 ul.
- Sparging will stop automatically at the end of sparge time.
- Remove the vial and cap it until the analysis is run.

Two samples can be sparged simultaneously.

Samples containing large particulates (> 0.5 mm) must be pretreated as directed in Section 10.2.

POC



Injection Technique

As soon as the INJECT light comes on, inject the sample into the POC sparger through the injection port.

When the analysis is over, withdraw the remaining sample from the sparger with the syringe.

Sample Pretreatment

None.

How to Fill the Syringe

Remove the plunger from the syringe and close the syringe valve and needle. Open the sample or standard container, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 10 ml.

This process of taking an aliquot destroys the validity of the liquid sample for future analysis. If there is only one sample container, the analyst should fill a second syringe at this time in case the first analysis is unsuccessful.

6.4 AUTOSAMPLER OPERATION

INTRODUCTION

The DC-190 Autosampler (ASM) option is designed for unattended operation for many hours. The sample tray holds 32 8 mL vials. Automatic acid addition and sparging are provided by the sparge tower to remove inorganic carbon for NPOC analysis. The sample probe may be rinsed with either water and/or sample between analyses. The ASM can handle samples with particulates up to 0.5 mm and the sample may be stirred with gas before the sample is drawn to insure uniform sampling. Cross-contamination is minimized by the use of non-wetting materials for all sample contacting parts. Sample vials may be marked as blanks or standards for automatic calibration of the system during the ASM run.

The ASM offers an autoranging capability which will adjust the sample volume to maintain the peak integral within the range of the detector. Since the dynamic range of the DC-190 system is very wide (10,000 to 1), activation of the autoranging will normally be a very rare event. When this feature is active, the DC-190 will check the first replicate of a vial in the ASM mode to verify that the peak integral is within range. If the peak integral is below range, the result will be printed, but ignored in future statistical calculations. The injection will then be repeated, but with a volume 5 times larger than the original injection. If the peak integral is over range, a similar procedure is followed with a volume one fifth the original volume. The volume adjustment will be repeated until the peak integral is within range. If an adjustment would result in a volume outside the 10 to 400 uL range, the volume will be set to either 10 or 400 uL as appropriate and no further adjustment will be made. The original injection volume will be restored at the beginning of the next sample vial. The accuracy of the autoranged data may suffer somewhat because the ASM was not calibrated with the new volume. The inaccuracy without autoranging is potentially much worse, however, than with autoranging. If desired, the results of autoranged data may be rechecked later.

Below is a table of expected and observed volumes for the ASM. These values are approximate and will vary from instrument to instrument. This volume variation only affects autoranged data. This will not apply to normal calibrated ASM data because the same volume is used for analysis.

VOLUME (uL)	
Expected	Observed
10	10.3
20	19.5
40	35.4
80	70
100	92
200	194
400	400

OPERATION

* Refer to DAILY START-UP in Section 6.1 to prepare the analyzer for operation.

* If it is desired to save the current operating parameters before making any changes, select a new Set-up number (see Section 6.8).

* Refer to Section 6.2 and select the analysis mode and volume desired. See Table 6.3 for guidelines to set the other operating parameters.

* Place the vials in the sample tray beginning with tray position 1. Refer to Table 6.4 and mark the vials as blanks, standards, or samples as appropriate. Mark the first empty tray position after the samples as indicated in Table 6.4 to terminate the run.

* Clean and fill the rinse bottle with DI water if water rinses were called for on the Rinse\stir menu.

* Check that the acid bottle is at least 1/3 full of acid solution if set up for NPOC analysis.

* Check that the printer is ready and has sufficient paper.

* Press **START**.

* There are two ways to end the run before completion. Press **STOP** to end the run after the current analysis. To terminate the run immediately, press **STOP** five times. After an immediate bail out, the ASM may have to be returned to its resting position. The sparge arm may be raised by selecting "Raise sparge arm" (**1**) on the "Sparge arm menu" (**MAIN 2 5 3 3**). The sample arm may be returned to the rinse bottle position by selecting "Move arm to rinse" (**4**) on the "Sample arm" menu (**MAIN 2 5 3 2**). Always check the "Furnace/IC ports" menu (**MAIN 2 5 5**) to be sure the inlet ports are shut (even if the indicator lights next to the ports are not lit).

TABLE 6.3
ASM OPERATION PARAMETER GUIDELINES

# of repeats	Select a number that is statistically comfortable. The allowed range is 1 - 5 repeats, with 3 being the default.
Sparge time (min)	The default time (3 minutes) should be satisfactory for almost all samples as long as the pH is in the proper range (see "Acid volume" below). This option is applicable to the NPOC mode only.
Acid volume	The pH must be adjusted to a value less than 4. It may be necessary to check a few samples after acid addition and make adjustments by trial and error until the acid addition matches the particular samples being analyzed. The default is 1 (each unit of acid volume is equivalent to 100 ul). This option is applicable to the NPOC mode only.

The following selections are on the "Rinse and /or stir" menu:

# of rinses w/water	This option specifies the number of times the ASM sample probe and loop will be rinsed with water between each vial.
# of rinses w/sample	Similar to the above option except that the ASM will rinse with sample before the first injection from each vial.
Sample stir time (sec)	Specifies the time that the sample will be stirred before the sample is drawn into the sample loop. The allowed range is 0 - 30 seconds (default = 0). In most applications, 15 seconds will provide effective stirring. Stirring is accomplished by bubbling gas out of the sample probe to suspend particulates and obtain a more uniform sample.
Auto-range	When set to "Yes", the DC-190 will automatically adjust the injection volume. "No" is the default setting. See the INTRODUCTION to this section for details on this feature.
CG off after	The default "No" means the carrier gas (CG) will not be turned off at the end of an ASM run. A "Yes" will cause the carrier gas to be turned off 10 minutes after the end of an ASM run. During this period, the red light in the **START/STOP** button will blink as if the run is still in progress.

TABLE 6.4
ASM VIAL MARKERS

VIAL	PEG POSITION		INDICATION
	INNER*	OUTER**	
No	No	No	Skip Position
Yes	No	No	Sample
Yes	Yes	No	Blank
Yes	No	Yes	Standard
Yes	Yes	Yes	Rinse Sample***
No	No	Yes	Terminate Run

* Peg hole closer to center of sample tray.

** Peg hole closer to sample vial.

*** Sample is used for rinse only (no analysis).

NOTE: If the printer runs out of paper or jams during a run "Print last run" (**MAIN 2 3**) will reprint the run data from a buffer. This allows data otherwise lost to be retreived. The buffer which retains the data is not large enough, however, to hold a complete run of data in all cases. This buffer has sufficient capacity to hold data from approximately 32 vials with 3 replicates per vial in modes where each replicate requires one line to print (TC, IC, or NPOC). In the TOC mode, each replicate requires three lines to print. In this mode, the buffer will only hold approximately 10 vials with 3 replicates per vial. The buffer is filled on a first in first out basis so that the data remaining at the end of the run will be the last data point back until the buffer is full.

6.5 OPERATION OF THE RSM OPTION

The RSM option allows the continuous sampling of a sample stream which is tapped to flow through the RSM sample cell. The ASM will perform the designated number of replicates on the sample stream and then wait for a designated time period. The sampling cycle is then repeated. The TC, IC, and TOC analysis modes may be performed using the RSM option. However, if the sample stream IC and TC levels are not constant, the accuracy of the TOC analysis may suffer due to the time lag between the IC and TC portions of the analysis.

* Adjust the sample flow rate to the sample cell by slowly opening the needle valve (counter clockwise) until the water level stabilizes slightly above the drain port of the sample cell.

* If it is desired to save the current operating parameters before making any changes, select a new Set-up number (see Section 6.8).

* Select **TC**, **IC**, or **TOC** (see Section 6.2 for selection guidelines) and then **RSM** to set the analysis mode. Verify that the operating parameters are set to the desired values. Use the guidelines in Table 6.5.

* Calibrate the DC-190 according to the RSM calibration procedure in Section 6.8.

* Press **START** to begin the analysis. The RSM will continue until manually stopped.

* To stop the analysis, press **STOP** (same button as **START**). This will stop the DC-190 at the end of an analysis in progress or immediately during the time between runs. To stop the run immediately during an analysis, press the **STOP** button 5 times.

TABLE 6.5
RSM OPERATING PARAMETER GUIDELINES

Sample volume	See Figure 6.1
# of repeats	Select a number that is statistically comfortable. The allowed range is 1 - 5 repeats with 3 being the default.
Time between runs	This is the time from the conclusion of the last replicate of a group to the beginning of the first replicate of the next group. The allowable range is 0 to 54 minutes with a default of 0 minutes.

6.6 OPERATION OF THE BOAT OPTION

Use the boat sampler for slurries, sludges, solids, and suspensions. Operate in either the **TC** or **NPOC** mode. Refer to "Installation and Operation of the 183 Boat Sampling Module" (P/N 915-240) for sample introduction instructions (Section V, Parts 5A and 5B). The DC-190 calculates ppmC from liquids or solids.

SAMPLE TYPE	SAMPLE INTRODUCTION	CONCENTRATION UNITS
Liquids, light slurries, suspensions	See 183 Instructions for **Liquids**	mg/L
Solids, heavy slurries	See 183 Instructions for **Solids**	ug/g

* If it is desired to save the current operating parameters before making any changes, select a new Set-up number (see Section 6.8).

* Press **BOAT TC** or **NPOC** .

* Press **1** until the appropriate units are displayed.

* Introduce the sample into the boat - see "Installation and Operation of the 183 Boat Sampling Module".

* Press **START** and follow the 183 instructions.

* If ug/g units are selected, enter the sample weight when asked - "Sample weight (mg)?".

* **SOLIDS ONLY:** Enter the sample weight when asked - "Sample weight (mg)?".

6.7 CALIBRATION

The DC-190 offers a choice of either one point or two point calibration. Two point calibration is equivalent to subtracting the blank value automatically. The DC-190 system always calculates a two point linear calibration. If only a single point calibration is desired, the System Blank may be set to 0 before updating the Calibration Factor. In this case the System Blank will remain 0 after updating the Calibration Factor resulting in a single point calibration. Since the system blank for IC is normally insignificant, its value is set to zero and IC analysis always has one point calibration. When two-point calibration is used, both calibration factor and system blank are recalculated each time either the calibration factor or system blank is updated. In TOC mode, the system uses TC value for calibration and blank update.

The DC-190 system provides a common calibration set (calibration factor and system blank) for SYRINGE, ASM, and RSM modes. POC and BOAT modes have their own calibration sets. When changing inlet mode from SYRINGE to ASM or RSM, calibration stays the same. When changing inlet mode from SYRINGE, ASM, or RSM to POC or Boat, calibration changes accordingly. The multiple set-up function (see Section 6.8) provides capability to store and retrieve up to 5 calibration sets.

Since SYRINGE and ASM/RSM calibrations are not necessarily the same, calibration for these modes should be done separately. Use the multiple set-up function to store the different calibration sets.

SUMMARY
1. System Blank 2. Calibrating Syringe, POC, or Boat Modes 3. Calibrating The ASM Mode 4. Calibrating The RSM Option 5. Omitting Outlier Data 6. Calibration Equations

SYSTEM BLANK

System blank is defined as the response contributed by the analyzer when carbon-free water sample is injected and analyzed. In reality, it is very difficult to produce and preserve the carbon-free water. Thus the true system blank and the carbon content of the water sample cannot be accurately distinguished. However, the carbon content of high purity water can be below the defection limit (.2ppmC) and the response with such water may be assumed as the system blank. When it exists, the blank value is subtracted from every analysis except in IC mode where blank is always assumed to be zero.

The system blank becomes increasingly important for analyses below 10 mgC/L as shown :

MODE	VOLUME	TYPICAL BLANK (mgC/L)
TC NPOC	400 ul	.10 - .40
IC	400ul	0*
POC	10ml	0 - .03
BOAT	40ul	2.0 - 4.0

Factors affecting the blank :

- Cleanliness of syringes, spargers and IC chamber.
- Sample handling.
- Age and sample history of TC and boat combustion tubes.
- Dehumidifier temperature.

CALIBRATING THE SYRINGE, POC, or BOAT INLET MODES

See "SYSTEM BLANK" earlier in this section for guidelines to determine whether a two point calibration is needed for the samples to be analyzed.

* Analyze a standard in the analysis mode to be used. An average of at least two determinations is recommended. Respond **NO** to the prompt "Continue yes/no?" when satisfied with the results.

* Outlier data can be omitted at this point if desired. See the section "OMITTING OUTLIER DATA" at the end of this section for details on how to do this.

* Press **CALIBRATE** to review the calibration menu :

1. Calibration factor	1
2. System blank	0
3. Sample size	50
4. Std. concentration	1000
5. Update cal-factor	
6. Update system blank	
7. Other actions	

* Verify that the sample size and standard concentration shown on the "Calibration" menu are correct. If a one point calibration (no subtraction of the blank) is desired, make sure the System Blank is set to 0. Make any necessary changes.

* Press **5** to update the Calibration Factor. The new calibration factor will be calculated and displayed on the menu.

* To complete a two point calibration, if desired, repeat the above procedure with a blank sample. Use the cleanest reagent water available (less than 0.150 mgC/L). Press **6** to update the System Blank.

* The DC-190 is now calibrated for the selected analysis mode.

Analyze a check standard with each sample set. If the reported value deviates from the expected value by more than 2%, re-calibrate the system.

Note To Boat Users: It is easy to use a liquid standard to calibrate the DC-190 even when using "ug/g" units to analyze solid samples. For example, to obtain 10 mg of sample, simply inject 10 ul of standard. This relationship holds as long as the density of the standard is 1 g/mL, which will be true for most water-based standards.

CALIBRATING THE ASM INLET MODE

* Select the ASM operating paramaters as described in Section 6.4 and press **START** to begin analyzing the standard.

* Place the vials of standard in the first tray positions. It is recommended that two vials of standard be placed next to each other at the beginning of the ASM sample tray. Place a peg in the outer hole next to the second vial to mark it as a standard for calibration (see Table 6.4).

* If blanks are to be determined, place two or three vials of blank immediately following the vials of standard. In most circumstances, two vials are sufficient. For best accuracy at low levels, three vials are recommended. Place a peg in the inner hole next to the last of the two or three blank vials to instruct the DC-190 to determine a new blank value (see Table 6.4).

* Press **CALIBRATE** to review the calibration menu:

1. Calibration factor	1
2. System blank	0
3. Sample size	50
4. Std. concentration	1000
5. Update cal-factor	
6. Update system blank	
7. Other actions	

* Verify that the sample size and standard concentration shown on the "Calibration" menu are correct. If a one point calibration (no subtraction of the blank) is desired. make sure the System Blank is set to 0. Make any necessary changes.

* Place the sample vials in the sample tray following the standard and blank vials, and run the analysis according to the operation instructions in Section 6.4. The DC-190 will automatically calculate and use the calibration factor and blank value.

CALIBRATING THE RSM OPTION

The RSM mode is easiest to calibrate using a vial of the desired standard rather than by pumping the standard through the RSM sample cell. This method is described in the following steps:

* Lift the sample cell from its holder and secure it in the clip located to the left of the black cell holder.

* Place an ASM vial (P/N 080-140) containing the standard solution into the black cell holder.

* Select the RSM operating paramaters as described in Section 6.5 and press **START** to begin analyzing the standard.

* Since the RSM does not stop automatically, it is necessary to manually stop it by pressing **STOP** (the same button as **START**) during the last desired replicate of the standard. The DC-190 will then stop at the end of the current analysis.

* Outlier data can be omitted at this point if desired. See the Section "OMITTING OUTLIER DATA" at the end of this Section for details on how to do this.

* Press **CALIBRATE** to review the calibration menu:

1. Calibration factor	1
2. System blank	0
3. Sample size	50
4. Std. concentration	1000
5. Update cal-factor	
6. Update system blank	
7. Other actions	

* Verify that the sample size and standard concentration shown on the "Calibration" menu are correct. If subtraction of the blank is not desired, make sure the System Blank is set to 0. Make any necessary changes.

* Press **5** "Update cal factor" to calculate and store a new calibration factor.

* Repeat the above procedure with a blank sample and press **6** "Update system blank" on the "Calibration" menu if an update of the system blank is desired.

OMITTING OUTLIER DATA

The DC-190 provides the ability to reject outlier data when operated in the manual modes (Syringe, Boat, and POC) and the RSM mode (no provision for outlier rejection is made in the ASM mode). A new average and standard deviation are calculated after the data is rejected. This feature saves having to re-run a data set due to a bad data point when updating the Calibration Factor or System Blank. The DC-190 will not allow the number of replicates to be reduced to less than 2 as a result of data rejection. Data rejection is accomplished by the following steps:

* Complete the run by responding **NO** in one of the manual modes or **STOP** in the RSM mode (see the calibration instructions for the mode in use) to the prompt at the end of the analysis. Three or more replicates must have been generated.

* Select the "Auxiliary functions" menu (**MAIN 2**) and press **1** "Omit an outlier".

* At the prompt, enter the number of replicates to reject. Each replicate to be rejected will be prompted for separately. Enter a replicate number after each prompt.

* New statistics will be displayed on the screen and printer. An update of the Calibration Factor or System Blank will now be based on the new average value.

* If the "Omit an outlier" menu item is selected again after the current data set has been edited, the DC-190 will start the data rejection over and ignore the previous data editing.

CALIBRATION EQUATIONS

The following equations are used in the DC-190 system.

The equation for determining a calibrated result is:

$$y = (Fx - b) / V$$

where:
- y = Concentration (calibrated) of sample.
- x = NDIR peak with background subtracted. Normally invisible to the user. The displayed value, y, may be made to equal x by setting F, b, and V to the appropriate values (1, 0, and 1, respectively)
- F = "Calibration Factor". This is the slope of the linear fit line.
- b = Intercept. This is an internal parameter which is invisible to the user.
- SB = "System Blank" = b/V.
- V = Sample volume (or mass).

The quantities F and SB are the ones displayed on the calibration menu and are the ones which can be edited directly.

The Calibration Factor and Blank are calculated by:

$$F_n = F_o (C_s / y_s)$$

$$b_n = b_o (F_n / F_o)$$

where:
- C_s = Concentration of the standard.
- o = Old value.
- n = New value.
- s = Value for Standard.

These are the equations used internally by the DC-190 system. Both Fn and bn are re-calculated each time either the Calibration Factor or the System Blank is updated. It should be noted that if the old value bo is already 0, the new value bn and therefore SB will also be 0. This provides a means to have the system effectively do a one point calibration update when it calculates a new Calibration Factor. These equations may also be used to manually calculate the values and enter them on the "Calibration" menu directly.

6.8 USING THE MULTIPLE PARAMETER SETS

The DC-190 provides the capability to store 5 complete sets of operating parameters. This capability allows the user to return to a previously defined set of operating parameters without having to re-enter the parameters. The parameter set includes the inlet mode, the analysis mode, the parameters appropriate to the analysis/inlet mode as well as the Calibration Factor and System Blank..

One of the parameter sets is always the "working" set-up. This is the parameter set associated with the current set-up number. Any run started will now use the parameter values currently contained in the working parameter set. As changes are made to the operating parameters, these changes are made to the working set-up.

When a new set-up number is selected, the parameter values in the previous set-up are saved as they were at the time of the new selection. The working parameter set now takes the values associated with the new set-up number. Any run started will use the new parameter values and any parameter changes are now made to the new parameter set.

Returning to the previous set-up number will restore the operating parameters to the state they were in when the set-up number was last used.

If it is desired to save the current set of parameter values for future re-use, a new set-up number should be selected before starting to define a new parameter set.

To determine the set-up number: Display the "System status" menu (**MAIN** 1) . Line 5 "Analysis set-up" indicates the current Set-up number.

To change to another set-up number: Select the "System status" menu (**MAIN** 1) and then "Analysis set-up" (**5**) and enter the new Set-up number. This saves the current parameter set.

To print the current parameter set:	Press the analysis mode button with the lit LED and then select the "Print set-up" option on the displayed operating parameter menu.
To print all the parameter sets:	Display the "System status" menu (**MAIN** 1). Press 6 "Print set-up selections".

USING THE CLIPBOARD

A clipboard is provided in the DC-190 system which allows the Calibration Factor and System Blank to be copied from one parameter set to another. This feature can save time and effort when changing from parameter set to another after the system has been calibrated. Use the following steps:

* Select the "Other actions" section of the "Calibration" menu (**CALIBRATE 7**).

* Verify that the "Analysis set-up" shown on line 4 is the one from which to copy the calibration factors. If not, select **4** "Analysis set-up" and enter the desired set-up number.

* Select **2** to save the calibration factors.

* Enter the number of the new parameter set on line 4 and select **3** to copy the calibration factors.

The new parameter set now contains the same Calibration Factor and System Blank as the one copied.

DC-190 Operation Guide

DAILY START-UP

1. Gas @ 30 Psig.

2. Check that the acid bottle is 1/3 full.

3. Confirm that the IC chamber is 1/2 full **(gas off)**

4. Fill IC chamber by using the prime acid function.

5. Press **CARRIER** Check that gas is flowing in IC chamber.

6. Ensure there is water in the dehumidifier.

7. Observe green lights on carrier & furnace.

8. Check for: flow rate 180-220cc/min, dehumidifier temp. 0-10°C, and furnace temp. 680°C. (Most applications)

9. Confirm or change Set-up number on display. **(Section 6.8)**

10. Check analysis and inlet mode.

11. Print Set-up.

12. If using the Boat, connect Teflon tubing to inlet part of dehumidifier. **(Fig. 4.15)**

13. If using ASM, clean the rinse bottle and fill it with acidified DI water. **(Few Drops of H_3PO_4)**

14. Observe for stable baseline **(Peak to Peak <.2mV)** before starting analysis.

DAILY SHUT-DOWN

1. Check that system is not in the **RUN** mode.

2. Push **CARRIER** to turn off gas.

3. Leave furnace at operating temperature. **(Normally 680°C)**

4. Disconnect the Teflon tubing from the dehumidifier to boat at the boat inlet.

5. For total shut down turn **OFF** main power switch in the rear.

OPER. & CAL

1. Select analysis mode **(Table 6.1)**

2. Select inlet mode **(Table 6.2)**

3. Confirm or change volume. **(Fig. 6.1)**

4. For **CALIBRATION**, press **CAL** to confirm or change concentration. **(Section 6.7)**

5. For manual injection, see **Section 6.3** for injection technique.

6. For ASM, confirm or change other parameters. **(Table 6.3)**

7. Refer to **Table 6.3** for ASM vial markers.

8. For RSM, see **Section 6.5** .

9. To complete **CALIBRATION**, see **Section 6.7.**

MAINTENANCE

Daily checks:
1. Printer paper
2. Gas supplies
3. IC chamber 1/2 full & acidified
4. Water in dehumidifier tube
5. Acid bottle 1/3 full
6. Gas flow 180-220cc/min
7. Temp. at set point
8. Dehumidifier temp 0-10°C

Weekly checks:
1. Daily checks plus
2. Replace septum in POC sparger every 40 injections.
3. Inspect TC inlet valve
4. Inspect combustion tube. Wipe inside area near top with wet Q-tips if necessary.
5. Inspect IC inlet valve
6. Clean IC reactor
7. Drain dehumidifier water & replace with acidified water. Flush several times if necessary.

Monthly checks:
1. Daily & weekly and/or:
2. Inspect & replace LiOH if necessary.
3. After ~ 160 hrs of operation, rinse catalyst, and combustion tube, replace silver wool **(Section 7.1)**. Condition catalyst at 900°C for 1/2 hr with DI injections.
4. Inspect O-rings in TC inlet and bottom connector. Replace if necessary.

DO'S & DONT'S

1. **DO** Check the bottom connector when checking the combustion tube.

2. **DO** Use a Soap Film Bubble meter to check output gas flow rates.

3. **DO** leave furnace at 680°C except for long term shut down.

4. **DO** Condition new catalyst. 100ul of water every 5 min. for 2 hours at 900°C.

5. **DON'T** use Pyrex wool in the combustion tube.

6. **DO** clean combustion tube weekly if used heavily. DI injections @ 900°C for 1/2 hrs. Use good water–should stabilize at 1 to 3ppm or better.

7. **DO** check valve seal & O-rings monthly when inspecting TC & IC ports.

8. **DO** re-align TC & IC ports with ASM probe after inspections.

9. **DO** study flow diagram **Figs 8-1 & 8.2.**

10. **DO** acidify ASM rinse bottle

11. **DON'T** use ASM stirring time > 30 sec.

12. **DO** inject acidified water daily into TC port if non-acidified samples are analyzed. (3, 100ul inj. of pH1, HCl or HNO_3)

13. **DO** rinse **(section 7.1)** and condition catalyst **(section 5.3)** when catalyst is contaminated.

14. **DON'T** raise drain line higher than 1 1/2" above lab bench.

SECTION 10
STANDARDS PREPARATION AND SAMPLE HANDLING

10.1 STANDARDS PREPARATION

REAGENT WATER

Use:

Standards preparation, system blanks, sample dilution, cleaning, etc.

Requirements:

Deionized or distilled.

ASTM Type II reagent water or equivalent.

TOC level: Less than 0.2 mgC/L.

ACID SOLUTION

Use:

Automatic acid feed for IC chamber, sparge stations, autosampler.

Requirements:

Reagent water.

Phosphoric (H_3PO_4), sulfuric (H_2SO_4), or nitric (HNO_3) acid, concentrated, reagent grade.

Do not use hydrochloric acid (HCl).

Preparation:

Final volume: 100 ml.

20% Phosphoric Acid Solution:

Add 20 ml acid to 80 ml reagent water. Transfer to the acid bottle (4 oz borosilicate with open top screw cap).

If phosphoric acid is not available, 10% sulfuric acid or 5% nitric acid can be substituted.

Replace monthly.

TC and IC STOCK SOLUTIONS

Use:

Dilute to appropriate concentration for calibration or system check-out.

Requirements:

Reagent water.

Reagent-grade concentrated acid (H_3PO_4 or H_2SO_4) for TC stock only.

Standard compounds are reagent-grade, and must be dried to a constant weight. (See the table in the next page.)

Preparation:

Final volume: 100 mL.

Standard compound choice:
For system performance check and troubleshooting purposes, use a compound listed below. For routine analyses, use one of these, or any compound which might be more appropriate for your application.

Weigh the specified amount of the compound into a 100 ml volumetric flask. Add about 75 ml reagent water to dissolve the compound. Add about 0.1 ml acid to TC solutions to adjust pH below 3. Then fill to the mark.

Store stock solutions in amber borosilicate bottles with Teflon-lined closures at $4^{o}C$.

Replace monthly.

TC STOCK SOLUTIONS (Choose one):

Compound	Weight (g/100mL)	Concentration	Add Acid?
KHP ($C_8H_5KO_4$)	2.126	10,000 mgC/L	Yes
Sucrose ($C_{12}H_{22}O_{11}$)	2.375	10,000 mgC/L	Yes

IC STOCK SOLUTIONS (Choose one):

Compound	Weight (g/100mL)	Concentration	Add Acid?
Na_2CO_3 (Anhydrous)	0.883	1,000 mgC/L	No
$NaHCO_3$	0.699	1,000 mgC/L	No

Use this formula to determine the weight required to make 100 ml stock solutions using other compounds:

$$\text{g Compound} = \frac{\text{mw x \%C}}{\text{N x 12.01}}$$

where:

mw	=	molecular weight of compound
%C	=	concentration of standard in % carbon
N	=	number of carbon atoms per molecule
12.01	=	atomic weight of carbon

For example

For a 1% (10,000 mgC/L) solution of sucrose (mw = 342.29):

$$\frac{342.29 \text{ x } 1\%}{12 \text{ x } 12.01} = 2.375 \text{ g.}$$

TC and IC
WORKING STANDARDS

Use:

Calibration or system check-out.
Choose the standard concentration to match the working range of your samples.

Requirements:

Reagent water.
Clean volumetric flasks and volumetric pipets.

Preparation:

Final volume: Depends on concentrations.

Use larger volumes as concentration decreases. Make 1 liter volume at 10 mgC/L. Do not make final volume smaller than 100 ml.

TC solutions only: Maintain at pH 3 or lower.

Store standard solutions in amber borosilicate bottles with Teflon-lined closures at $4^{o}C$. **Minimize exposure to atmosphere.**

Bottle volume: Between 100 - 200 mL, depending upon the concentration.

Replace weekly.

System Performance Check: (Initial Start-Up)

Make 100 ml of 1000 mgC/L TC standard and 100 ml of 100 mgC/L IC standard.

POC STANDARD

Use:

Calibrate POC sparger.

Requirements:

Very clean 1 liter volumetric flask.

Reagent water.

Stir plate and Teflon coated stirbar.

Reagent grade compound.

Preparation:

Final volume: 1000 ml.

Compound Choice:

Benzene or chloroform is strongly recommended. Other compounds can be used if reliable results can be demonstrated. Use only benzene or chloroform for system performance check and troubleshooting.

WARNING!

BENZENE	DANGER! Extremely flammable. Suspected human carcinogen. Harmful if swallowed, inhaled or absorded through the skin. May affect the blood system.
CHLOROFORM	Warning! Suspected human carcinogen. Harmful if inhaled or swallowed. Skin and eye irritant and may produce toxic vapors if burned.

Please consult material safety data sheets for more precautions regarding these compounds.

Fill the 1 liter flask to the mark with reagent water. Add the stir bar and gently agitate water on stirplate for 1 - 2 minutes to degas. Inject a microliter quantity of the compound. Use the table or formula in the following page to determine the proper quantity to inject. The syringe needle should be well immersed in the water. Cap the flask and gently agitate the solution until it comes to equilibrium (approximately 5 minutes).

COMPOUND	VOLUME TO INJECT	CONCENTRATION
Benzene (C_6H_6)	12 ul	9.92 mgC/L
Chloroforom ($CHCl_3$)	67 ul	9.72 mgC/L

To make other concentrations or standards, use this formula:

$$\textbf{Concentration of POC Standard } C = \frac{V \times D \times F}{L}$$

where:

C = Concentration of standard (mgC/L)
V = Microliters of POC solvent injected
D = Density of POC solvent (mg/ul)
F = Fraction of carbon per molecule by weight
L = Volume in liters of water

10.2 SAMPLE HANDLING

Good laboratory practice is important in obtaining reliable analysis for carbon content of samples. Since carbon is everywhere in nature, it is very easy to contaminate a sample. Follow these guidelines for sample handling during collection, pretreatment, and analysis.

Syringe Handling:

Dedicate a syringe to a particular carbon range. When the syringe gets contaminated (indicated by sample or standard not completely wetting the inner barrel), draw chromic acid into the syringe a few times, then rinse well with reagent water.

Sample Bottles:

It is preferable to store and collect samples in glass containers. Plastic bottles should only be used if it is established that the specific type of container to be used does not contribute contaminating organics.

The sample collection bottles should be cleaned well before collecting the sample. The amount of cleaning necessary is dependent on the expected concentration of carbon in the sample. As a rule of thumb, the following levels are suggested:

*** Greater than 100 mgC/L**

- Wash bottle in hot, soapy water.
- Rinse with clean water.
- Plastic cap may be used, but try to use Teflon-lined cap.
- Analyze samples within 2 weeks.
- Treat standard bottles and sparge vials the same way.

*** Less than 100 mgC/L**

- Use amber bottle.
- Wash in hot, soapy water.
- Rinse with clean water.
- Swirl with chromic/sulfuric acid cleaning solution.
- Rinse with reagent water.
- Use Teflon-lined cap.
- Store sample at $4^{o}C$.
- Analyze within two weeks.
- Treat standard bottles and sparge vials the same way.

Sample Pretreatment:

If a sample contains particulates larger than 0.5 mm or insoluble matter, homogenize with a blender or tissuemizer until the average particle size is less than 0.5 mm. Analyze these samples with the micropipettor or autosampler.

If the average particle size cannot be reduced to below 0.5 mm by homogenizing, dilute the sample with reagent water and blend again, or analyze the sample using the boat sampler.

*** Below 100 mgC/L:**

Minimize the sample handling and the blend time in order to minimize contamination and loss of volatiles. Analyze a blank with the same pretreatment as a sample.

Appendix A-19

Explosives: AP-0062

AP-0062
Extraction, Preparation, and Analysis of Explosives and Their Degradation Products by HPLC

1.0 PURPOSE

This procedure is a method of determination for the identification and quantitation of nitroaromatics and nitroamines using High Performance Liquid Chromatography (HPLC).

2.0 SCOPE

This procedure applies to water, compost, compost leachate, soil, sediment, gravel, and plant samples. The following analytes (listed with their abbreviations as used in this document) can be identified and quantified with this procedure.

2,6-Diamino-4-nitrotoluene----------2,6-DANT
1,3,5-Trinitroso-1,3,5-triazacyclohexane----------Tri-RDX
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine-----HMX
2,4-Diamino-6-nitrotoluene----------2,4-DANT
1-Nitroso-3,5-dinitro-1,3,5-triazacyclohexane--------Mono-RDX
Hexahydro-1,3,5-trinitro-1,3,5-triazine----------RDX
1,3,5-Trinitrobenzene----------TNB
1,3-Dinitrobenzene----------1,3-DNB
3,5-Dinitroaniline----------3,5-DNA
2,4,6-Trinitrotoluene----------TNT
2-Amino-4,6-dinitrotoluene----------2-ADNT
4-Amino-2,6-dinitrotoluene----------4-ADNT
2,6-Dinitrotoluene----------2,6-DNT
2,4-Dinitrotoluene----------2,4-DNT
4,4',6,6'-Tetranitro-2,2'-azoxytoluene----------TN-2,2'-AZT
2,4',6,6'-Tetranitro-2',4-azoxytoluene----------TN-2',4-AZT
2,2',6,6',Tetranitro-4,4'-azoxytoluene----------TN-4,4'-AZT
2,2'-Dinitro-4,4'-azoxytoluene----------DN-4,4'-AZT

3.0 SUMMARY

Samples can be prepared for analysis with no prior extraction or concentration, or can be extracted and concentrated before analysis preparation. Sample extraction and concentration methods may also serve to remove substances which would interfere with analyte identification or quantitation. The resulting prepared sample is injection ready for HPLC analysis. Nitroaromatics and nitroamines in the prepared sample are chromatographically separated as they pass through a HPLC analytical

column. The nitroaromatic and nitroamine compounds are identified by comparing their retention times and UV spectra, generated on a photodiode array detector using commercial chromatography workstation software, with those of known standard compounds generated under similar conditions. The compounds are quantified by comparing their peak heights, generated on a single wavelength UV/VIS detector, with compound-specific calibration curves generated under identical conditions.

4.0 REFERENCES

4.1 "Method 8330 - Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)." EPA Test Methods for Evaluating Solid Waste (SW-846), November 1992

4.2 Personal communications with Dr. Thomas Jenkins
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, NH

4.3 Personal communications with Philip G. Thorne
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, NH

4.4 Thorne, Philip G. "Hydrolytic Release of Bound Residues From Composted TNT-Contaminated Soil." 1996

4.5 Personal communications with Dr. Steve Larson
U.S. Army Corps of Engineers Waterways Experiment Station, Environmental Laboratory, Environmental Chemistry Branch

4.6 GLP-0018, "Method Detection Limits", Environmental Applications, Tennessee Valley Authority, Muscle Shoals, AL

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the Supervisor of the Environmental Applications section, or his designee, to ensure that this procedure is followed during the handling, preparation, extraction and analysis of all samples for nitroaromatics and nitroamines by HPLC.

5.2 The Laboratory Group Leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure. Training of personnel inexperienced with this procedure shall be carried out by experienced personnel under the supervision of the Laboratory Group Leader.

5.3 The analyst shall follow this procedure and report any abnormal results or problems to the Laboratory Group Leader, or his designee.

6.0 REQUIREMENTS

6.1 Prerequisites

Method detection limits shall be determined as in GLP0018 (see Note 9.1)

6.2 Limitations and Actions

None

6.3. Materials/Apparatus/Equipment

6.3.1 HPLC system composed of a tertiary pump (Varian Model 9012 or equivalent), an autosampler (Varian Model 9300 or equivalent) and a single wavelength UV/Vis detector (Varian Model 9050 or equivalent) or a photodiode array detector (Varian Model 9065 or equivalent).

6.3.2 HPLC guard column - Ultracarb ODS (20), 30 X 4.6 mm, manufactured by Phenomenex - (or equivalent).

6.3.3 HPLC analytical column - Ultracarb ODS (20), 250 X 4.6 mm, manufactured by Phenomenex - (or equivalent).

6.3.4 Tissue homogenizer - Omni Mixer ES, manufactured by Omni International (or equivalent).

6.3.5 25 mm sawtooth generator probe for use with tissue homogenizer - Part # 15035, manufactured by Omni International (or equivalent).

6.3.6 Freeze Dryer - Model 77520 (6L-Benchtop), manufactured by Labconco - (or equivalent).

6.3.7 Sonicator bath - Bransonic 52, manufactured by Bransom of Smith/Kline (or equivalent).

6.3.8 Temperature controlled circulating bath - Model 2095 Bath and Circulator, manufactured by Forma Scientific - (or equivalent).

6.3.9 300 ml size freeze dry flask with rubber top and glass adapter - Assembly # 75406, manufactured by Labconco - (or equivalent).

6.3.10 Glass Class A volumetric pipets (various sizes).

6.3.11 Glass graduated cylinders (various sizes).

6.3.12 Glass Class A volumetric flasks (various sizes).

6.3.13 Glass separatory funnels 125 ml and 250 ml size.

6.3.14 Stainless steel spatulas.

6.3.15 Teflon coated stir bars (various sizes).

6.3.16 Heavy duty aluminum foil - Part # 0-10900, manufactured by Reynolds Aluminum Co. - (or equivalent).

6.3.17 12-port vacuum manifold - Cat. # 5-7030, manufactured by Supelco Inc - (or equivalent).

6.3.18 Sep-Pak Vac Adapters - Part # WAT054260, manufactured by Waters Corp. - (or equivalent).

6.3.19 60 ml Sep-Pak reservoir - Part # WAT024659, manufactured by Waters Corp. - (or equivalent).

6.3.20 Explosion-proof refrigerator - Model Cryo-Fridge, manufactured by Scientific Products Inc. - (or equivalent).

6.3.21 8ml and 16 ml glass vials with Teflon lined closures - Cat # 75008-SB and 75016-SB respectively, manufactured by Scientific Resources Inc. (SRI) - (or equivalent).

6.3.22 12 X 32 amber autosampler vials with Teflon lined closures - Cat. # 99575-A - (or equivalent).

6.3.23 250 ml tall form, wide mouth glass bottle with Teflon lined closures - Part # 131-08C/TL/WS, manufactured by Eagle Picher - (or equivalent).

6.3.24 60 ml pre-cleaned amber bottle with Teflon lined closure - Part # 120-02A, manufactured by Eagle Picher - (or equivalent).

6.3.25 40 ml vial with Teflon lined closure - Part # 141-40A, manufactured by Eagle Picher - (or equivalent).

6.3.26 10 ml disposable plastic syringe - Part # 309604, manufactured by Becton and Dickinson - (or equivalent).

6.3.27 25 mm, PTFE syringe filters having 0.2 or 0.45 μm pore size - Cat. # 42225-NP and 44525-PC respectively, manufactured by SRI - (or equivalent).

6.3.28 Alumina-A solid phase extraction cartridges 1, 5, and 10 gram sizes - Part # WAT054580, WAT054670 and WAT054710 respectively, manufactured by Waters Corp. - (or equivalent).

6.3.29 Porapak-Rdx solid phase extraction cartridge (500mg size) - Part # WAT047220, manufactured by Waters Corp. - (or equivalent).

6.3.30 Vacuum manifold for solid phase extraction cartridges - Cat. # 5-7030, manufactured by Supelco Inc. - (or equivalent).

6.3.31 Refrigerated centrifuge - Model CRU-5000, manufactured by IEC Inc. - (or equivalent).

6.3.32 Benchtop centrifuge - Model SS-4 Manual, manufactured by Sorvall - (or equivalent).

6.3.33 Magnetic stirrer - Cat. # 14-511-1A, manufactured by Fisher Scientific Co. - (or equivalent).

6.3.34 Analytical balance - Model A200S, manufactured by Sartorius - (or equivalent).

6.3.35 Glass vacuum desiccator with indicating desiccant.

6.3.36 Ceramic mortar and pestle.

6.3.37 Glass conical bottom centrifuge tubes (12 ml size).

6.3.38 30 mesh sieve.

6.3.39 Pasteur pipets - Cat. # P5201-1, manufactured by Scientific Products - (or equivalent).

6.3.40 Parafilm "M" - Laboratory Film, manufactured by American National Can (or equivalent).

6.3.41 Ultrapure nitrogen - compressed gas.

6.4 Reagents and Standards

6.4.1 Water (HPLC grade) - Part # WX0004-1, manufactured by E M Science - (or equivalent).

6.4.2 Methanol, CH_3OH (HPLC grade) - Part # MX0488-1, manufactured by E M Science - (or equivalent).

6.4.3 Acetonitrile, CH_3CN (HPLC grade) - Part # AX0142-1, manufactured by E M Science - (or equivalent).

6.4.4 Sodium chloride, NaCl (reagent grade) - Part # SX0420-1, manufactured by E M Science - (or equivalent).

6.4.5 Calcium chloride, $CaCl_2$ (reagent grade) - Part # C1096, manufactured by Spectrum Chemical - (or equivalent).

6.4.6 Sodium phosphate dibasic, $Na_2HPO_4 \cdot 7H_2O$ (reagent grade) - Part # SX0175-1, manufactured by E M Science - (or equivalent).

6.4.7 Concentrated sulfuric acid, H_2SO_4 (reagent grade) - Part # 5557, manufactured by Mallinckrodt Inc. - (or equivalent).

6.4.8 Blank soil - U.S. Army Environmental Center Standard Soil.

6.4.9 Neat explosive analyte standards - either provided by the U.S. Army Environmental Center, or purchased from Accustandard Inc, Stanford Research Institute International or Chem Service Inc.

6.4.9.1 Stock Standard Solutions (single analyte)

Each neat solid analyte standard is dried to a constant weight in a vacuum dessicator at room temperature in the dark. Each neat liquid analyte standard is transferred using glass Pasteur pipets or glass gas-tight syringes with Teflon tipped plungers. Approximately 0.1 g (weighed to 0.0001 g) of a single neat analyte is placed into a 100 ml volumetric flask and diluted to volume with acetonitrile. A stir bar is added to the flask which is then placed on a magnetic stirrer and stirred until the analyte has totally dissolved or mixed. During mixing, the flask is covered with an aluminum foil hood. The stir bar is removed, the flask is stoppered and wrapped in aluminum foil. The concentration of the stock solution is calculated from the actual weight of the analyte used, the purity of the analyte and the volume of the solution (nominal

concentration is 1,000 mg/L). These solutions should be stored, stoppered and sealed with Parafilm, in an explosion-proof refrigerator at 4° C.

6.4.9.2 Intermediate Standard Solutions (single or multiple analyte)

These solutions, at approximately 20 µg/ml per analyte, are prepared by dilutions of the stock standard solutions with acetonitrile in volumetric flasks. The flasks are wrapped with aluminum foil and stored, stoppered and sealed with Parafilm, in an explosion-proof refrigerator at 4° C. These solutions are used to prepare calibration standards.

6.4.9.3 Calibration Standard Solutions (multiple analyte)

These solutions, at a minimum of five levels covering the concentration range of interest (approximately 6 µg/ml to approximately 25 ng/ml), are usually prepared by dilutions of the Intermediate standard solutions with acetonitrile in volumetric flasks. The flasks are wrapped with aluminum foil and stored, stoppered and sealed with Parafilm, in an explosion-proof refrigerator at 4°C. Before analysis, these solutions are equilibrated to room temperature, diluted 1:1 with water, allowed to stand for 20 minutes and passed through a 25 mm PTFE syringe filter with 0.45 µm pore size.

6.4.10 Aqueous explosives spike solution (8 component) at 2 µg/ml each analyte.

Spike made from Accustandard solution containing HMX, RDX, (1,3,5-TNB), (1,3-DNB), nitrobenzene, TNT, 2-ADNT and 2,4-DNT at 1000 µg/ml each analyte. The spike solution is prepared by first diluting 1.0 ml of the 1000 µg/ml standard to 25.0 ml with acetonitrile. A 5.0 ml aliquot of this solution is diluted to 100.0 ml with HPLC water to yield a solution whose concentration is 2.0 ug/ml per analyte.

6.4.11 Spike solution for use with compost leachate extraction

Solution(s) whose concentration is approximately 3 ug/ml per analyte for the following compounds: (2,6-DANT), HMX, (2,4-DANT), RDX, (1,3,5-TNB), TNT, 4-ADNT, 2-ADNT, (2,6-DNT) and 2,4-DNT. Solution matrix is acetonitrile.

6.4.12 Spike solution for use with plant extraction

Prepare a spiking solution at approximately 100 ug/ml per analyte for the following analytes: (2,6-DANT), HMX, (2,4-DANT), RDX, (1,3,5-TNB), TNT, 4-ADNT, 2-ADNT, (2,6-DNT) and 2,4-DNT. The mixed analyte solution matrix should be acetonitrile. The solution should be prepared

from stock standard solutions (section 6.4.9.1) and should be stored in an aluminum foil wrapped flask, stoppered and sealed with Parafilm in an explosion-proof refrigerator at 4° C.

6.4.13 Sulfuric acid solution (1+1)

In a suitable container which is sitting on ice, place a known volume of HPLC water, add to this slowly and with swirling an equal volume of concentrated sulfuric acid. Allow to equilibrate to room temperature before using.

6.4.14 Sodium phosphate dibasic at 1.07 M concentration

Place appropriate quantity of sodium phosphate dibasic heptahydrate in a glass beaker and place in a forced air oven at 35°C and leave for at least 24 hr. Remove from oven and allow to cool. For about 1 L of solution, weigh out 322 g of the dried compound and place in a large Erlenmeyer flask. Add 1000 mL of HPLC water to the flask. Add a stir bar and place on a magnetic stirrer / hot plate on low heat and moderate stirring until all solids are dissolved. Cool to less than 30°C before use. This should not be kept for use for more than 2 days.

6.4.15 Saturated aqueous sodium chloride solution

Weigh out 325 g of sodium chloride and place in a 1000 ml volumetric flask. Add about 950ml of HPLC water. Add a stir bar and place on magnetic stirrer until most of the salt has dissolved. Remove the stir bar from solution, use HPLC water to make solution to volume, then return the stir bar to the solution and stir for at least 30 minutes (salt will still be present in bottom of flask).

6.4.16 Aqueous calcium chloride solution

Weigh out 6.67 g of calcium chloride dihydrate and place in a 1000 ml volumetric flask. Make to volume with HPLC water, add a stir bar and place on a magnetic stirrer until all solids are dissolved.

6.4.17 Acetonitrile based explosives spike solution (8 components) at 2 ug/ml for each analyte.

Spike made from Accustandard solution containing HMX, RDX, (1,3,5-TNB), (1,3-DNB), nitrobenzene, TNT, 2-ADNT and 2,4-DNT at 1000 µg/ml each analyte. The spike solution is prepared by first diluting 1.0 ml of the 1000 µg/ml standard to 25.0 ml with acetonitrile. A 5.0 ml aliquot of

this solution is then diluted to 100.0 ml with more acetonitrile to yield a solution whose concentration is 2.0 ug/ml per analyte.

6.4.18 1:1 mixture of acetonitrile/calcium chloride.

Combine equal volumes of HPLC grade acetonitrile (step 6.4.3) and 5 g/L calcium chloride solution (step 6.4.16). Allow solution to equilibrate to room temperature before using.

6.5 Quality Control Sample Requirements

6.5.1 Every batch of samples (20 members or less) whose matrix is water, soil, compost, sediment, or gravel, shall have the following QA/QC samples extracted and/or prepared at the same time in identical fashion: matrix spike, matrix spike duplicate, method blank and laboratory control sample (LCS).

Every batch of samples (20 members or less) whose matrix is compost leachate shall have the following QA/QC samples extracted at the same time and in identical fashion: matrix spike, method blank and LCS.

Every batch of samples (20 members or less) whose matrix is plant tissue shall have the following QA/QC samples extracted at the same time and in identical fashion: matrix spike, LCS, and method blank.

6.5.2 Daily Calibration Check of the UV/VIS detector system.

Midpoint calibration standards for each analyte of interest are analyzed in duplicate at the beginning of the analytical run, singly after every 10 sample vials and singly after the last sample of the run. The calculated concentration of each analyte of interest in each midpoint standard throughout the analytical run shall agree with its known value within +/- 15%. If this criterion is not met, samples following the previous acceptable standard and prior to the next acceptable standard may be reanalyzed, or all or part of the sample data may be "qualified" and flagged with a "Q" designation in the database. The decision to reanalyze or qualify samples shall be made by the Laboratory Group Leader.

7.0 PROCEDURE

7.1 Calibration

Initial Calibration of the UV/VIS detector system.

From one to three injections of each calibration standard over the concentration range of interest are sequentially injected into the HPLC in random order. Using commercial chromatography software, peak heights are obtained for each analyte. Calibration curves are generated using spreadsheets which utilize linear regression equations of the form $y = mx$, $y = a + bx$, or $y = a + bx + cx^2$. Selection of the equation form to use is made by assessing the data for goodness of fit and how closely back-calculation of the fit data reproduces the known concentrations of the calibration solutions.

7.2 Procedure Instructions

NOTE: Because some of the analytes of interest in the following procedures are photosensitive and thermolabile, standards, samples, extracts, filtrates, eluants, etc. should be exposed to light or heat as little as possible during the performance of the procedures. This is especially true during standing or storage periods.

7.2.1 Preparation of water samples (with no preconcentration) for qualitative / quantitative analysis.

NOTE: Batches of samples undergoing this preparation shall contain the following QA/QC samples: matrix spike, matrix spike duplicate, LCS, and method blank.

7.2.1.1 Retrieve samples and allow them to equilibrate to room temperature if necessary.

7.2.1.2 Obtain the appropriate sample worksheet (Attachment 1 - "Preparation of Liquids for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be prepared for HPLC analysis, the date, analyst's name, the serial number and concentration of the spiking solution to be used.

Select one sample out of the batch for use in the creation of the matrix spike and matrix spike duplicate. Record the number of this sample in the appropriate area in the QC section of the worksheet.

7.2.1.3 If sample contains no solids, proceed to step 7.2.16. If sample contains solids, place appropriate volume of sample in a properly labeled, 40 ml vial and seal with a Teflon-lined closure.

7.2.1.4 Centrifuge the sample at 2000 rpm or greater for at least 15 minutes.

7.2.1.5 Decant the supernatant to a properly labeled, glass vial and seal with Teflon-lined closure.

7.2.1.6 Prepare the batch QA/QC samples as listed below. Record all critical data in the appropriate areas in the QC section of the sample worksheet.

Matrix spike and matrix spike duplicate - To a 10 ml volumetric flask, add 5.0 ml of selected sample, then add 1.0 ml of the aqueous spiking solution (see section 6.4.10). Make flask to volume with HPLC water, stopper and mix thoroughly by inversion. Store in dark until needed.

Laboratory control sample - To a 10 ml volumetric flask, add 5.0 ml of HPLC water, then add 1.0 ml of the aqueous spiking solution (see section 6.4.10). Make flask to volume with HPLC water, stopper and mix thoroughly by inversion. Store in dark until needed.

Method blank - To a 10 ml volumetric flask, add 10.0 ml of HPLC water, stopper the flask and mix thoroughly by inversion.

7.2.1.7 Using precisely measured volumes, place equal amounts of sample (regular and QA/QC) and HPLC grade acetonitrile (usually 2 ml of each component) in a glass vial, cap with a Teflon-lined closure and mix thoroughly by inversion.

7.2.1.8 Let mixture stand in dark at room temperature for 20 minutes.

7.2.1.9 Pass the mixture through a PTFE syringe filter with 0.45 μm pore size. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.1.10 Let the filtrate stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto the autosampler the same day they are

prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.1.11 If it becomes necessary during the analysis process to dilute the sample, record on the sample worksheet the aliquots and dilution volumes used.

7.2.2 **Preconcentration of water samples by Solid Phase Extraction (SPE) for qualitative/quantitative analysis by HPLC.**

NOTE: Batches of samples undergoing this extraction shall contain the following QA/QC samples: LCS and method blank

7.2.2.1 Retrieve the samples and allow them to equilibrate to room temperature.

7.2.2.2 Obtain the appropriate sample worksheet (Attachment 2 - "Preconcentration of Liquids by SPE for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be concentrated and prepared for HPLC analysis, the date, analyst's name, the serial number and concentration of the spiking solution to be used.

7.2.2.3 Prepare the batch QA/QC samples as listed below. Record all critical data in the appropriate areas in the QC section of the sample worksheet.

Laboratory control sample - To a 100 ml Erlenmeyer flask, add approximately 50 ml of HPLC water, then add 1.0 ml of the aqueous spiking solution (see section 6.4.10) and swirl to mix. Seal with Parafilm and let stand in dark until needed.

Method blank - To a 100 ml Erlenmeyer flask, add 50 ml of HPLC water. Seal with Parafilm and place in dark until needed.

7.2.2.4 If sample does not contain solids, proceed to step 7.2.2.6 (be sure to read NOTE before step 7.2.2.6). If sample contains solids, fractionate an appropriate volume of sample to 40 ml vials with Teflon lined closures and centrifuge for at least 15 minutes at 2000 rpm or greater.

7.2.2.5 Remove the supernatant and place in an Erlenmeyer flask, seal with Parafilm, and let stand in dark until needed. This supernatant is the sample fraction that will be concentrated by SPE.

NOTE: Do not allow the resin bed of the Porapak-Rdx cartridge to become dry during the conditioning step, between the conditioning and the sample loading steps or during the sample loading.

7.2.2.6 Attach an adapter and a 60 ml reservoir to a Porapak-Rdx cartridge (500 mg size) and connect the cartridge to the vacuum manifold. Condition the cartridge by passing 15 ml of acetonitrile through it (gravity flow after starting flow with vacuum), followed by 30 ml of water at a rate of approximately 10 ml/minute using vacuum.

NOTE: In the following step, if the extract from this procedure is to be used for analyte identification only, approximate sample volumes can be used (minimum of 60ml). If the extract is to be used for analyte quantitation, it is necessary to use a known volume aliquoted with an accurate measuring device, such as a graduated cylinder (rinse device three times with HPLC water and add this to reservoir for the appropriate sample).

7.2.2.7 Pass the appropriate volume of sample through the SPE cartridge at a flow rate of approximately 10 ml/min. Record this known or approximate volume on the worksheet.

7.2.2.8 After the sample has been totally pulled through the cartridge, continue to apply a vacuum to the cartridge for about 5 minutes to remove residual moisture.

7.2.2.9 Remove the SPE cartridge from the vacuum manifold and remove the adapter and 60 ml reservoir from the cartridge.

7.2.2.10 Position the SPE cartridge over a properly labeled 5 ml volumetric flask (other sizes of volumetric flasks can be used if deemed necessary) with the Luer tip of the cartridge extending into the mouth of the flask.

7.2.2.11 Add 5 ml of acetonitrile to the SPE cartridge.

7.2.2.12 Apply a lightly pressurized flow of ultrapure nitrogen to the top of the cartridge in order to initiate solvent flow through the cartridge and into the volumetric flask. Once the solvent flow begins, remove the nitrogen source and allow the solvent flow to be by gravity alone.

7.2.2.13 After the solvent stops dripping from the cartridge, reapply the pressurized nitrogen to the top of the cartridge to force any trapped solvent into the flask.

7.2.2.14 Make the flask to volume with acetonitrile, stopper and mix thoroughly. Record the eluant volume on the worksheet.

7.2.2.15 Using accurately measured volumes, place equal amounts of eluant and HPLC grade water (usually 2 ml of each component) in a glass vial, cap with a Teflon-lined closure and mix thoroughly by inversion.

7.2.2.16 Let the mixture stand in the dark at room temperature for 20 minutes.

7.2.2.17 Pass the mixture through a PTFE syringe filter with 0.45 µm pore size. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.2.18 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.3 **Preparation of soil or sediment samples for qualitative/quantitative analysis**

NOTE: Batches of samples undergoing this extraction/preparation shall contain the following QA/QC samples: matrix spike, matrix spike duplicate, LCS, and method blank.

7.2.3.1 Spread enough sample either onto acetonitrile rinsed ceramic dishes or clean aluminum foil for sample duplicates, matrix spikes, matrix spike duplicates, and percent moisture procedure.

7.2.3.2 Place the samples in the air flow of a darkened hood at room temperature and allow to dry for 12 - 18 hours (no visible moisture should be present).

7.2.3.3 Set aside enough air dried sample, for each regular sample, to perform a percent moisture determination as described in section 9.2 of this procedure. The start of this determination must be prompt so that sample moisture is not lost.

7.2.3.4 If the air dried sample is loose and free flowing without large clumps, no grinding will be required. But if the sample does contain large clumps, grind an appropriate quantity of sample in a dry, acetonitrile rinsed mortar. Place the sample (unground or ground) into a glass vial with Teflon-lined

closures. Store the sample in the dark at freezer temperatures (-10° C) until ready for use.

7.2.3.5 Obtain the appropriate sample worksheet (Attachment 3 - "Preparation of Solids for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be extracted and prepared for HPLC analysis, the date, analyst's name, the sample matrix, the serial number and concentration of the spiking solution to be used.

7.2.3.6 Select one sample out of the batch for use in the creation of the matrix spike and matrix spike duplicate. Record the laboratory number of this sample in the appropriate areas in the QC section of the sample worksheet.

7.2.3.7 Into a properly labeled 40 ml glass vial, weigh out 2 grams of air dried sample. Record the sample weight to the nearest 0.0001 g on the worksheet in the appropriate area.

7.2.3.8 Prepare the batch QA/QC samples as listed below. Record all critical data in the appropriate areas in the QC section of the sample worksheet.

Matrix spike and matrix spike duplicate - For each spiked sample, weigh into a properly labeled 40 ml glass vial, 2 grams of air dried sample. Record the weight to the nearest 0.0001 g. Add 1.0 ml of the organic spiking solution (see section 6.4.17) to the sample, evaporate the acetonitrile of the spike using a flow of ultra high purity nitrogen or the air flow of an operating hood. Then add 10.0 ml of acetonitrile to the vial. Recap the vial and vortex for 1 minute. Place vial in the dark until ready for step 7.2.3.10.

Laboratory control sample - Into a properly labeled 40 ml glass vial, weigh out 2 g of standard soil (see section 6.4.8). Record the weight to the nearest 0.0001 g. Add 1.0 ml of the organic spiking solution (see section 6.4.17) to the sample, evaporate the acetonitrile of the spike using a flow of ultra high purity nitrogen or the air flow of an operating hood. Then add 10.0 ml of acetonitrile to the vial. Recap the vial and vortex for 1 minute. Place vial in the dark until ready for step 7.2.3.10.

Method blank - Into a properly labeled 40 ml glass vial, weigh out 2 g of standard soil (see section 6.4.8). Record the weight to the nearest 0.0001 g. Add 10.0 ml of acetonitrile to the vial. Recap the vial and vortex for 1 minute. Place vial in the dark until ready for step 7.2.3.10.

7.2.3.9 To all regular samples (non-QA/QC samples), add 10.0 ml of HPLC grade acetonitrile to the vial, replace the Teflon-lined closure, and vortex for 1

minute. Record this volume on the worksheet in the appropriate area. Place vial in the dark until ready for next step.

7.2.3.10 Suspend the extraction vials (regular samples and QA/QC samples) in a sonicator bath regulated between 10° C and 15° C and sonicate under low light conditions for 18 hours. The water level in the sonicator should be above the solvent level in the sample bottles.

7.2.3.11 Remove the vials from the sonicator bath and let stand in the dark at room temperature for 30 - 60 minutes. This allows particulates to settle and a supernatant to form.

If, at the end of the standing period, particulates make pipetting impossible, it will be necessary to centrifuge the sample at 2000 rpm or greater for at least 15 minutes before proceeding to next step.

7.2.3.12 With a volumetric pipet, remove an appropriate quantity of supernatant and mix it at 1:1 ratio with the calcium chloride solution (see section 6.4.16). Let the mixture stand in the dark for 20 minutes.

7.2.3.13 Remove the supernatant from the sample (avoid the flocculated particulates on the bottom) and filter through a 0.2 µm Teflon syringe filter. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.3.14 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.4 **Preparation of gravel samples for qualitative/quantitative analysis**

NOTE: Batches of samples undergoing this extraction/preparation shall contain the following QA/QC samples: matrix spike, matrix spike duplicate, LCS, and method blank.

7.2.4.1 Spread enough sample either onto acetonitrile rinsed ceramic dishes or clean aluminum foil for sample duplicates, matrix spikes, matrix spike duplicates, and percent moisture procedure.

7.2.4.2 Place the samples in the air flow of a darkened hood at room temperature and allow to dry for 12 - 18 hours (no visible moisture should be present).

7.2.4.3 Set aside enough air dried sample, for each regular sample, to perform a percent moisture determination as described in section 9.2 of this procedure. The start of this determination must be prompt so that sample moisture is not lost.

7.2.4.4 Obtain the appropriate sample worksheet (Attachment 3 - "Preparation of Solids for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be prepared for HPLC analysis, the date, analyst's name, the sample matrix type the serial number and concentration of the spiking solution to be used.

Select one sample out of the batch for use in the creation of the matrix spike and matrix spike duplicate. Record the number of this sample in the appropriate area in the QC section of the worksheet.

7.2.4.5 Weigh enough air dried sample into a pre-cleaned, 250 ml, wide-mouth, tall-form bottle to reach the base of the bottle's neck (usually over 200 g). Record this weight on the worksheet in the appropriate area.

7.2.4.6 Prepare the batch QA/QC samples as listed below. Record all critical data in the appropriate areas in the QC section of the sample worksheet.

Matrix spike and matrix spike duplicate - For each spiked sample, weigh out into a properly labeled 250 ml bottle, enough air dried sample to reach the base of the bottle's neck and cap the bottle with a Teflon-lined closure. Record the weight to the nearest 0.1 g. Add 5.0 ml of the aqueous spiking solution (see section 6.4.10) to the sample, recap the bottle and shake for 1 minute, then let the sample stand in the dark for 1 hour. Then add 95.0 ml of acetonitrile to the vial. Recap the bottle tightly and shake vigorously for 1 minute. Place the bottle in the dark until ready for step 7.2.4.9.

Laboratory control sample - Into a properly labeled 250 ml bottle, pipet 5.0 ml of the aqueous spiking solution (see section 6.4.10), recap the bottle and shake for 1 minute, then let the bottle stand in the dark for 1 hour. Then add 95.0 ml of acetonitrile to the bottle. Recap the bottle tightly and shake vigorously for 1 minute. Place the bottle in the dark until ready for step 7.2.4.9.

Method blank - Into a properly labeled 250 ml bottle, place 100.0 ml of acetonitrile. Recap the bottle tightly and shake vigorously for 1 minute. Place the bottle in the dark until ready for step 7.2.4.9.

7.2.4.7 For any regular sample (non-QA/QC samples) add 100.0 ml of acetonitrile to the bottle and replace the cap, taking care to ensure a tight fit. Record this volume on the worksheet in the appropriate area.

7.2.4.8 Shake the bottle vigorously for one minute.

7.2.4.9 Place bottle in a sonicator bath regulated between 10° C and 15° C and sonicate for 18 hours. The water level in the sonicator should be even with the solvent level in the sample bottles, but should not be high enough to float the bottles or touch the lids of the sample bottles.

7.2.4.10 Remove the bottle from sonicator bath and shake vigorously for one minute.

7.2.4.11 Let the bottle stand in the dark and equilibrate to room temperature.

7.2.4.12 Mix, in a glass vial, an appropriate volume of the acetonitrile sample extract at a 1:1 ratio with a calcium chloride solution (see section 6.4.16) and let stand in the dark for 20 minutes.

7.2.4.13 Remove the supernatant from the calcium chloride treated sample (avoid the flocculated particulates on the bottom) and filter through a 0.2 μm Teflon syringe filter. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.4.14 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.5 **Preparation of compost leachate for qualitative/quantitative analysis**

NOTE: Batches of samples undergoing this extraction/preparation shall contain the following QA/QC samples: matrix spike, LCS, and method blank.

7.2.5.1 Prepare a sodium chloride solution as per section 6.4.15 of this procedure.

7.2.5.2 Retrieve the samples and allow to equilibrate to room temperature if necessary.

7.2.5.3 Obtain the appropriate sample worksheet (Attachment 4 - "Preparation of Compost Leachates for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be extracted and prepared for HPLC analysis, the date, analyst's name, the serial number and concentration of the spiking solution to be used.

Select one sample out of the batch for use in the creation of the matrix spike. Record the number of this sample in the appropriate area in the QC section of the worksheet.

7.2.5.4 Fractionate at least 40 ml of the leachate sample (80 ml of the sample selected for matrix spike) into 40 ml glass vials with Teflon lined closures. Centrifuge the vials for 30 minutes at 2000 rpm or greater. After centrifugation, decant the supernatant for each sample into a clean 40 ml vial(s).

7.2.5.5 For each sample add 12.56 g of sodium chloride to a 500 ml separatory funnel. Measure out 38 ml of sample (use HPLC water for the method blank and LCS) and transfer to the separatory funnel containing the salt. Record these weights and volumes on the worksheet in the appropriate areas.

7.2.5.6 To the matrix spike and LCS, add 1.0 ml of the appropriate spiking solution (see section 6.4.11). Record the critical data on the worksheet in the appropriate areas.

7.2.5.7 Stopper the separatory funnel and shake until all the salt has dissolved (about 5 minutes).

7.2.5.8 Using volumetric pipets, add 9.0 ml of acetonitrile to the separatory funnel of each sample which has been spiked and 10.0 ml of acetonitrile to the funnel of each unspiked sample.

7.2.5.9 Stopper the funnel and shake for 5 minutes, venting as needed to relieve pressure, then let the samples stand for 10 minutes to allow phases to separate.

7.2.5.10 Drain off the salt layer (bottom layer) except for the last 1-2 ml and discard properly. Drain the acetonitrile layer (top layer of approximately 1-2 ml) along with the remaining salt layer into a 250 ml separatory funnel.

7.2.5.11 Add 16 ml of HPLC grade acetonitrile to first separatory funnel and rinse the walls into the second separatory funnel.

7.2.5.12 Add 84 ml (measure with 100 ml graduated cylinder) of salt solution (see step 7.2.5.1) to the 250 ml separatory funnel.

7.2.5.13 Stopper the separatory funnel and shake for 5 minutes, then allow to stand for 10 minutes for phase separation.

7.2.5.14 Discard to waste most of the bottom layer (salt) and transfer the acetonitrile layer (top layer) plus the last 1-2 ml of the salt layer to a glass centrifuge tube. Rinse the separatory funnel with 1.0 ml of acetonitrile and transfer to the same centrifuge tube.

7.2.5.15 Centrifuge the extract for 10 minutes at 5000 rpm. Then remove the acetonitrile layer (top) and place in a 10 ml graduated cylinder. Measure the extract volume to the nearest 0.1 ml (should be 3-4 ml). Record this volume on the worksheet in the appropriate area.

7.2.5.16 Pipet 2 ml of the sample from the 10 ml graduated cylinder into a glass vial. Add 2 ml of calcium chloride solution (see section 6.4.16) to the vial, mix and let stand for 20 minutes.

7.2.5.17 Remove the supernatant from the calcium chloride treated sample (avoid the flocculated particulates on the bottom) and filter through a 0.2 μm Teflon syringe filter. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.5.18 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.6 Preparation of plant tissue for qualitative/quantitative HPLC analysis

Three separate extractions are performed on each vegetation sample: two with acetonitrile and one with sulfuric acid. The three extracts can then analyzed separately, or combined and analyzed as one sample. Total

concentrations of explosives and degradation products are calculated mathematically.

NOTE: Turn on the freeze dry unit (if it is not already running) and allow the temperature and vacuum to equilibrate to normal running levels during the performance of the following steps.

NOTE: Batches of samples undergoing this preparation shall contain the following QA/QC samples: matrix spike, LCS, and method blank.

7.2.6.1 Retrieve samples and allow to equilibrate to room temperature in the dark and out of air currents.

7.2.6.2 Obtain the appropriate sample worksheet (Attachment 5 - "Preparation of Plant Tissue for Explosives Analysis"). Record on the worksheet, the laboratory number of the samples to be prepared for HPLC analysis, the date, analyst's name, the serial number and concentration of the spiking solution to be used.

Select one sample out of the batch for use in the creation of the matrix spike. Record the number of this sample in the appropriate area in the QC section of the worksheet.

7.2.6.3 Set aside enough fresh plant tissue, for each regular sample, to perform a percent moisture determination as described in section 9.2 of this procedure. The start of this determination must be prompt so that sample moisture is not lost.

7.2.6.4 Rinse the outside of the plant tissue with deionized water, then gently blot excess moisture from the tissue using lab wipes.

NOTE: The amount of tissue used in step 7.2.6.5 will vary depending on the percent moisture of the plant. Use enough tissue to have 1.5 - 2.0 grams of tissue left after freeze drying.

7.2.6.5 Into a large plastic boat, weigh out 20 g of plant tissue (the tissue will have to be cut or torn into pieces) and record this weight on the sample worksheet.

7.2.6.6 Place the plant tissue in an acetonitrile rinsed ceramic mortar of appropriate size.

7.2.6.7 Add enough liquid nitrogen to the mortar to create a pool in the bottom about ½ inch deep. The nitrogen should be poured over the surface of the tissue to facilitate rapid freezing.

7.2.6.8 Using an acetonitrile rinsed ceramic pestle of appropriate size, gently crush and grind the frozen plant tissue until it reaches the consistency of a loosely flowing powder.

NOTE: Do not allow the plant tissue to warm enough during this step for liquid water to become visible in the mortar. Add more liquid nitrogen if necessary.

7.2.6.9 Using a powder funnel and a stainless steel spatula, quickly transfer the ground tissue from the mortar to a freeze dry flask (300 ml size).

7.2.6.10 Rinse any adhering tissue from the mortar into the freeze dry flask using small amounts of HPLC water from a squrit bottle.

7.2.6.11 With the tissue in the freeze dry flask, use the 25 mm sawtooth generator probe on the homogenizer to grind the plant tissue to a liquid consistency. Use the speeds and times listed below as a guideline. Keep the generator probe deep enough in the tissue slurry to prevent any material from being ejected from the flask.

1000 rpm----------2 min.
2500 rpm----------1.5 min.
5000 rpm----------1.5 min.
6500 rpm----------1.5 min.

NOTE: The initial homogenization at 1000 rpm may require additional time in order to break up the frozen tissue slurry

7.2.6.12 Sparingly rinse any tissue adhering to the generator probe back into the freeze dry flask with HPLC water.

NOTE: After each plant sample is homogenized, remove the generator probe from the mixer unit, disassemble the probe entirely and wash the parts thoroughly with a detergent solution, followed by a rinse with distilled water, acetonitrile and then with HPLC water. Then reassemble the generator probe.

7.2.6.13 At this point, if the sample is a matrix spike, add 2.0 ml of the appropriate spiking solution (see section 6.4.12) to the flask. The freeze dry flask

should then be sealed with Parafilm, the contents swirled for several seconds and then placed in a darkened area for 30 minutes.

7.2.6.14 Place a rubber cap, with its filter and glass adapter in place, on the freeze dry flask.

7.2.6.15 Place the flask containing the tissue slurry in an acetone/dry ice bath and shell freeze the slurry to the walls of the flask. Ensure there are no large masses of frozen tissue in the bottom of the flask and, that the slurry is thoroughly frozen.

7.2.6.16 Immediately transport the frozen sample to the freeze dryer, place the sample flask on a free port, carefully apply vacuum to the flask and allow the instrument to equilibrate to its normal operating levels before adding additional samples.

7.2.6.17 Leave sample(s) on the freeze dryer until all tissue is thoroughly dry (probably 24-48 hours for five or more samples). Then carefully remove each sample and seal the top of the glass adapter with Parafilm.

7.2.6.18 Carefully remove the rubber cap from the freeze dry flask. Use a clean spatula and scrape any tissue adhering to the top back into the flask.

7.2.6.19 Use a spatula to push the tissue from the inside walls of the freeze dry flask, to its bottom. Then gently chop and stir the tissue mass until it is finely divided.

7.2.6.20 Carefully transfer the tissue mass (scraping out as much as possible) to a clean glass wide-mouth container. Seal with a Teflon-lined closure and let stand in the dark until ready to proceed.

7.2.6.21 Into a 40 ml wide-mouth glass vial, weigh out 0.5 g of tissue. Record this weight to 0.0001 g the on worksheet.

7.2.6.22 Add 15.0 ml of acetonitrile to the vial and seal with Teflon-lined closure. Record this volume on the worksheet.

7.2.6.23 Suspend the vial in a sonicator bath whose temperature is controlled between 10° C and 15° C such that the water level covers the level of solids/liquids inside the vial. Place cover on the sonicator bath to block out light. Individual vials should not touch each other or the walls of the bath.

7.2.6.24 Sonicate the samples for 18 hours.

7.2.6.25 Remove the sample vials from the sonicator and allow to stand in the dark for 15 minutes.

7.2.6.26 Centrifuge sample vials at 2000 rpm or greater for 30 minutes.

7.2.6.27 Remove as much supernatant as possible from the vial, leaving the tissue pellet undisturbed for further extraction.

7.2.6.28 Place the supernatant in a 250 ml Erlenmeyer flask containing 100 ml of HPLC water. Seal the flask with Parafilm, label the flask as fraction "A" and place flask in dark until ready to proceed with step 7.2.6.35.

7.2.6.29 Using the tissue pellet remaining from the previous step, add 15.0 ml of acetonitrile to the vial and seal with Teflon-lined closure. Record this volume on the worksheet.

7.2.6.30 Suspend the vial in a sonicator bath whose temperature is controlled between 10° C and 15° C such that the water level covers the level of solids/liquids inside the vial. Place cover on the sonicator bath to block out light. Individual vials should not touch each other or the walls of the bath.

7.2.6.31 Sonicate the samples for 18 hours.

7.2.6.32 Remove the sample vials from the sonicator and allow to stand in the dark for 15 minutes. Centrifuge sample vials at 2000 rpm or greater for 30 minutes.

7.2.6.33 Remove as much supernatant as possible from the vial, leaving the tissue pellet undisturbed for further extraction. Place the supernatant in a 250 ml Erlenmeyer flask containing 100 ml of HPLC water. Seal the flask with Parafilm label the flask as fraction "B" and place flask in dark until ready to proceed with step 7.2.6.35.

7.2.6.34 Place the uncapped vial containing the tissue pellet at a forward leaning angle (facing outward) in the front portion of a functioning darkened hood. Pull the hood sash partially down and allow the pellet to dry out thoroughly. This should be done in a darkened room, away from possible analyte contamination.

7.2.6.34.1 Pipette 10.0 ml of 1+1 sulfuric acid into the vial with and break up the tissue pellet with a stainless steel spatula, being careful to leave all the tissue in the vial when the spatula is removed. Record this volume on the worksheet.

7.2.6.34.2 Suspend the vial in a sonicator bath whose temperature is regulated at 25° - 30° C and sonicate for 6 hours. The sonicator shall have a cover which blocks out the light.

7.2.6.34.3 Remove the vial from the sonicator bath and centrifuge at 2000 rpm or greater for 30 minutes.

7.2.6.34.4 Remove 5.0 ml of the acidic supernatant and add to 100 ml of 1.07 M sodium phosphate dibasic solution (see section 6.4.14) in an Erlenmeyer flask and swirl. Record the volume of supernatant on the worksheet.

7.2.6.34.5 Seal the flask with Parafilm and place the neutralized supernatant in an explosion-proof refrigerator at 4° C for 12-15 hours.

7.2.6.34.6 Remove the neutralized extract from the refrigerator. If the beaker contains a precipitate or a fluffy suspension, draw off and save most of the free liquid into a clean 250 ml Erlenmeyer flask then proceed to step 7.2.6.34.8.

7.2.6.34.7 If the beaker contains no precipitate or suspension, proceed to step 7.2.6.35.

7.2.6.34.8 Pour the suspension or precipitate layer into a 40 ml glass vial. Rinse the Erlenmeyer flask with HPLC water and add to 40 ml vial. Seal vial with Teflon-lined closure.

7.2.6.34.9 Centrifuge 40 ml vial at 2000 rpm or greater for 30 minutes.

7.2.6.34.10 Remove the supernatant from the precipitate and add to the supernatant removed in step 7.2.6.34.6.

7.2.6.34.11 Seal the flask with Parafilm, and place the accumulated supernatant in the dark until ready to proceed with step 7.2.6.35. Label this as sample fraction "C".

7.2.6.35 For each of the three fractions prepared from each sample (two acetonitrile extracts and one sulfuric acid extract) connect in series from top to bottom (using appropriate adapters), one 60 ml reservoir, one 5 gram Alumina-A SPE cartridge, one 1 gram Alumina-A SPE cartridge and one Porapak-Rdx SPE cartridge (500 mg size). Place this cartridge train onto the vacuum manifold

NOTE: Do not allow the bed of the Porapak-Rdx cartridge to become dry during the conditioning step, between the conditioning and the sample loading steps or during the sample loading step.

7.2.6.36 Condition the cartridges by first pulling 20 ml of acetonitrile (at a flow rate of 2-4 ml/min.) through them, immediately followed by 50 ml of HPLC water at a flow rate of 30 ml/minute. Immediately follow the HPLC water with the sample solution. When the sample flask is empty, rinse it with HPLC water three times and add this to the cartridge reservoir.

NOTE: If the sample being loaded onto the SPE cartridges has as its matrix the 1.07 M sodium phosphate buffer, follow the sample solution with about 70 ml of HPLC water to wash any accumulated salts out of the Porapak-Rdx cartridge.

7.2.6.37 After the sample solution (and wash solution if necessary) has totally passed through the cartridge train, separate the 60 ml reservoir, Alumina-A cartridges, and adaptors from the Porapak-Rdx cartridge which will remain on the vacuum manifold. Dispose of the Alumina-A cartridges properly.

7.2.6.38 Now apply a strong vacuum to the Porapak-Rdx cartridge for about 5 minutes to remove residual water.

7.2.6.39 Remove the Porapak-Rdx cartridge from the vacuum manifold.

7.2.6.40 Position the SPE cartridge over a properly labeled 5 ml volumetric flask (other sizes of volumetric flasks can be used if deemed necessary) with the Luer tip of the cartridge extending into the mouth of the flask.

7.2.6.41 Add 5.0 ml (record on worksheet) of acetonitrile to the SPE cartridge. Apply a lightly pressurized flow of ultrapure nitrogen to the top of the cartridge to start the solvent flowing through the cartridge and into the volumetric flask. Once the solvent flow begins, remove the nitrogen source and allow the solvent flow to be by gravity alone.

7.2.6.42 After the solvent stops dripping from the cartridge, reapply the pressurized nitrogen to the top of the cartridge to force any trapped solvent into the flask.

7.2.6.43 Make the volumetric flask to volume with acetonitrile and mix thoroughly. This extract should be prepared for HPLC analysis on the same day it was generated, or should be transferred to a glass vial with a Teflon-lined closure and stored in an explosion-proof refrigerator at 4° C until needed.

7.2.6.44 At this point, if each of the three sample fractions are to be analysed separately, proceed to step 7.2.6.44.1 (see calculations section 7.3.4.1). If the three sample fractions are to combined for analysis, proceed to step 7.2.6.44.2 (see calculations section 7.3.4.2).

7.2.6.44.1 Using precisely measured volumes, place equal amounts of eluant and HPLC grade water (usually 2 ml of each component) in a glass vial, cap with a Teflon-lined closure and mix thoroughly by inversion.

7.2.6.44.2 Using precisely measured volumes, and in a 16 ml glass vial, combine the eluants from sample fractions A, B, and C at the ratio of 1:1:2. Then add a volume of HPLC water equal to the total volume of the combined sample fractions. Cap the vial and mix.

7.2.6.45 Let the mixture stand in the dark at room temperature for 20 minutes.

7.2.6.46 Pass the mixture through a PTFE syringe filter with 0.45 µm pore size. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.6.47 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.7 **Preparation of compost samples for qualitative/quantitative analysis of explosives.**

NOTE: Batches of samples undergoing this extraction/preparation shall contain the following QA/QC samples: matrix spike, matrix spike duplicate, LCS, and method blank.

7.2.7.1 Spread sample on clean holder and place in the air flow of a darkened hood at room temperature and allow to dry for 12-18 hours (no visible moisture should be present).

7.2.7.2 Obtain the appropriate sample worksheet (Attachment 6). Record on the sheet, the laboratory number of the samples being prepared, the date, analyst's name, and the serial number and concentration of the spiking solution to be used.

7.2.7.3 Select one sample out of the batch for use in the creation of the matrix spike and matrix spike duplicate. Record the laboratory number of the sample in

the appropriate area in the QC section of the preparation worksheet (Attachment 6).

7.2.7.4 Into a properly labeled 40 ml glass vial, weigh out 2 grams of air dried sample. Record this weight to the nearest 0.0001 g on the preparation worksheet in the appropriate area.

NOTE: Carried out in conjunction with this procedure and using the same air dried samples, perform a percent moisture determination as described in section 9.2 of this procedure.

7.2.7.5 Prepare the batch QA/QC samples as listed below. Record all critical data in the appropriate areas of the QC section of the worksheet.

Matrix spike and matrix spike duplicate - For each spiked sample, weigh into a properly labeled 40 ml glass vial, 2 grams of air dried sample. Add 1.0 ml of acetonitrile based spiking solution (section 6.4.17) to the sample. Evaporate the acetonitrile from the sample, recap the vial and place in dark until ready for step 7.2.7.6

Laboratory control sample - Weigh into a properly labeled 40 ml glass vial, 2 grams of air dried sample. Add 1.0 ml of acetonitrile based spiking solution (section 6.4.17) to the sample. Evaporate the acetonitrile from the sample, recap the vial and place in dark until ready for step 7.2.7.6

Method blank - Weigh into a properly labeled 40 ml glass vial, 2 grams of AEC blank soil. Recap the vial and place in dark until ready for step 7.2.7.6

7.2.7.6 To each sample vial, add 10.0 ml of HPLC grade acetonitrile. Replace the vial closure and vortex for one minute. Place the vial in dark until ready for next step.

7.2.7.7 Suspend the vial(s) in a sonicator bath regulated between 10° - 15° C and sonicate under low light conditions for 18 hours. The water level in the bath should remain above the solvent level in the vials.

7.2.7.8 Remove the vials from the sonicator bath and centrifuge at 2000-2500 rpm for at least 15 minutes. Decant the supernatant into a properly labeled glass vial (label as fraction "A"). Save the remaining pellet of solids for further extraction in step 7.2.7.9

7.2.7.8.1 Mix at a 1:1 ratio, the sample supernatant with a 5 g/L calcium chloride solution (section 6.4.16) and let stand in dark for 20 minutes.

7.2.7.8.2 Filter the flocculated mixture through a 0.2 um Teflon syringe filter. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being split equally between two amber autosampler vials.

7.2.7.8.3 Allow the autosampler vials to stand in dark until ready for use. If filtrates cannot be used the same day they are prepared, they should be stored at 4°C.

7.2.7.9 Add l0 ml of a 1:1 mixture of acetonitrile/calcium chloride solution (step 6.4.18) to the compost pellet from step 7.2.7.8. Vortex the pellet for 1 minute, then centrifuge the vial at 2000-2500 rpm for at least 15 minutes. Decant the supernatant to waste.

7.2.7.10 Repeat step 7.2.7.9 three more times.

7.2.7.11 Place the washed compost pellets in the air flow of a hood to dry until only slightly damp.

7.2.7.12 Add 10 ml of 1:1 sulfuric acid (step 6.4.13) to the pellet, replace the vial closure and vortex for 1 minute.

7.2.7.13 Suspend the vials in a sonicator bath regulated between 25° - 30°C and sonicate for 6 hours.

7.2.7.14 Remove the vials from the sonicator. If the next steps cannot be performed immediately, place the vials in a refrigerator at 4°C until they can be performed (delay should not be longer than 48 hours).

7.2.7.15 Centrifuge vials at 2000-2500 rpm for at least 15 minutes. Remove 5.0 ml of acidic supernatant from the sample and place into a beaker containing 50 ml of 1.07M sodium phosphate dibasic solution (step 6.4.14). Using more of the phosphate solution and a pH meter, adjust the pH of the buffered extract to 5.0.

7.2.7.16 For each sample, connect in series from top to bottom (using appropriate adapters), one 60 ml reservoir, one 5 gram Alumina-A SPE cartridge, one 1 gram Alumina-A SPE cartridge and one Porapak-Rdx SPE cartridge (500 mg size). Place this cartridge train onto the vacuum manifold

NOTE: Do not allow the bed of the Porapak-Rdx cartridge to become dry during the conditioning step, between the conditioning and the sample loading steps or during the sample loading step.

7.2.7.16.1 Condition the cartridges by first pulling 20 ml of acetonitrile (at a flow rate of 2-4 ml/min.) through them, immediately followed by 50 ml of HPLC

water at a flow rate of 10 ml/minute. Immediately follow the HPLC water with the sample solution. When the sample flask is empty, rinse it with HPLC water three times and add this to the cartridge reservoir. Follow the buffer solution with about 70 ml of HPLC water to wash any accumulated salts out of the Porapak-Rdx cartridge.

7.2.7.16.2 After all solutions have totally passed through the cartridge train, separate the 60 ml reservoir, Alumina-A cartridges, and adapters from the Porapak-Rdx cartridge which will remain on the vacuum manifold. Dispose of the Alumina-A cartridges properly.

7.2.7.16.3 Now apply a strong vacuum to the Porapak-Rdx cartridge for about 5 minutes to remove residual water.

7.2.7.16.4 Remove the Porapak-Rdx cartridge from the vacuum manifold.

7.2.7.16.5 Position the SPE cartridge over a properly labeled (label as sample fraction "B") 5 ml volumetric flask (other sizes of volumetric flasks can be used if deemed necessary) with the Luer tip of the cartridge extending into the mouth of the flask.

7.2.7.16.6 Add 5.0 ml (record on worksheet) of acetonitrile to the SPE cartridge. Apply a lightly pressurized flow of ultrapure nitrogen to the top of the cartridge to start the solvent flowing through the cartridge and into the volumetric flask. Once the solvent flow begins, remove the nitrogen source and allow the solvent flow to be by gravity alone.

7.2.7.16.7 After the solvent stops dripping from the cartridge, reapply the pressurized nitrogen to the top of the cartridge to force any trapped solvent into the flask.

7.2.7.16.8 Make the volumetric flask to volume with acetonitrile and mix thoroughly. This extract should be prepared for HPLC analysis on the same day it was generated, or should be transferred to a glass vial with a Teflon-lined closure and stored in an explosion-proof refrigerator at 4° C until needed.

7.2.7.16.9 Using precisely measured volumes, place equal amounts of eluant and HPLC grade water (usually 2 ml of each component) in a glass vial, cap with a Teflon-lined closure and mix thoroughly by inversion.

7.2.7.16.10 Let the mixture stand in the dark at room temperature for 20 minutes.

7.2.7.16.11 Pass the mixture through a PTFE syringe filter with 0.45 µm pore size. The first 1/3 of the filtrate should be discarded, with the remaining filtrate being apportioned as follows:

If only qualitative or quantitative analysis of the sample is required, then only one autosampler vial containing filtrate is required. If qualitative and quantitative analysis of the sample are required, then two autosampler vials containing filtrate are required.

7.2.7.16.12 Allow the autosampler vial containing the filtrate to stand in the dark until ready to load onto the autosampler. If filtrates cannot be loaded onto autosampler the same day they are prepared for analysis, they should be stored in an explosion-proof refrigerator at 4° C.

7.2.8 HPLC procedure

After preparation is completed and autosampler vials are filled; load the autosampler, enter the parameters noted below, and start the analysis.

7.2.8.1 Tertiary pump parameters

Pump flow rate: 0.8 ml/min.

Run length: 50.00 minutes

Method end action: Equilibrate at end
Equilibration time: 5.00 minutes

Mobile phase gradient (where phase A is water and phase B is methanol)
Time = 0.00 min.; phase A = 83%; phase B = 17%
Time = 8.00 min.; phase A = 63%; phase B = 37%
Time = 10.00 min.; phase A = 42%; phase B = 58%
Time = 23.00 min.; phase A = 42%; phase B = 58%
Time = 28.00 min.; phase A = 0%; phase B = 100%
Time = 35.00 min.; phase A = 0%; phase B = 100%
Time = 40.00 min.; phase A = 84%; phase B = 16%

(NOTE: Mobile phase percentages and flow rates may be altered prior to an initial calibration to provide the best peak resolution and placement)

7.2.8.2 Autosampler parameters

Sample loop volume: 100 µl

Syringe volume: 1000 µl
Wash cycle volume: 500 µl
Tube volume: 13.0 µl
Viscosity factor: 1
Pre-injection delay: 10 sec.
Post-injection wash: Yes
Automixing volume %: 100%
Automixing type-air mixing: No
Stop: momentary: No
Expel tube volume to vial: No
Pulsed start output: Yes

7.2.8.3 Photodiode array detector parameters

Detector information
Bunch rate: 8 points (2.0 Hz)
Monitor length: 64 bunched points (32.0 seconds)

Polychrom parameters
Screen width: 50.00 minutes
Scan frequency: 16 Hz
Autoprint: Off
Ch A output: Absorbance
Ch A bandwidth: 4 nm
Ch A peak use: Upper-half
Ch A time constant: 0.500 seconds
Ch A offset: 10%

7.3 Calculations and Recording Data

7.3.1 Peak identification is made by commercial chromatography workstation software. Data are stored in individual files for each injection with the extension RP1.

7.3.2 Copy files from a run onto a diskette. Extract and concatenate data into a single file with QBASIC program 16.BAS (or its most recent revision). 16.BAS applies calibration curve factors to peak heights and calculates raw concentration.

7.3.3 Edit the output file from 16.BAS to eliminate mis-identified peaks. Add in peaks which were not identified by the software but were found in manual review of chromatograms.

7.3.4.1 For vegetation when the extracts are analyzed separately: Enter the weight of the vegetation sample, extraction volumes, and the measured concentration of each target compound for the three fractions into the spreadsheet 'PLANT_TMPLATE.xls' to calculate total concentrations.

Example: A 0.5041 g sample gives readings X1, X2, and X3 on the three fractions for analyte X.

Total X in micgrograms/gram = (X1*5.0 + X2*5.0 +X3*10.0)/0.5041

7.3.4.2 For vegetation when the extracts are combined before analysis:

If X grams of tissue are extracted into 5 ml of solvent for fraction "A"
and
The second extraction is made to 5 ml for fraction "B"
and
The third extraction initially uses 10 ml of acid, with 5 ml of the acid extract being used for the SPE step and having final volume of 5 ml for fraction "C"
and
The fractions are combined at a 1:1:2 ratio that when analyzed give a concentration of (Rc)
then
The Final concentration = Rc*20/X

7.3.5 Interface the edited file with the EBS database. Add weights, volumes, dilution factors, concentration factors, and unit conversion factors to EBS.

Review percent recoveries and relative percent differences as calculated by EBS.

7.3.6 Review data and resolve all discrepancies. Print a final copy of the customer report and route it to the supervisor along with the data package for final review.

7.3.7 Store chromatograms, preparation worksheets, EBS printouts, run narratives, notes, logbooks, final reports, and other information as quality assurance records.

8.0 SAFETY

8.1 Care should be taken when handling neat HMX, RDX and TNT since these compounds are classified as explosives. Safety glasses and vinyl gloves should be worn during the use of these compounds. Quantities should be minimized as far as possible.

8.2 Standard laboratory safety precautions should be followed when handling the organic solvents used in this procedure. Safety glasses shall be worn at all times in the laboratory and gloves, appropriate for the solvent being handled, should be worn.

9.0 NOTES

9.1 Method Detection Limit determination in GLP-0018 is done in accordance with Title 40, Code of Federal Regulations, Part 136, Appendix B, "Definition and Procedure for the Determine of the Method Detection Limit" - Revision 1.11.

9.2 Percent moisture by Oven Drying

9.2.1 Obtain the appropriate worksheet (Attachment 7 - "Determination of Percent Moisture by Oven Drying"). Record on the worksheet, laboratory numbers, sample description, and your name.

NOTE: For each sample, the steps (9.2.2-9.2.9) will be identical

9.2.2 Obtain an appropriately sized aluminum weighing boat and label with laboratory number of sample.

9.2.3 Weigh the boat to 0.0001 g and record this as the tare weight (TW) in the appropriate area of the worksheet.

9.2.4 Add the appropriate weight of sample (see list below) to the boat. (Weights may vary depending on the amount of sample material available)

Soil----------5 g
Sediment----5 g
Gravel-------30 g
Plant----------2 g
Compost-----5 g

9.2.5 Record the weight of the boat plus sample to 0.0001 g and record this as the gross weight (GW) in the appropriate area of the worksheet.

9.2.6 Place the boat containing the sample in an oven at 105° C and leave for 12-15 hours. Record on the worksheet, the date and time the samples were placed in the oven and its temperature at that time.

9.2.7 Remove the boat and allow to equilibrate to room temperature in a dessicator. Record on the worksheet, the date and time the samples were removed from the oven and its temperature at that time.

9.2.8 Remove from the dessicator and weigh the boat and dried sample. Record this weight to 0.0001 g as the dried weight (DW) in the appropriate area of the worksheet.

9.2.9 Calculate the percent moisture of the sample as shown on the worksheet and record the results in the appropriate areas. The formula for the calculation is:

$$\% \text{ Moisture} = \frac{(GW - DW) * 100}{(GW - TW)}$$

9.3 Approximate analyte retention times:

ANALYTE	MINUTES
2,6-Diamino-4-nitrotoluene	12.11
1,3,5-Trinitroso-1,3,5-triazacyclohexane	12.07
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	13.05
2,4-Diamino-6-nitrotoluene	13.53
1-Nitroso-3,5-dinitro-1,3,5-triazacyclohexane	16.11
Hexahydro-1,3,5-trinitro-1,3,5-triazine	15.78
1,3,5-Trinitrobenzene	18.30
1,3-Dinitrobenzene	20.44
3,5-Dinitroaniline	21.82
2,4,6-Trinitrotoluene	23.56
2-Amino-4,6-dinitrotoluene	24.58
4-Amino-2,6-dinitrotoluene	25.43
2,6-Dinitrotoluene	25.85
2,4-Dinitrotoluene	26.44
4,4',6,6'-Tetranitro-2,2'-azoxytoluene	32.69
2,4',6,6'-Tetranitro-2',4-azoxytoluene	32.96
2,2',6,6',Tetranitro-4,4'-azoxytoluene	33.21
2,2'-Dinitro-4,4'-azoxytoluene	34.33

ATTACHMENT 1

Preparation of Liquids for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____ **Matrix:** Aqueous Organic

Laboratory Number	Aliquot (ml)	Dilution Vol. (ml)	Aliquot (ml)	Dilution Vol. (ml)	1:1 Mixer Matrix		PTFE Filter	
					Water	AcCN	0.2 um	0.45um

QA/QC Samples

	Sample Vol. (ml)	Spike Vol. (ml)	Final Vol. (ml)		1:1 Mixer Matrix		PTFE Filter	
					Water	AcCN	0.2 um	0.45um
Method Blank								
LCS								
Matrix Spike								
Martix Spike Dupl.								

ATTACHMENT 2

Preconcentration of Liquids by SPE for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____

Laboratory Number	Sample Vol. (ml)	Eluant Vol. (ml)	Aliquot (ml)	Dilution Vol. (ml)	1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um

QA/QC Samples

	Spike Vol. (ml)	Final Vol. (ml)	Eluant Vol. (ml)		1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um
Method Blank								
LCS								

ATTACHMENT 3

Preparation of Solids for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____ **Matrix:** Soil Sediment Gravel

Laboratory Number	Sample Wt. (g)	Extraction Vol. (ml)	Aliquot (ml)	Dilution Vol. (ml)	1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um

QA/QC Samples

	Sample Wt. (g)	Spike Vol. (ml)	Final Vol. (ml)		1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um
Method Blank								
LCS								
Matrix Spike								
Martix Spike Dupl.								

ATTACHMENT 4

Preparation of Compost Leachates for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____

Laboratory Number	Sample Vol. (ml)	Salt Wt. (g)	Extract Vol. (ml)	Dilution Vol. (ml)	1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um

QA/QC Samples

	Sample Vol. (ml)	Salt Wt. (g)	Spike Vol. (ml)	Extract Vol. (ml)	1:1 Mixer Matrix		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um
Method Blank								
LCS								
Matrix Spike								

Preparation of Plants for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____ **Spike Vol. (ml):** MS LCS

			Sonication Extraction								Acid Digestion				
			Sonication #1				Sonication #2								
Laboratory Number	Wet Wt. (g)	Dry Wt. (g)	AcCN Vol. (ml)	Eluant Vol. (ml)	Mixer Water	Filter 0.45um	AcCN Vol. (ml)	Eluant Vol. (ml)	Mixer Water	Filter 0.45um	Acid (ml)	Extract Used (ml)	Eluant (ml)	Mixer Water	Filter 0.45um

QA/QC Samples

			Sonication Extraction								Acid Digestion				
			Sonication #1				Sonication #2								
	Wet Wt. (g)	Dry Wt. (g)	AcCN Vol. (ml)	Eluant Vol. (ml)	Mixer Water	Filter 0.45um	AcCN Vol. (ml)	Eluant Vol. (ml)	Mixer Water	Filter 0.45um	Acid (ml)	Extract Used (ml)	Eluant (ml)	Mixer Water	Filter 0.45um
Method Blank															
LCS															
Matrix Spike															

Preparation of Compost for Explosives Analysis

Start Date:_____ **Spike s/n:**_____

End Date:_____ **Spike concentraton:**_____

Analyst:_____ **Spike Vol. (ml):** MS_____ LCS_____

			Sonication Extraction						Acid Digestion						
Laboratory Number	Sample Wt. (g)		AcCN Vol. (ml)		1:1 Mixer		PTFE Filter		Acid (ml)	Extract Used (ml)	Eluant (ml)	1:1 Mixer		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um				Water	$CaCl_2$	0.2 um	0.45um

QA/QC Samples

			Sonication Extraction						Acid Digestion						
	Sample Wt. (g)		AcCN Vol. (ml)		1:1 Mixer		PTFE Filter		Acid (ml)	Extract Used (ml)	Eluant (ml)	1:1 Mixer		PTFE Filter	
					Water	$CaCl_2$	0.2 um	0.45um				Water	$CaCl_2$	0.2 um	0.45um
Method Blank															
LCS															
Matrix Spike															
Matrix Spike dupl.															

ATTACHMENT 7

Percent Moisture by Oven Drying

Analyst:_____ **Sample Type:**_____

Initial date / time:_____ **Initial oven temp.:**_____

Final date / time:_____ **Final oven temp.:**_____

Laboratory Number	Tare Wt. (TW) Grams	Gross Wt. (GW) Grams	Dried Wt. (DW) Grams	Percent Moisture

Percent Moisture = $\frac{(GW - DW) * 100}{(GW - TW)}$

Appendix A-20

Ash Content: AP-0022

TENNESSEE VALLEY AUTHORITY

NO.: AP-0022

GENERAL ANALYTICAL LABORATORY

TITLE: ASH CONTENT

	Signature	Title	Date
Prepared by:	L. G. Kanipe	Research Chemist	12/8/89
Concurred:	J. R. Trimm	Laboratory Group Leader	12/8/89
Concurred:	C. W. Gilbert	QA/QC Coordinator	12/8/89
Concurred:			
Concurred:			
Concurred:			
Approved:	Larry G. Kanipe	Supervisor, General Analytical Laboratory	12/8/89

REVISION	R0			
CONTROL DATE:	12/8/89			

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

1.0 PURPOSE

This procedure provides a method for determining the inorganic residue as ash in samples.

2.0 SCOPE

This procedure is applicable to any sample for which the residue as metal oxides is desired.

3.0 SUMMARY

Ash is determined by weighing the residue remaining after burning the sample under controlled conditions of sample weight, temperature, time, and atmosphere.

4.0 REFERENCES

4.1 "Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," Annual Book of ASTM Standards, D-3174-89.

5.0 RESPONSIBILITIES

5.1 The General Analytical Laboratory Supervisor or his designee shall ensure that this procedure is followed during the determination of inorganic ash content.

5.2 The Laboratory Group Leader, or his designee, shall delegate the performance of this procedure to personnel experienced in this procedure. The Group Leader is responsible for the training of new personnel on this procedure.

5.3 The analyst shall follow this procedure and report any abnormal results on nonconformances to the Laboratory Group Leader.

6.0 PROCEDURE/REQUIREMENTS

6.1 Prerequisites

None

6.2 Limitations and Actions

None

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Electric Muffle Furnace -- capable of having temperature regulated at 700 to 750°C

6.3.1.2 Porcelain or platinum crucibles with covers

6.3.1.3 Analytical balance -- sensitive to 0.1 milligram

6.4 Calibration

None

6.5 Procedure Instructions

6.5.1 If the sample is solid, pulverize to pass a 40-mesh screen. Liquids may be run after thorough homogenization.

6.5.2 Weigh a crucible.

6.5.3 Weigh up to 10 grams of sample into the crucible and cover.

NOTE: In the next step, leave the furnace door slightly ajar to allow air movement during ashing.

6.5.3 Place the crucible into a cold furnace, remove the cover, and heat gradually at such a rate that the temperature reaches 450 to 500°C in approximately one hour.

6.5.4 Continue heating so that a temperature of 700 to 750°C is reached by the end of the second hour. Heat at that temperature for an additional two hours. Some samples may require additional time for complete combustion.

6.5.5 When completely combusted, place the cover on the crucible and cool in a desiccator.

6.5.6 When the sample has cooled, weigh the crucible/residue.

6.6 Calculations and Recording Data

6.6.1 The percent ash in the sample is calculated as follows:

$$\% \text{ Ash} = [(A - B)/C] \times 100$$

where:

A = weight of crucible and ash residue

B = weight of crucible

C = weight of original sample

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

7.1.1 The analyst shall inspect all numerical data for reasonableness.

7.1.2 The Laboratory Group Leader, or his designee, shall inspect the results of the procedure.

7.1.3 The General Analytical Laboratory Supervisor, or his designee, shall inspect the results of the procedure on a regular basis.

7.2 Acceptance Criteria

Critical measurements are made in the following steps:

6.5.2 -- Crucible weight

6.5.3 -- Sample weight

6.5.4 -- Crucible/residue weight

7.3 Material Monitoring

None

7.4 Equipment Monitoring

None

7.5 Certification

None

8.0 SAFETY

8.1 Normal laboratory safety rules shall be observed.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

None

APPENDIX B

QUALITY ASSURANCE

APPENDIX B
QUALITY ASSURANCE PLAN

B.1 Purpose and Scope of the Plan

The purpose of the Quality Assurance Plan is to ensure that:

- Sufficient measurements were made to assess the effectiveness of the proposed treatment methods.
- Samples taken were representative of the conditions in the experimental setup.
- Samples were delivered to the laboratory for analysis without deterioration.
- Measurement techniques were sufficiently specific to measure the target compounds.
- Data taken were reliable.

The Quality Assurance Plan applied to all activities, including performing experiments, sampling, and laboratory analysis of samples.

TVA's Analytical Laboratory provided analytical chemistry support for the project by performing analyses for explosives and degradation products. New procedures for extraction of explosives from plant tissues and compost were developed and tested for this project.

B.2 Quality Assurance Responsibilities

The attached organizational chart (Figure B-1) shows the TVA organizations providing support to the project. Responsibilities of staff members were as follows:

- The Project Manager provided overall direction for the project, ensured staffing was adequate to meet project goals and schedules, and provided progress reports to the USAEC.

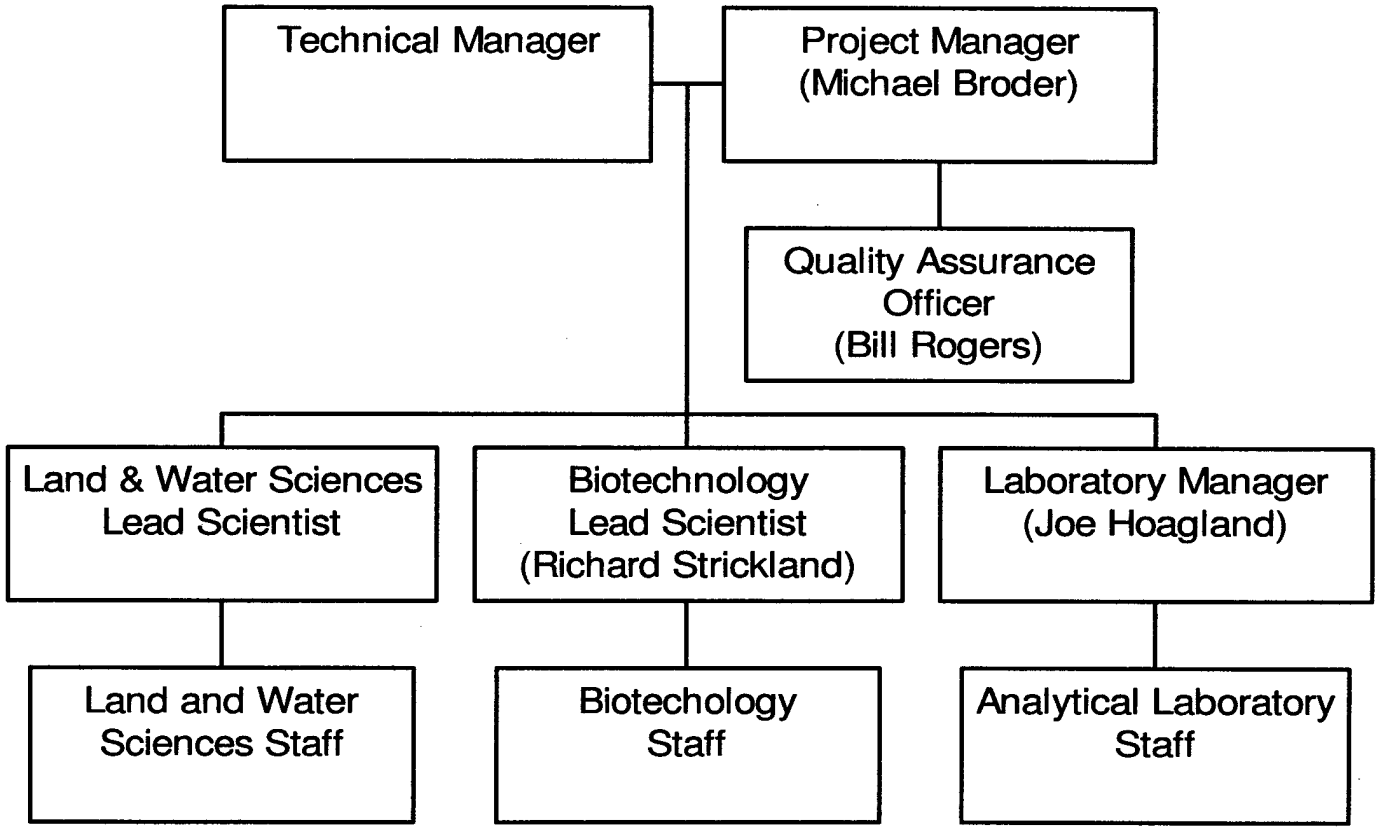


Figure B-1

TVA Organizations Providing Project Support

- The Technical Manager reported to the Project Manager and was responsible for providing technical direction and staff for development of processes and experimental design. The Technical Manager also provided oversight of experimental design, assisted in resolution of technical questions, and coordinated technical activities. The Technical Manager was responsible for providing periodic technical progress reports to the Project Manager.

- The Quality Assurance (QA) Officer reported to the Project Manager and had no direct responsibilities in testing or analysis of the samples. The QA Officer was responsible for auditing actions and documentation to ensure adherence to this plan. The QA Officer was responsible for providing quarterly quality control data reports to the Laboratory Manager.

- Land and Water Sciences Lead Scientist reported to the Project Manager and Technical Manager and was responsible for providing technical direction and staff for development of processes and experimental design.

- Land and Water Sciences staff reported to the Land and Water Sciences Lead Scientist and was responsible for performing experiments and experimental operations. Staff members were responsible for planning, design, testing, and documentation of the various sub-projects assigned to them. They were responsible for review of data falling under their areas of responsibility.

- Biotechnology Lead Scientist reported to the Project Manager and Technical Manager and was responsible for providing technical direction and staff for development of processes and experimental design.

- Biotechnology staff reported to the Biotechnology Lead Scientist and were responsible for performing experiments and experimental operations. Staff members were responsible for planning, design, testing, and documentation of the various sub-projects assigned to them. They were responsible for review of data falling under their areas of responsibility.

- The Laboratory Manager reported to the Project Manager and Technical Manager and was responsible for providing project analytical oversight and for final analytical data integrity. The Laboratory Manager was responsible for providing monthly project reports to the Project Manager.

- Research Chemists and Research Scientists in the Analytical Laboratory reported to the Laboratory Manager and were responsible for planning, design, testing, and documentation of the various sub-projects assigned to them. They were responsible for review of data falling under their areas of responsibility.

- Chemical Laboratory Analysts and technicians in the Analytical Laboratory reported to the Laboratory Manager and were responsible for following procedures and instructions to provide analytical measurements required in the course of the project. They were responsible for review of the data they produced, documentation of analytical runs, and equipment maintenance.

B.3 Quality Program Procedures and Documents

The Analytical Laboratory activities conducted during this project were carried out in accordance with the laboratory's QA manual which contains the following documents:

QAPLAN - "Quality Assurance Plan"
GLP-0001 - "Procedure Format and Style"
GLP-0002 - "Quality Assurance Records Control"
GLP-0003 - "Procedure Preparation and Distribution"
GLP-0004 - "Training"
GLP-0005 - "Nonconformances and Corrective Actions"
GLP-0006 - "Control of Reagents and Standards"
GLP-0007 - "Analysis Work Plan Preparation"
GLP-0012 - "Treatment of Data"
GLP-0013 - "Instrument Logbook and Control Chart Maintenance"
GLP-0016 - "Sample Receipt, Log-In, and Data Handling"

GLP-0017 - "Control of Changes to Software"

CP-0001 - "Measurement and Test Equipment Control and Calibration"

SP-0001 - "Sample Chain of Custody"

Laboratory analyses were conducted in accordance with written procedures. Modifications to procedures found to be necessary to perform the analyses required in this test plan were noted in equipment operation logs or research notebooks until the written procedures were revised. A revision to procedure AP-0062, "Extraction, Preparation, and Analysis of Explosives and Their Degradation Products by HPLC," was produced to cover extraction and analysis of plant and compost material.

The experimental portion of this plan was performed in accordance with the project plan. Data, observations, experimental conditions, and minor modifications to planned activities were recorded in research notebooks in a complete enough fashion that all actions, results, and conclusions could be reconstructed. Details of experiments involving method development were logged to facilitate production of a revision to AP-0062.

Sampling was conducted in accordance with written work plans, procedures, or instructions to ensure complete samples were taken at correct locations and in a manner which did not invalidate conclusions. All actions in sampling were recorded in research notebooks or on forms designed to ensure complete documentation of all experimental parameters. Instructions were provided for the preservation of samples.

B.4 Control of Purchased Items

Chemicals, equipment, materials, and other items purchased to conduct this project were of suitable quality to meet the project needs, as specified in the written procedures. Purchased items were inspected upon receipt to ensure they met the requirements specified in purchase requests. Nonconforming items were not used. Suitable handling activities, storage conditions, and other controls were utilized to ensure the quality of purchased items was not degraded after receipt.

B.5 Record Control

Records of analysis, records of calibration, research notebooks, chromatograms, sampling logs, custody records, work plans, machine printouts, chromatogram traces, logsheets, standard material use records, raw data calculation sheets, and copies of procedures were maintained as QA records as specified in GLP-0003. Records were accumulated in logical arrangement to facilitate retention and review. In-process records and logbooks were stored in the work area in a safe manner to protect against loss, fire, spills, or other damage.

Records of experiments and analyses will be maintained for a three-year period after the end of the project. This includes machine printouts or chromatogram traces, logbooks, notebooks, logsheets, standard material use logs, and raw data calculation sheets. Due to the limited lifetime of computer storage media, any computer media utilized to store analytical file backups or raw data files will be stored for the lifetime of the project plus one year.

B.6 Data Quality Parameters

B.6.1 Accuracy and Precision

Percent recovery, relative percent difference, standard deviation, and other commonly used statistical indicators of accuracy and precision were calculated as defined in Chapter 1 of SW-846, 3rd Edition.

B.6.2 Method Detection Limit, Method Quantitation Limit

Method Detection Limits were calculated as defined in Title 40, Code of Federal Regulations, Part 136, Appendix A, "Definition and Procedure for the Determination of the Method Detection Limit" - Revision 1.11.

Method Quantitation Limits were defined as five times the Method Detection Limit as in Chapter 1 of SW-846, 3rd Edition, or as the lowest point used in making the calibration curve, whichever was higher.

B.7 Calibration Procedures and Quality Control Checks

The precision and accuracy of analytical new or revised procedures were investigated before they were used for analysis of samples. However, no standard reference material was available for plant material or compost. Constructed test samples were used to estimate precision and accuracy.

B.7.1 Initial Calibration Procedures

B.7.1.1 Laboratory Instrumentation

The calibration frequencies and tests required in SW-846 for Methods 8330, 6010B, 7470A, 7471A, 7740, and 7060 were used as the guidelines for calibration of the equipment used in the HPLC, AA, and ICP methods. Guidelines for calibration frequencies and tests, as specified by the manufacturer, were used for IC and FIA.

B.8 Analytical Laboratory Calibration and Quality Control

B.8.1 General Quality Control Requirements

The Analytical Laboratory ran appropriate method blanks for the procedures used in this portion of the project. Method accuracy and precision were demonstrated by running quality control samples. Analysts demonstrated the ability to generate acceptable results with the methods by utilizing appropriate proficiency samples or standard reference materials. The Analytical Laboratory determined method detection limits for target compounds.

B.8.2 Batch QC

With each batch of 20 samples or subset thereof, one method blank, one matrix spike, and one laboratory control sample were run. In addition, one sample duplicate or one matrix spike duplicate was run with each batch. Note: For some analytical techniques, matrix spikes were not possible.

B.8.3 Quality Control Requirements for HPLC

Retention time windows were determined and the device was calibrated during development of the procedure. Five calibration standards were used.

At the beginning of each day that analyses were conducted, the midpoint calibration standard was analyzed. Then every ten samples and at the end of the run, a midpoint calibration standard was run again in accordance with the quality control requirements for HPLC devices.

B.8.4 Quality Control for Automated Laboratory Instrumentation

The quality control tests required in Method 6010B were used as guidelines for the calibration and use of the equipment used in ICP methods. The quality control tests for Atomic Absorption (AA) methods for calibration and use were those specified in the 7000 series methods in SW-846.

For ICP, calibration was performed with one standard and one blank run at the beginning of each run. For AA, calibration was performed with three standards and one blank run at the beginning of each run. Following calibration, a calibration check sample and a calibration blank were run as required by the method.

Flow injection analyzers (FIA) were calibrated before each use following written procedures. For FIA, calibration was performed with standards of five concentrations at the beginning of each day. Concentrations bracketed the range of interest, but were limited to the range of linear response of the device.

For these devices, a midpoint calibration standard was run at least every ten samples and at the end of the run throughout the day. Any group of ten samples preceding and following a midpoint calibration check, which fell outside the 15% limits, was reanalyzed.

For these devices, a laboratory control sample made from a separate stock than the calibration standards was run with each batch.

For combustion analyzers (Total N and Total C), manufacturers' instructions were followed for single-point calibration on each day of use. Sample duplicates and quality control check samples were usually run with each batch. For the carbon analyzer, a laboratory control sample made from a separate stock than the calibration standards was run with each batch.

For any of these devices, samples exhibiting a signal above the linear range of the device were diluted and reanalyzed.

B.8.5 Definitions

- **Batch** - Usually a group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

- **Method Blank** - A sample of clean reagent carried through preparation and extraction in the same manner as samples. One method blank was run with each batch.

- **Matrix Spike** - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration was selected to read at five times the method quantitation limit in the sample or about the midpoint of the calibration curve. One matrix spike was run for each batch. Spiking occurred prior to sample preparation and analysis.

- **Matrix Spike Duplicate** - A second aliquot of the same sample treated in the same manner as the matrix spike.

- **Duplicate** - A second aliquot of a sample taken independently through extraction and preparation before analysis.

- **Quality Control Check Sample** - A quality control sample of the same type and matrix as calibration solutions, but made independently from the calibration solutions. This sample is also referred to as a laboratory control sample.

B.8.6 Data Reduction, Validation, and Reporting

B.8.6.1 Data Reduction

The project's analytical data was calculated and reduced on vendor-supplied chromatographic software for HPLC systems and on vendor-supplied analysis software for FIA systems, ICP systems, or AA systems. These systems typically calculate calibration curves automatically and apply the curves to sample measurements. However, a spreadsheet developed at TVA was used to fit curves and calculate data for the HPLC analysis. Other laboratory calculations were carried out on spreadsheets developed and tested at TVA or on hand-held calculators (e.g., soil moisture). Some devices, such as pH meters or combustion analyzers for total N or total C, give direct readout or printout of analytical data.

The Analytical Laboratory's Chemical Laboratory Analysts were responsible for calculation and reduction of data.

B.8.6.2 Data Validation

Analytical measurements were first reviewed by the chemist producing them and then by another chemist before being interfaced with the laboratory database. If quality control samples fell outside limits, the samples were usually scheduled for reanalysis. After questions were resolved, results were passed on to the Laboratory Manager for final review and validation. Group supervisors or team leaders were responsible for decisions concerning reanalysis of samples and coordinated with the Project Manager when significant problems were discovered or when resampling was required.

B.8.6.3 Data Reporting

Analytical data were reported in units of milligrams per liter for liquid samples. Solid sample results were reported as milligrams per kilogram dry weight unless other units such as percent were more appropriate.

Method detection limits and instrument detection limits were reported for each run. Recovery of matrix spikes and recovery of quality control samples were calculated and reported as percentages.

B.8.6.4 Corrective Action

Corrective action in accordance with the requirements of GLP-0005 was not identified in the course of this project.

B.9 Performance and System Audits

B.9.1 Performance Audits

The analytical Laboratory participated in EPA Water Pollution Studies twice yearly during this project. The Analytical Laboratory investigated any analyte falling outside control limits and reported its findings to the QA Officer in writing. Participation in this cross-checking process provides information on the Analytical Laboratory's performance as compared to other laboratories in the nation.

B.9.2 On-Site System Audits

The QA Officer periodically inspected logs, records, printouts, results of quality control checks, documentation, case narratives, research notebooks, and other quality- related aspects of the project to ensure detailed compliance was in effect. One surveillance of field sampling was performed in conjunction with this project. A few minor concerns were identified. All concerns were rapidly brought to closure.

B.9.3 Audit Reports

Results of the surveillance of field sampling mentioned in B.9.2 were reported in writing to the Project Manager.

B.10 Quality Assurance Reports

B.10.1 Status Reports

TVA's Project Manager provided periodic progress reports to USAEC which contained a summary of accomplishments and a discussion of significant problems and their resolution.

Quarterly quality control data reports were written by the QA Officer addressing:

- Changes in this QA project plan
- Changes in analytical procedures
- Summary of QC program results
- Summary of training
- Results of audits
- Results of performance sample evaluations
- Data quality assessment in terms of precision, accuracy, and MDLs
- Discussion of whether QA objectives were met

B.11 Data Management and Analysis

B.11.1 Analytical Data

Analytical data packages for the project included:

- Sample description or identification information
- Sample analytical results
- Quality control sample results with surrogate recoveries and percent recovery of known compounds

Sufficient data were maintained such that experimental and analytical results could be reconstructed.

Records of all attempts at analysis were maintained whether or not the analysis was successful. However, unusable data were not reported. Data were unusable when quality control samples or quality control checks failed; however, the records for these attempts at analysis were maintained with relevant documentation. Data Qualification Codes in use by the laboratory and which may have been encountered in review of this project's data were as follows:

NA - Compound Not Analyzed

<MDL - Compound not detected (value falls less than Method Detection Limit)

TR or Trace - Compound present at trace level, indicated but less than MDL

Q - "Qualified" - For a sample in which an analyte was quantified, but an associated quality control sample fell outside control limits

APPENDIX C
RAINFALL DATA

Rainfall Dates (mo/da/yr)	Days fro Start	Rainfall (inches)	Monthly Totals	
9/16/96	1	0.70		
9/21/96	6	1.33		
9/27/96	12	2.25		
9/28/96	13	0.25		
9/29/96	14	0.29		
			September Total	**4.82**
			Total to Date	**4.82**
10/1/96	16	0.05		
10/16/96	31	0.60		
10/22/96	37	0.71		
10/26/96	41	0.60		
10/27/96	42	1.64		
			October Total	**3.60**
			Total to Date	**8.42**
11/1/96	47	1.20		
11/6/96	52	0.30		
11/7/96	53	1.55		
11/14/96	60	Trace		
11/18/96	64	1.05		
11/21/96	67	0.30		
11/25/96	71	1.10		
11/29/96	75	Trace		
11/30/96	76	4.52		
			November Total	**10.02**
			Total to Date	**18.44**
12/5/96	81	0.41		
12/7/96	83	0.10		
12/11/96	87	1.08		
12/15/96	91	2.70		
12/23/96	99	0.75		
12/25/96	101	0.40		
12/27/96	103	0.30		
12/28/96	104	Trace		
12/30/96	106	0.37		
			December Total	**6.11**
			Total to Date	**24.55**
1/4/97	111	0.80		
1/8/97	115	1.26		
1/9/97	116	0.50		
1/10/97	117		1.25 snowfall	
1/15/97	122	0.76		
1/22/97	129	0.53		
1/24/97	131	1.30		
1/27/97	134	1.23		
			January Total	**6.38**
			Total to Date	**30.93**
2/3/97	141	0.88		
2/6/97	144	0.52		
2/7/97	145	0.40		

Rainfall Dates (mo/da/yr)	Days fro Start	Rainfall (inches)	Monthly Totals	
2/13/97	151	0.72		
2/20/97	158	0.70		
2/25/97	163	0.45		
2/26/97	164	0.73		
2/28/97	166	0.88		
			February Total	**5.28**
			Total to Date	**36.21**
3/1/97	167	0.75		
3/2/97	168	2.30		
3/5/97	171	0.87		
3/9/97	175	0.10		
3/13/97	179	0.04		
3/17/97	183	0.23		
3/18/97	184	0.82		
3/25/97	191	0.25		
3/28/97	194	0.45		
			March Total	**5.81**
			Total to Date	**42.02**
4/4/97	201	0.25		
4/5/97	202	0.89		
4/11/97	208	0.20		
4/16/97	213	0.05		
4/19/97	216	0.10		
4/21/97	218	0.24		
4/22/97	219	0.81		
4/26/97	223	0.27		
4/27/97	224	0.85		
4/28/97	225	0.25		
4/30/97	227	0.05		
			April Total	**3.96**
			Total to Date	**45.98**
5/2/97	229	1.35		
5/8/97	235	0.11		
5/19/97	246	0.73		
5/23/97	250	0.20		
5/24/97	251	0.65		
5/25/97	252	0.20		
5/26/97	253	0.85		
5/27/97	254	0.45		
5/28/97	255	0.19		
5/29/97	256	0.43		
5/30/97	257	1.00		
5/31/97	258	2.00		
			May Total	**8.16**
			Total to Date	**54.14**
6/1/97	259	0.28		
6/5/97	263	0.90		
6/9/97	267	1.08		
6/10/97	268	0.35		

Rainfall Dates (mo/da/yr)	Days fro Start	Rainfall (inches)	Monthly Totals	
6/13/97	271	0.09		
6/16/97	274	3.21		
6/17/97	275	0.40		
6/21/97	279	0.50		
6/27/97	285	0.31		
6/29/97	287	0.10		
6/30/97	288	0.88		
			June Total	**8.10**
			Total to Date	**62.24**
7/1/97	289	1.74		
7/4/97	292	0.45		
7/8/97	296	0.38		
7/22/97	310	0.15		
			July Total	**2.72**
			Total to Date	**64.96**
8/8/97	327	0.16		
8/9/97	328	1.00		
8/10/97	329	1.92		
8/13/97	332	2.51		
8/19/97	338	0.10		
8/31/97	350	0.95		
			August Total	**6.64**
			Total to Date	**71.60**
9/9/97	359	0.09		
9/23/97	8	1.13		
9/24/97	9	4.47		
			September Total	**5.69**
			Total to Date	**77.29**
10/13/97	28	0.95		
10/21/97	36	0.74		
10/24/97	39	0.83		
10/26/97	41	1.55		
			October Total	4.07
			Total to Date	81.36
11/1/97	46	0.18		
11/4/97	49	0.89		
11/6/97	51	0.27		
11/11/97	56	0.06		
11/14/97	59	0.43		
11/21/97	66	0.12		
11/24/97	69	0.25		
			November Total	2.2
			Total to Date	83.56
12/1/97	76	0.07		
12/4/97	79	0.05		
12/5/97	80	0.13		
12/9/97	84	0.2		
12/10/97	85	0.39		

Rainfall Dates (mo/da/yr)	Days fro Start	Rainfall (inches)	Monthly Totals	
12/22/97	97	0.59		
12/24/97	99	1.22		
12/26/97	101	0.02		
12/28/97	103	0.6		
12/29/97	104	0.04		
			December Total	3.31
			Total to Date	86.87
1/6/98	112	0.78		
1/7/98	113	2.5		
1/8/98	114	0.3		
1/10/98	116	0.1		
1/12/98	118	0.88		
1/15/98	121	0.18		
1/16/98	122	1.04		
1/19/98	125	0.22		
1/22/98	128	0.25		
1/27/98	133	0.39		
			January Total	6.64
			Total to Date	93.51
2/2/98	139	0.1		
2/3/98	140	0.4		
2/4/98	141	1.67		
2/11/98	148	0.42		
2/16/98	153	0.47		
2/17/89	154	0.98		
2/23/98	160	0.8		
2/27/98	164	1.31		
			February Total	6.15
			Total to Date	99.66
3/5/98	170	0.62		
3/6/98	171	0.65		
3/8/98	173	1.52		
3/16/98	181	0.16		
3/20/98	185	1.5		
3/24/98	189	0.5		
3/31/98	196	0.75		
			March Total	5.70
			Total to Date	105.36
4/3/98	199	0.52		
4/9/98	205	0.02		
4/13/98	209	0.32		
4/17/98	213	1.85		
4/20/98	216	1.76		
4/23/98	219	0.26		
4/27/98	223	0.06		
4/28/98	224	1.2		
4/30/98	226	0.5		
			April Total	6.49
			Total to Date	111.85

Rainfall Dates (mo/da/yr)	Days fro Start	Rainfall (inches)	Monthly Totals	
5/1/98	227	0.32		
5/8/98	234	2.04		
5/26/98	252	0.55		
5/27/98	253	2		
5/28/98	254	0.67		
5/29/98	255	0.27		
			May Total	5.85
			Total to Date	117.70
6/5/98	262	0.4		
6/8/98	265	0.32		
6/15/98	272	0.92		
6/21/98	278	2.72		
			June Total	4.36
			Total to Date	122.06
7/5/98	292	0.73		
7/8/98	295	0.03		
7/14/98	301	3.23		
7/15/98	302	0.62		
7/16/98	303	0.17		
7/23/98	310	0.64		
7/27/98	314	1.26		
			July Total	6.68
			Total to Date	128.74
8/7/98	325	1.2		
8/10/98	328	0.24		
8/11/98	329	0.3		
8/17/98	335	2.4		
			August Total	4.14
			Total to Date	132.88

APPENDIX D

VOLUME OF LEACHATE COLLECTED

Compost Weathering Leachate Volume, Liters										
	Compost Only					Compost + Soil				
	Sample No.			Monthly	Accum.	Sample No.			Monthly	Accum.
Month	1	2	3	Average	Average	4	5	6	Average	Average
Sept. '96	9.350	12.220	6.800	9.457	9.457	2.615	0.245	0.475	1.112	1.112
Oct. '96	19.965	27.710	34.830	27.502	36.958	21.390	11.185	13.380	15.318	16.430
Nov. '96	56.435	56.190	65.260	59.295	96.253	48.810	54.635	54.810	52.752	69.182
Dec. '96	88.660	112.900	140.579	114.046	210.300	70.550	62.260	37.079	56.630	125.811
Jan. '97	91.495	81.535	76.981	83.337	293.637	42.230	46.254	34.236	40.907	166.718
Feb. '97	40.240	38.219	48.103	42.187	335.824	29.457	35.783	26.608	30.616	197.334
Mar. '97	70.831	74.666	69.954	71.817	407.641	26.415	38.216	39.992	34.874	232.208
Apr. '97	19.980	8.346	23.625	17.317	424.958	18.598	26.355	23.514	22.822	255.031
May '97	18.533	18.146	24.295	20.325	445.283	18.559	22.414	17.585	19.519	274.550
June '97	84.990	69.055	72.206	75.417	520.700	101.291	101.049	73.285	91.875	366.425
July '97	8.984	7.763	9.165	8.637	529.337	19.532	14.856	17.754	17.381	383.806
Aug. '97	26.977	27.966	25.999	26.981	556.318	32.594	23.707	34.977	30.426	414.232
Sep. '97	26.500	23.500	27.300	25.767	582.084	23.500	23.980	23.820	23.767	437.998
Oct. '97 *	26.035	27.026	24.646	25.902	607.987	24.085	3.846	25.851	24.968	462.966
Nov. '97	9.694	13.105	13.715	12.171	620.158	25.013	12.837	17.901	18.584	481.550
Dec. '97	57.584	57.680	54.810	56.691	676.849	38.051	51.259	25.069	38.126	519.676
Jan. '98	76.867	81.034	77.613	78.505	755.354	43.870	84.169	23.339	50.459	570.136
Feb. '98	92.214	92.542	92.108	92.288	847.642	49.953	84.887	24.070	52.970	623.106
Mar. '98	39.456	33.399	39.356	37.404	885.046	66.680	36.294	57.446	53.473	676.579
Apr. '98	68.650	69.210	67.100	68.320	953.366	58.600	52.800	60.830	57.410	733.989
May '98	47.150	47.200	37.100	43.817	997.182	36.800	28.700	39.700	35.067	769.056
Jun. '98	0.000	0.000	0.000	0.000	997.182	0.000	0.000	0.000	0.000	769.056
Jul. '98	31.500	28.300	32.700	30.833	1028.016	33.200	26.300	43.200	34.233	803.289
Aug. '98	33.400	31.800	32.000	32.400	1060.416	21.750	26.700	32.400	26.950	830.239
Sep. '98										
Totals	**1045.490**	**1039.512**	**1096.245**			**853.543**	**868.731**	**747.321**		

* Container 5 was not used in the average since its drain was partially plugged

Leachate Volume Data, Liters										
		Compost Only			Soil+Compost			Average	Average	
Days from		Sample No.			Sample No.			Compost	Compost	Deliver
Start	Date	1	2	3	4	5	6	Only	+ Soil	Composite
7	9/22/96	4,475	4,970	2,800	15	0	0	4,082	5	
12	9/27/96	4,875	7,250	4,000	2,600	245	475	5,375	1,107	
23	10/8/96	680	580	2,795	0	0	390	1,352	130	
34	10/19/96	1,350	730	2,400	0	0	0	1,493	0	
38	10/23/96	990	740	1,245	1,830	220	440	992	830	
39	10/24/96	0	0	420	0	330	0	140	110	
42	10/27/96	500	670	560	5,750	450	540	577	2,247	
43	10/28/96	320	490	285	12,510	640	970	365	4,707	
45	10/30/96	2,375	20,500	14,125	1,300	8,125	9,840	12,333	6,422	
46	10/31/96	13,750	4,000	13,000	0	1,420	1,200	10,250	873	
49	11/3/96	18,000	15,000	19,250	12,250	12,300	13,750	17,417	12,767	
53	11/7/96	4,000	4,000	4,000	3,800	4,000	3,900	4,000	3,900	
56	11/10/96	10,625	12,250	20,500	10,500	14,625	14,500	14,458	13,208	
63	11/17/96	3,450	4,000	2,250	1,200	4,000	4,000	3,233	3,067	
66	11/20/96	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	
70	11/24/96	6,000	7,000	4,000	4,000	7,000	5,750	5,667	5,583	
72	11/26/96	10,360	9,940	11,260	13,060	8,710	8,910	10,520	10,227	
77	12/1/96	5,750	6,500	7,600	17,500	5,750	5,100	6,617	9,450	
79	12/3/97	9,310	8,250	12,250	11,250	5,250	4,100	9,937	6,867	
83	12/7/97	20,750	19,500	35,100	14,000	11,250	7,000	25,117	10,750	Start
92	12/16/97	9,270	16,250	22,250	5,000	7,000	2,850	15,923	4,950	12/16/97
93	12/17/97	3,080	4,500	4,129	800	2,010	1,379	3,903	1,396	
98	12/22/97	12,750	11,750	12,500	3,500	5,000	2,500	12,333	3,667	
99	12/23/97	7,250	19,400	19,750	4,750	3,750	2,750	15,467	3,750	
105	12/29/97	17,000	22,500	23,500	11,000	18,250	9,000	21,000	12,750	
107	12/31/97	3,500	4,250	3,500	2,750	4,000	2,400	3,750	3,050	12/31/97
112	1/5/97	3,500	4,250	3,500	2,750	4,000	2,400	3,750	3,050	
116	1/9/97	6,250	7,500	5,500	5,000	6,000	3,500	6,417	4,833	
120	1/13/97	400	1,220	840	5,620	1,440	2,000	820	3,020	1/15/97
127	1/20/97	21,000	21,000	19,000	7,750	12,250	7,000	20,333	9,000	
130	1/23/97	23,500	13,500	8,500	7,000	8,887	7,661	15,167	7,849	
133	1/26/97	22,000	22,000	20,000	8,250	9,000	8,750	21,333	8,667	
136	1/29/97	11,695	11,565	13,391	4,610	3,677	3,575	12,217	3,954	1/30/97

Leachate Volume Data, Liters										
		Compost Only			Soil+Compost			Average	Average	
Days from		Sample No.			Sample No.			Compost	Compost	Deliver
Start	Date	1	2	3	4	5	6	Only	+ Soil	Composite
142	2/4/97	9,000	8,640	11,220	5,440	6,000	4,300	9,620	5,247	
147	2/9/97	11,844	12,438	10,857	7,150	7,654	5,350	11,713	6,718	
151	2/13/97	204	87	51	2,678	3,111	2,466	114	2,752	2/14/97
155	2/17/97	9,170	9,715	9,345	3,800	4,455	3,515	9,410	3,923	
161	2/23/97	5,040	3,520	6,530	6,200	8,990	6,650	5,030	7,280	
165	2/27/97	4,982	3,819	10,100	4,189	5,573	4,327	6,300	4,696	2/27/97
168	3/2/97	17,300	17,200	22,400	3,000	4,600	5,900	18,967	4,500	
170	3/4/97	22,351	22,351	22,352	2,080	3,429	3,291	22,351	2,933	
172	3/6/97	22,500	17,100	13,450	1,632	3,355	3,044	17,683	2,677	
175	3/9/97	2,350	7,468	240	2,091	4,094	3,851	3,353	3,345	
178	3/12/97	0	1,459	0	2,468	3,826	4,363	486	3,552	3/13/97
182	3/16/97	759	1,928	1,579	3,287	4,165	5,054	1,422	4,169	
189	3/23/97	4,686	6,677	8,749	5,417	6,628	7,346	6,704	6,464	
196	3/30/97	585	483	1,184	6,440	8,519	7,143	751	7,367	3/31/97
203	4/6/97	4,362	1,856	7,063	6,001	7,222	6,543	4,427	6,589	
211	4/14/97	498	712	246	6,352	7,555	6,796	485	6,901	4/15/97
218	4/21/97	0	0	0	2,125	3,824	4,157	0	3,369	
226	4/29/97	15,120	5,778	16,316	4,120	7,754	6,018	12,405	5,964	4/30/97
232	5/5/97	11,162	10,977	13,395	4,384	7,696	5,179	11,845	5,753	
239	5/12/97	0	137	0	2,723	2,739	3,870	46	3,111	5/15/97
253	5/26/97	0	295	480	1,820	640	2,320	258	1,593	
256	5/29/97	7,371	6,737	10,420	9,632	11,339	6,216	8,176	9,062	5/29/97
260	6/2/97	23,500	15,654	23,500	9,762	12,239	7,282	20,885	9,761	
263	6/5/97	14,351	22,154	3,907	16,870	18,259	9,342	13,471	14,824	
266	6/8/97	6,615	6,442	5,307	10,796	12,233	7,028	6,121	10,019	
270	6/12/97	17,074	8,995	16,492	12,161	13,342	9,783	14,187	11,762	6/16/97
276	6/18/97	23,450	5,000	23,000	23,500	18,000	18,100	17,150	19,867	
281	6/23/97	0	6,810	0	16,602	15,801	11,400	2,270	14,601	
287	6/29/97	0	4,000	0	11,600	11,175	10,350	1,333	11,042	6/30/97
290	7/2/97	8,984	3,383	9,195	6,750	4,360	4,744	7,187	5,285	
294	7/6/97	0	2,610	0	10,612	4,096	7,460	870	7,389	
298	7/10/97	0	1,770	0	2,170	6,400	5,550	590	4,707	7/14/97
332	8/13/97	4,365	5,133	3,411	9,224	7,396	11,172	4,303	9,264	

Leachate Volume Data, Liters										
Days from Start	Date	Compost Only Sample No. 1	Compost Only Sample No. 2	Compost Only Sample No. 3	Soil+Compost Sample No. 4	Soil+Compost Sample No. 5	Soil+Compost Sample No. 6	Average Compost Only	Average Compost + Soil	Deliver Composite
333	8/14/97	22,612	22,833	22,588	8,655	5,189	7,847	22,678	7,230	
339	8/19/97	0	0	0	14,715	8,122	15,958	0	12,932	
348	8/28/97	0	0	0	0	3,000	0	0	1,000	8/28/97
355	9/4/97	3,000	0	3,800	0	480	320	2,267	267	9/15/97
14	9/29/97	23,500	23,500	23,500	23,500	23,500	23,500	23,500	23,500	9/29/97
24	10/9/97	0	0	0	7,400	0	7,440	0	4,947	
29	10/14/97	2,725	6,766	2,820	1,999	146	3,256	4,104	1,800	
35	10/20/97	410	20	226	986	0	1,795	219	927	
41	10/26/97	21,500	18,800	21,500	9,100	18,000	10,200	20,600	12,433	
42	10/27/97	1,400	1,440	1,000	4,600	1,900	3,160	1,280	3,220	
50	11/4/97	13,563	14,878	13,077	18,815	12,505	11,609	13,839	14,310	
53	11/7/97	3,059	2,872	3,193	4,450	2,449	3,679	3,041	3,526	
56	11/10/97	0	0	0	4,180	0	2,970	0	2,383	
60	11/14/97	4,875	5,083	5,247	4,293	4,228	3,182	5,068	3,901	
67	11/21/97	1,360	1,150	1,125	8,720	300	5,350	1,212	4,790	
70	11/24/97	4,000	4,000	4,150	3,370	3,100	2,720	4,050	3,063	
77	12/1/97	8,271	8,330	8,670	3,888	7,677	4,955	8,424	5,507	12/1/98
84	12/8/97	6,384	6,382	6,369	6,303	6,026	5,583	6,378	5,971	
88	12/12/97	10,800	10,800	9,053	8,685	7,000	3,886	10,218	6,524	
98	12/22/97	6,729	7,488	7,123	5,655	5,159	4,965	7,113	5,260	
102	12/26/97	18,000	17,380	16,200	7,720	16,000	2,860	17,193	8,860	
107	12/31/97	7,400	7,300	7,400	5,800	9,400	2,820	7,367	6,007	
112	1/5/98	7,765	7,232	8,173	7,334	6,249	3,305	7,723	5,629	
114	1/7/98	18,000	18,000	18,000	0	15,600	0	18,000	5,200	
116	1/9/98	10,139	12,850	9,687	7,470	20,871	3,549	10,892	10,630	
119	1/12/98	12,000	14,000	13,000	4,600	112,300	2,800	13,000	39,900	
123	1/16/98	16,563	16,552	16,343	6,265	15,629	3,274	16,486	8,389	
128	1/21/98	4,200	4,000	4,110	6,400	4,820	4,100	4,103	5,107	
133	1/26/98	5,100	5,200	5,200	4,700	5,800	3,360	5,167	4,620	
137	1/30/98	3,100	3,200	3,100	7,100	2,900	2,950	3,133	4,317	
144	2/6/98	22,000	22,000	22,500	9,000	22,000	4,700	22,167	11,900	2/6/98
150	2/12/98	6,508	6,993	6,352	8,006	6,693	4,603	6,618	6,434	
155	2/17/98	20,000	20,000	20,200	6,700	15,700	3,000	20,067	8,467	

Leachate Volume Data, Liters										
		Compost Only			Soil+Compost			Average	Average	
Days from		Sample No.			Sample No.			Compost	Compost	Deliver
Start	Date	1	2	3	4	5	6	Only	+ Soil	Composite
161	2/23/98	11,200	11,200	11,300	7,100	11,000	4,000	11,233	7,367	
165	2/27/98	18,500	18,000	18,000	8,000	18,000	2,980	18,167	9,660	
172	3/6/98	14,006	14,349	13,756	11,147	11,494	4,787	14,037	9,143	
182	3/16/98	0	0	0	15,333	0	10,673	0	8,669	
183	3/17/98	0	0	0	22,000	0	22,000	0	14,667	
186	3/20/98	19,050	19,050	19,000	9,000	16,000	10,000	19,033	11,667	
190	3/24/98	6,400	6,000	6,600	9,200	4,800	10,000	6,333	8,000	
203	4/6/98	16,000	16,200	14,700	8,700	4,000	8,400	15,633	7,033	4/6/98
214	4/17/98	21,500	21,000	20,000	16,000	9,100	16,000	20,833	13,700	
217	4/20/98	21,000	21,000	22,000	21,000	21,000	21,000	21,333	21,000	
224	4/27/98	3,000	3,000	2,500	1,800	2,500	1,330	2,833	1,877	
226	4/29/98	18,000	1,901	17,500	15,200	15,500	17,800	12,467	16,167	
233	5/6/98	5,150	5,200	5,100	4,600	4,700	4,700	5,150	4,667	
235	5/8/98	21,000	21,000	20,000	20,000	14,000	20,000	20,667	18,000	
256	5/29/98	21,000	21,000	12,000	12,200	10,000	15,000	18,000	12,400	
298	7/10/98	10,500	11,000	10,600	5,600	1,150	14,000	10,700	6,917	6/29/98
303	7/15/98	14,000	12,500	17,500	16,500	17,000	21,000	14,667	18,167	
312	7/24/98	3,000	3,000	3,000	4,000	4,200	4,000	3,000	4,067	
316	7/28/98	4,000	1,800	1,650	7,100	4,200	4,200	2,483	5,167	7/31/98
329	8/10/98	11,400	9,800	10,000	10,550	750	4,700	10,400	5,333	
337	8/18/98	22,000	22,000	22,000	22,000	21,000	22,000	22,000	21,667	

APPENDIX E
DETECTION LIMITS

The explosive and explosive by-product method detection limits (MDLs) for each sample are provided in the following tables. The MDLs listed varied for each explosives analysis because they are corrected for the final volume of acetonitrile when water samples are extracted into acetonitrile by a salting-out process. No attempt was made to bring each extract to the same final volume, so the final volumes vary. In addition, some of the early samples exhibited a very dark color and had to be diluted in order to successfully perform the analysis. These dilution factors are also included in the MDL calculation.

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9609042-01	1CW.COW1.9/27/96	0.34	0.112	0.297	0.29	1.18	1.1	0.647	0.318	0.287	0.538
9609042-02	2CW.COW2.9/27/96	2.3	0.764	1.74	1.4	3.77	3.3	3.7	1.69	1.55	3
9609042-03	3CW.COW3.9/27/96	1.3	0.131	0.971	0.8	1.99	1.6	1.86	0.906	0.806	1.56
9609042-04	4CW.CSW1.9/27/96	8.4	2.28	8.07	6.6	23.4	15	17.3	9.06	7.3	13.1
9609042-05	5CW.CSW2.9/27/96	4.9	1.19	4.43	3.9	12.2	9.2	9.83	4.97	4.21	8.05
9609042-06	6CW.CSW3.9/27/96	3.8	0.84	3.23	2.9	8.66	7.2	7.28	3.62	3.14	6.19
9609043-02	2CW.COW2.9/22/96	2.04	0.147	0.36	1.59	1.34	0.253	0.797	0.391	0.352	0.663
9609043-03	3CW.COW3.9/22/96	2.13	0.15	0.358	1.69	1.52	0.28	0.785	0.405	0.364	0.669
9609043-04	4CW.CSW1.9/22/96	11.9	0.8	2.1	9.5	5.5	1	4.9	2.3	2.1	3.9
9610010-01	1CW.COW1.10/8/96	3.49	0.26	0.618	2.7	2.82	0.483	1.23	0.662	0.592	1.15
9610010-02	2CW.COW2.10/8/96	6.45	0.376	1.21	4.84	2.8	0.481	2.49	1.24	1.12	2.04
9610010-03	3CW.COW3.10/8/96	2.53	0.21	0.416	1.93	1.99	0.356	0.916	0.461	0.429	0.817
9610010-04	4CW.CSW3.1008/96	3.01	0.197	0.517	2.16	1.49	0.263	1.13	0.546	0.495	0.93
9611002-01	1.cw.cow.1.11/3/96	6.31	0.499	1.06	4.53	3.56	0.715	2.08	1.07	0.982	1.9
9611002-02	2.cw.cow.2.11/3/96	6.57	0.429	1.26	5.3	3.19	0.666	2.35	1.23	1.13	2.19
9611002-03	3.cw.cow.3.11/3/96	1.96	0.147	0.353	3.51	1.57	0.31	0.692	0.37	0.331	0.646
9611002-04	4.cw.csw.1.11/3/96	1.97	0.142	0.44	1.87	1.35	0.244	0.935	0.479	0.432	0.837
9611002-05	5.cw.csw.2.11/3/96	3.33	0.234	0.719	3.22	2	0.348	1.17	0.84	0.589	1.14
9611002-06	6.cw.csw.3.11/3/96	2.74	0.196	0.641	2.61	1.73	0.306	1.28	0.674	0.587	1.14
9611024-01	1.cw.cow.1.11/20/96	1.48	0.095	0.277	1.22	0.897	0.192	0.57	0.274	0.244	0.467
9611024-02	2.cw.cow.2.11/20/96	1.27	0.107	0.255	1.19	1.03	0.19	0.514	0.273	0.241	0.469
9611024-03	3.cw.cow.3.11/20/96	1.44	0.126	0.306	1.37	1.13	0.198	0.629	0.305	0.279	0.546
9611024-04	4.cw.csw.1.11/20/96	1.55	0.103	0.274	1.17	0.862	0.158	0.605	0.291	0.258	0.481
9611024-05	5.cw.csw.2.11/20/96	1.37	0.0958	0.242	1.03	0.905	0.168	0.554	0.257	0.235	0.449
9611024-06	6.cw.csw.3.11/20/96	1.28	0.108	0.244	1.094	0.942	0.162	0.528	0.271	0.243	0.467
9612003-01	1.cw.cow.1.12/3/96	0.659	0.758	0.646	0.659	0.877	0.782	0.771	0.647	0.66	0.642
9612003-02	2.cw.cow.2.12/3/96	0.61	0.708	0.612	0.63	0.872	0.87	0.7	0.588	0.602	0.594

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6-Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9612003-03	3.cw.cow.3.12/3/96	0.604	0.74	0.642	0.638	0.822	0.822	0.745	0.609	0.622	0.629
9612003-04	4.cw.csw.1.12/3/96	1.43	0.0827	0.189	0.889	0.952	0.214	0.411	0.215	0.196	0.365
9612003-05	5.cw.csw.2.12/3/96	1.63	0.124	0.3	1.32	1.14	0.212	0.682	0.333	0.291	0.561
9612003-06	6.cw.csw.3.12/3/96	1.56	0.11	0.28	1.2	0.978	0.182	0.638	0.307	0.269	0.513
9612033-01	1.cw.cow.1.12/16/96	0.146	0.0369	0.0966	0.096	0.345	0.31	0.211	0.102	0.0892	0.174
9612033-02	2.cw.cow.2.12/16/96	0.5	0.12	0.308	0.31	1.09	1	0.687	0.332	0.287	0.56
9612033-03	3.cw.cow.3.12/16/96	0.44	0.113	0.281	0.28	0.954	0.86	0.635	0.309	0.27	0.516
9612033-04	4.cw.csw.1.12/16/96	0.33	0.0752	0.195	0.2	0.69	0.64	0.455	0.219	0.192	0.366
9612033-05	5.cw.csw.2.12/16/96	0.38	0.102	0.246	0.25	0.904	0.81	0.579	0.281	0.249	0.476
9612033-06	6.cw.csw.3.12/16/96	0.44	0.108	0.267	0.27	0.902	0.86	0.633	0.302	0.27	0.511
9612065-01	1.cw.cow1.12/31/96	1.26	0.116	0.25	1.15	0.994	0.163	0.535	0.271	0.242	0.463
9612065-02	2.cw.cow.2.12/31/96	1.27	0.114	0.236	1.07	0.915	0.153	0.524	0.252	0.23	0.447
9612065-03	3.CW.COW.3.12/31/96	1.23	0.106	0.227	1.04	0.937	0.16	0.505	0.25	0.23	0.432
9612065-04	4.CW.CSW.1.12/31/96	1.33	0.103	0.242	1.08	0.928	0.154	0.551	0.263	0.242	0.458
9612065-05	5.CW.CSW.2.12/31/96	1.19	0.096	0.231	1.01	0.873	0.139	0.491	0.247	0.225	0.439
9612065-06	6.CW.CSW.3.12/31/96	1.21	0.101	0.232	1.05	0.879	0.15	0.503	0.258	0.232	0.443
9701016-01	1.cw.cow.1.1/15/97	1.52	0.105	0.303	1.28	0.987	0.19	0.619	0.299	0.263	0.501
9701016-02	2.cw.cow.2.1/15/97	1.51	0.109	0.293	1.3	1.01	0.187	0.65	0.309	0.272	0.526
9701016-03	3.cw.cow.3.1/15/97	1.48	0.109	0.274	1.22	0.946	0.179	0.62	0.3	0.265	0.503
9701016-04	4.cw.csw.1.1/15/97	1.34	0.0926	0.228	0.996	0.803	0.152	0.553	0.257	0.231	0.439
9701016-05	5.cw.csw.2.1/15/97	1.38	0.0975	0.249	1.1	0.861	0.16	0.588	0.281	0.248	0.47
9701016-06	6.cw.csw.3.1/15/97	1.58	0.108	0.265	1.17	0.955	0.176	0.617	0.296	0.262	0.511
9701053-01	1.cw.cow.1.01/30/97	0.626	0.776	0.644	0.758	0.885	1.02	0.746	0.626	0.636	0.629
9701053-02	2.cw.cow.2.1/30/97	0.646	0.788	0.641	0.659	0.893	0.99	0.771	0.646	0.654	0.645
9701053-03	3.cw.cow.3.1/30/97	0.625	0.76	0.62	0.649	0.841	0.915	0.729	0.631	0.627	0.618
9701053-04	4.cw.csw.1.1/30/97	0.626	0.778	0.606	0.633	0.85	0.895	0.731	0.623	0.62	0.618

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9701053-05	5.cw.csw.2.1/30/97	0.586	0.714	0.583	0.605	0.845	0.891	0.697	0.593	0.595	0.59
9701053-06	6.cw.csw.3.1/30/97	0.653	0.806	0.642	0.669	0.848	0.899	0.772	0.659	0.652	0.657
9702031-01	1.CW.COW.1.2/14/97	0.578	0.696	0.57	0.574	0.809	0.901	0.675	0.568	0.577	0.569
9702031-02	2.CW.COW.2.2/14/97	0.578	0.716	0.564	0.581	0.808	0.903	0.677	0.563	0.564	0.567
9702031-03	3.CW.COW.3.2/14/97	0.625	0.698	0.567	0.579	0.878	0.995	0.693	0.583	0.592	0.596
9702031-04	4.CW.CSW.1.2/14/97	0.422	0.528	0.406	0.413	0.608	0.667	0.483	0.415	0.421	0.416
9702031-05	5.CW.CSW.2.2/14/97	0.525	0.662	0.509	0.517	0.76	0.822	0.607	0.52	0.525	0.521
9702031-06	6.CW.CSW.3.2/14/97	0.528	0.658	0.497	0.517	0.752	0.81	0.619	0.505	0.515	0.508
9702046-01	1.CW.COW.1.02/27/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9702046-02	2.CW.COW.2.02/27/97	0.461	0.553	0.461	0.461	0.461	0.461	0.553	0.461	0.461	0.461
9702046-03	3.CW.COW.3.02/27/97	0.474	0.568	0.474	0.474	0.474	0.474	0.568	0.474	0.474	0.474
9702046-04	4.CW.CSW.1.02/27/97	0.474	0.568	0.474	0.474	0.474	0.474	0.568	0.474	0.474	0.474
9702046-05	5.CW.CSW.2.02/27/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9702046-06	6.CW.CSW.3.02/27/97	0.421	0.505	0.421	0.421	0.421	0.421	0.505	0.421	0.421	0.421
9703018-01	1.CW.COW.1.03/13/97	0.303	0.363	0.303	0.303	0.303	0.303	0.363	0.303	0.303	0.303
9703018-02	2.CW.COW.2.03/13/97	0.395	0.474	0.395	0.395	0.395	0.395	0.474	0.395	0.395	0.395
9703018-03	3.CW.COW.3.03/13/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9703018-04	4.CW.CSW.1.03/13/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9703018-05	5.CW.CSW.2.03/13/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9703018-06	6.CW.CSW.3.03/13/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9703042-01	1.CW.COW.1.03/31/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9703042-02	2.CW.COW.2.03/31/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9703042-03	3.CW.COW.3.03/31/97	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9703042-04	4.CW.CSW.1.03/31/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9703042-05	5.CW.CSW.2.03/31/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9703042-06	6.CW.CSW.3.03/31/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9704021-01	1.CW.COW.1.4/15/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9704021-02	2.CW.COW.2.4/15/97	0.461	0.553	0.461	0.461	0.461	0.461	0.553	0.461	0.461	0.461

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9704021-03	3.CW.COW.3.4/15/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9704021-04	4.CW.CSW.1.4/15/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9704021-05	5.CW.CSW.2.4/15/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9704021-06	6.CW.CSW.3.4/15/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9704056-01	1.CW.COW.1.4/30/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9704056-02	2.CW.COW.2.4/30/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9704056-03	3.CW.COW.3.4/30/97	0.447	0.537	0.447	0.447	0.447	0.447	0.537	0.447	0.447	0.447
9704056-04	4.CW.CSW.1.4/30/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9704056-05	5.CW.CSW.2.4/30/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9704056-06	6.CW.CSW.3.4/30/97	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9705032-01	1.CW.COW.1.5/15/97	0.461	0.553	0.461	0.461	0.461	0.461	0.553	0.461	0.461	0.461
9705032-02	2.CW.COW.2.5/15/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9705032-03	3.CW.COW.3.5/15/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9705032-04	4.CW.CSW.1.5/15/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9705032-05	5.CW.CSW.2.5/15/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9705032-06	6.CW.CSW.3.5/15/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9705043-01	1.CW.COW.1.5/29/97	0.461	0.553	0.461	0.461	0.461	0.461	0.553	0.461	0.461	0.461
9705043-02	2.CW.COW.2.5/29/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9705043-03	3.CW.COW.3.5/29/97	0.408	0.489	0.408	0.408	0.408	0.408	0.489	0.408	0.408	0.408
9705043-04	4.CW.CSW.1.5/29/97	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9705043-05	5.CW.CSW.2.5/29/97	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9705043-06	6.CW.CSW.3.5/29/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706042-01	1.CW.COW.1.6/16/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9706042-02	2.CW.COW.2.6/16/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9706042-03	3.CW.COW.3.6/16/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706042-04	4.CW.CSW.1.6/16/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706042-05	5.CW.CSW.2.6/16/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9706042-06	6.CW.CSW.3.6/16/97	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9706063-01	1.CW.COW.1.6/30/97	0.382	0.458	0.382	0.382	0.382	0.382	0.458	0.382	0.382	0.382
9706063-02	2.CW.COW.2.6/30/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706063-03	3.CW.COW.3.6/30/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706063-04	4.CW.CSW.1.6/30/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9706063-05	5.CW.CSW.2.6/30/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9706063-06	6.CW.CSW.3.6/30/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9707013-01	1.CW.COW.1.7/14/97	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9707013-02	2.CW.COW.2.7/14/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9707013-03	3.CW.COW.3.7/14/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9707013-04	4.CW.CSW.1.7/14/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9707013-05	5.CW.CSW.2.7/14/97	0.566	0.679	0.566	0.566	0.566	0.566	0.679	0.566	0.566	0.566
9707013-06	6.CW.CSW.3.7/14/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9708061-01	1.CW.COW.1.08/28/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9708061-02	2.CW.COW.2.08/28/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9708061-03	3.CW.COW.3.08/28/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9708061-04	4.CW.CSW.1.08/28/98	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9708061-05	5.CW.CSW.2.08/28/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9708061-06	6.CW.CSW.3.08/28/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9708009-01	Sample #1 from compo	0.0674	0.0449	0.0449	0.0449	0.674	0.449	0.0449	0.0449	0.0449	0.0449
9708009-02	Sample #2 from compo	0.0737	0.0492	0.0492	0.0492	0.737	0.492	0.0492	0.0492	0.0492	0.0492
9708009-03	Sample #3 from compo	0.0689	0.046	0.046	0.046	0.689	0.46	0.046	0.046	0.046	0.046
9708009-04	Sample #4 from compo	0.0716	0.0477	0.0477	0.0477	0.716	0.477	0.0477	0.0477	0.0477	0.0477
9709001-01	compost/soil 101A	0.013	0.015	0.013	0.013	0.013	0.013	0.015	0.013	0.013	0.013
9709001-02	compost/soil 101B	0.0125	0.0149	0.0125	0.0125	0.0125	0.0125	0.0149	0.0125	0.0125	0.0125
9709001-03	compost/soil 101C	0.013	0.015	0.013	0.013	0.013	0.013	0.015	0.013	0.013	0.013

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9709001-04	compost/soil 010D	0.013	0.015	0.013	0.013	0.013	0.013	0.015	0.013	0.013	0.013
9709020-01	1.CW.COW.1.09/15/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9709020-03	3.CW.COW.3.09/15/97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9709020-05	5.CW.CSW.2.09/15/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9709020-06	6.CW.CSW.3.09/15/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9709055-01	1.CW.COW.1.9/29/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9709055-02	2.CW.COW.2.9/29/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9709055-03	3.CW.COW.3.9/29/97	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9709055-04	4.CW.CSW.1.9/29/97	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9709055-05	5.CW.CSW.2.9/29/97	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9709055-06	6.CW.CSW.3.9/29/97	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9712016-01	1.CW.COW.1.12/4/97	0.408	0.489	0.408	0.408	0.408	0.408	0.489	0.408	0.408	0.408
9712016-02	2.CW.COW.2.12/4/97	0.421	0.505	0.421	0.421	0.421	0.421	0.505	0.421	0.421	0.421
9712016-03	3.CW.COW.3.12/4/97	0.408	0.489	0.408	0.408	0.408	0.408	0.489	0.408	0.408	0.408
9712016-04	4.CW.CSW.1.12/4/97	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9712016-05	5.CW.CSW.2.12/4/97	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9712016-06	6.CW.CSW.3.12/4/97	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9802007-01	1.CW.COW.1.COMPO	0.152	0.102	0.102	0.102	1.52	1.02	0.102	0.102	0.102	0.102
9802007-02	2.CW.COW.2.COMPO	0.152	0.101	0.101	0.101	1.52	1.01	0.101	0.101	0.101	0.101
9802007-03	3.CW.COW.3.COMPO	0.146	0.0972	0.0972	0.0972	1.46	0.972	0.0972	0.0972	0.0972	0.0972
9802007-04	4.CW.CSW.4COMPOS	0.15	0.1	0.1	0.1	1.5	1	0.1	0.1	0.1	0.1
9802007-05	5.CW.CSW.5COMPOS	0.15	0.1	0.1	0.1	1.5	1	0.1	0.1	0.1	0.1
9802007-06	6.CW.CSW.6.COMPO	0.15	0.1	0.1	0.1	1.5	1	0.1	0.1	0.1	0.1
9803007-01	1.CW.COW.1.2/4/98	0.408	0.489	0.408	0.408	0.408	0.408	0.489	0.408	0.408	0.408
9803007-02	2.CW.COW.2.2/4/98	0.487	0.584	0.487	0.487	0.487	0.487	0.584	0.487	0.487	0.487
9803007-03	3.CW.COW.3.2/4/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9803007-04	4.CW.CSW.1.2/4/98	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9803007-05	5.CW.CSW.2.2/4/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5

LAB_ID	CUSTOMER_ID	HMX	RDX	2,4,6-Trinitrotoluene (TNT)	1,3,5-Trinitrobenzene (TNB)	2,6,Diamino-4-nitrotoluene (2,6-DANT)	2,4-Diamino-6-nitrotoluene (2,4-DANT)	2,6-Dinitrotoluene (2,6-DNT)	2,4-Dinitrotoluene (2,4-DNT)	2-Amino-4,6-dinitrotoluene (2A-DNT)	4-Amino-2,6-dinitrotoluene (4A-DNT)
9803007-06	6.CW.CSW.3.2/4/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9810025-01	1.CW.COW.1.4/3/98	0.474	0.568	0.474	0.474	0.474	0.474	0.568	0.474	0.474	0.474
9810025-02	2.CW.COW.2.4/3/98	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9810025-03	3.CW.COW.3.4/3/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9810025-04	4.CW.CSW.4.4/3/98	0.553	0.663	0.553	0.553	0.553	0.553	0.663	0.553	0.553	0.553
9810025-05	5.CW.CSW.5.4/3/98	0.539	0.647	0.539	0.539	0.539	0.539	0.647	0.539	0.539	0.539
9810025-06	6.CW.CSW.6.4/3/98	0.526	0.632	0.526	0.526	0.526	0.526	0.632	0.526	0.526	0.526
9809025-01	1.CW.COW.1.6/29/98	0.447	0.537	0.447	0.447	0.447	0.447	0.537	0.447	0.447	0.447
9809025-02	2.CW.COW.2.6/29/98	0.421	0.505	0.421	0.421	0.421	0.421	0.505	0.421	0.421	0.421
9809025-03	3.CW.COW.3.6/29/98	0.421	0.505	0.421	0.421	0.421	0.421	0.505	0.421	0.421	0.421
9809025-04	4.CW.CSW.4.6/29/98	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9809025-05	5.CW.CSW.5.6/29/98	0.421	0.505	0.421	0.421	0.421	0.421	0.505	0.421	0.421	0.421
9809025-06	6.CW.CSW.6.6/29/98	0.447	0.537	0.447	0.447	0.447	0.447	0.537	0.447	0.447	0.447
9809029-01	1.CW.COW.1.7/31/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9809029-02	2.CW.COW.2.7/31/98	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9809029-03	3.CW.COW.3.7/31/98	0.434	0.521	0.434	0.434	0.434	0.434	0.521	0.434	0.434	0.434
9809029-04	4.CW.CSW.4.7/31/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9809029-05	5.CW.CSW.5.7/31/98	0.513	0.616	0.513	0.513	0.513	0.513	0.616	0.513	0.513	0.513
9809029-06	6.CW.CSW.6.7/31/98	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
9809031-01	1.cw.cow.1.COMPOST	0.12	0.08	0.08	0.08	1.2	0.8	0.08	0.08	0.08	0.08
9809031-02	2.cw.cow.2.COMPOST	0.134	0.0896	0.0896	0.0896	1.34	0.896	0.0896	0.0896	0.0896	0.0896
9809031-03	3.cw.cow.3.COMPOST	0.122	0.081	0.081	0.081	1.22	0.81	0.081	0.081	0.081	0.081
9809031-04	4.cw.csw.4COMPOST	0.118	0.0788	0.0788	0.0788	1.18	0.788	0.0788	0.0788	0.0788	0.0788
9809031-05	5.cw.csw.5.COMPOST	0.116	0.0774	0.0774	0.0774	1.16	0.774	0.0774	0.0774	0.0774	0.0774
9809031-06	6.cw.csw.6.COMPOST	0.117	0.0778	0.0778	0.0778	1.17	0.778	0.0778	0.0778	0.0778	0.0778

APPENDIX F

DATA SET - EXPLOSIVES AND DEGRADATION BY-PRODUCTS IN LEACHATE

Table F-1, TNT

TNT (mg/L) (2,4,6 Trinitrotoluene)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			0.00	0.00	0.00
10/19/96								
10/23/96								
10/24/96								
10/27/96								
10/28/96								
10/30/96								
10/31/96								
11/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/24/96								
12/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/16/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/31/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/16/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/14/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/28/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detection limit

Table F-2, RDX

RDX (mg/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	SNC	13.9	9.82	0.00			11.9	0.00
9/27/96	8.52	56.3	7.72	0.00	0.00	0.00	24.2	0.00
10/8/96	8.39	0.00	17.4			26.4	8.66*	26.4
11/3/96	0.00	0.00	0.00	13.3	18.9	11.3	0.00	14.5
######	0.00	0.00	0.00	7.83	10.3	7.74**	0.00	8.62
12/3/96	0.00	0.00	0.00	2.52	5.68**	3.52**	0.00	3.91
######	0.00	0.00	0.00	2.15**	4.96**	2.42**	0.00	3.18
######	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	3.71	0.976	0.918	0.00	0.00	0.00	1.87	0.00
3/13/97	1.02	2.15	1.27	0.00	0.00	0.00	1.48	0.00
3/31/97	5.98	0.686	1.54	0.00	0.00	0.00	2.74	0.00
4/15/97	5.89	2.73	3.84	0.00	0.00	0.00	4.15	0.00
4/30/97	5.75**	4.43**	2.84**	0.00	0.00	0.00	4.34	0.00
5/15/97	4.12	4.05	3.01	0.00	0.00	0.00	3.73	0.00
5/29/97	4.19**	2.78**	0.881**	0.00	0.00	0.00	2.62	0.00
6/16/97	1.62	1.20	1.32	0.00	0.00	0.00	1.38	0.00
6/30/97	0.824	0.00	0.00	0.00	0.00	0.00	0.475*	0.00
7/14/97	1.72**	0.811**	1.56**	3.55**	0.00	0.00	1.36	1.40*
8/28/97	2.05**	0.674**	1.26**	0.00	0.00	0.00	1.33	0.00
9/15/97	0.00		0.00		0.00	0.00	0.00	0.00
9/29/97	0.64	5.05	2.74	0.00	0.00	0.00	2.81	0.00
12/4/97	2.47	0.00	0.98	0.00	0.00	0.00	1.25*	0.00
2/5/98	3.06	0.75	0.70	0.00	0.00	0.00	1.50	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	1.50	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	1.50	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detection limit

* One or more samples were below detection limit, average based on one-half the detection limit

** On one or more samples associated quality control sample was out of limits

Table F-3, HMX

HMX (mg/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			31.5	0.00	31.5
11/3/96	0.00	0.00	0.00	17.6	22.4	14.8	0.00	18.3
11/20/96	0.00	0.00	0.00	14.0	18.1	17.0	0.00	16.4
12/3/96	0.00	0.00	0.00	12.6**	10.9**	12.9	0.00	12.1
12/16/96	0.00	0.00	0.00	11.6**	10.5**	12.8**	0.00	11.6
12/31/96	0.00	0.00	0.00	8.42	7.72	10.4	0.00	8.85
1/13/97	0.00	0.00	0.00	7.21**	7.24**	8.11**	0.00	7.52
1/29/97	0.00	0.00	0.00	3.99	4.22	4.45	0.00	4.22
2/13/97	0.00	0.00	0.00	3.82	4.55	4.41	0.00	4.26
2/27/97	0.00	0.00	0.00	2.34	3.55	2.89	0.00	2.93
3/13/97	0.00	0.00	0.00	2.06	3.29	2.78	0.00	2.71
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	2.28**	0.00	0.00	0.00	0.00	0.00	0.922*	0.00
4/30/97	1.21**	0.00	0.00	0.00	0.00	0.00	0.566*	0.00
5/15/97	1.46	1.22	1.32	0.00	0.00	0.00	1.33	0.00
5/29/97	1.28**	0.689**	0.55**	0.00	0.00	0.00	0.840	0.00
6/16/97	1.42	1.22**	1.42**	0.00	0.00	0.00	1.35	0.00
6/30/97	1.16	0.00	0.844	0.00	0.00	0.00	0.835*	0.00
7/14/97	1.27**	0.00	0.901**	0.00	0.00	0.00	0.895	0.00
8/28/97	0.00	0.00	2.12**	0.00	0.00	0.00	0.876*	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000

Zero values mean the result was below the detection limit

* One or more samples were below detection limit and average was based on one-half the detection limit

** On one or more samples, associated quality control sample was out of limits

Table F-4. 2,6-DANT

2,6-DANT (mg/L) (2,6-Diamino-4-dinitrotoluene)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			0.00	0.00	0.00
10/19/96								
10/23/96								
10/24/96								
10/27/96								
10/28/96								
10/30/96								
10/31/96								
11/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/24/96								
12/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/16/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/31/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/13/97	0.00	0.493	0.00	0.00	0.00	0.00	0.295*	0.00
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/16/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/14/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/28/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detection limit

* For sample below detection limit, one half detection limit was used for average

Table F-5. 2,6-DNT

2,6-DNT (µg/L) (2,6-Dinitrotoluene)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			0.00	0.00	0.00
10/19/96								
10/23/96								
10/24/96								
10/27/96								
10/28/96								
10/30/96								
10/31/96								
11/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/24/96								
12/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/16/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/31/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/13/97	0.00	0.916	0.00	0.00	0.00	0.00	0.463*	0.00
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/16/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/14/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/28/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detecion limit

* For sample below detection limit, one half detection limit was used for average

Table F-6. 2A-DNT

2A-DNT (mg/L) (2-Amino-4,6-dinitrotoluene)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			0.00	0.00	0.00
10/19/96								
10/23/96								
10/24/96								
10/27/96								
10/28/96								
10/30/96								
10/31/96								
11/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/24/96								
12/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/16/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/31/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/15/97	0.543	0.00	0.00	0.00	0.00	0.00	0.349*	0.00
5/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/16/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/14/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/28/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detection limit

* For sample below detection limit, one half detection limit was used for average

Table F-7. 4A-DNT

4A-DNT (mg/L) (4-Amino-2,6-dinitrotoluene)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96		0.00	0.00	0.00			0.00	0.00
9/27/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/8/96	0.00	0.00	0.00			0.00	0.00	0.00
10/19/96								
10/23/96								
10/24/96								
10/27/96								
10/28/96								
10/30/96								
10/31/96								
11/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11/24/96								
12/3/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/16/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/31/96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/27/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/13/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/31/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/15/97	1.07	0.00	0.00	0.00	0.00	0.00	0.526*	0.00
5/29/97	0.745	0.00	0.00	0.00	0.00	0.00	0.398*	0.00
6/16/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/30/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/14/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/28/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/15/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/29/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12/4/97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2/5/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/9/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6/29/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/31/98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Zero values mean the result was below the detection limit

* For sample below detection limit, one half detection limit was used for average

APPENDIX G

DATA SET - NUTRIENTS IN LEACHATE

Ammonia-N (mg NH3-N/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	16.22	18.36	13.60				16.06	
9/27/96	17.00	15.70	18.40	0.35	0.74	0.51	17.03	0.53
10/8/96	49.60	51.20	45.60			0.26	48.80	0.26
10/19/96	59.53	50.58	65.44				58.52	
10/23/96	73.71	66.83	76.14	0.88	0.35	0.49	72.23	0.57
10/24/96			81.53		0.99		81.53	0.99
10/27/96	69.43	67.46	77.87	0.72	1.06	0.85	71.59	0.88
10/28/96	73.00	66.36	81.89	0.56	1.11	0.94	73.75	0.87
10/30/96	80.08	71.35	64.73	0.53	1.63	1.49	72.05	1.22
10/31/96								
11/3/96	36.64	38.98	39.73	0.65	1.73	1.27	38.45	1.22
11/7/96								
11/10/96								
11/17/96								
11/20/96	48.75	36.45	27.31	0.49	0.92	0.81	37.50	0.74
11/24/96		26.60					26.60	
12/3/96	27.85	24.55	17.27	0.36	0.88	0.52	23.22	0.59
12/16/96	15.99	12.34	8.78	1.28	0.89	0.33	12.37	0.83
12/31/96	11.47	9.05	6.47	0.72	0.96	0.84	9.00	0.84
1/13/97	7.71	7.07	6.09	0.56	0.68	0.21	6.96	0.48
1/29/97	8.66	7.58	8.26	1.00	1.23	1.36	8.17	1.20
2/13/97	7.60	9.13	11.65	1.12	1.29	1.32	9.46	1.24
2/27/97	4.86	6.74	5.13	1.04	1.22	1.13	5.58	1.13
3/13/97	3.97	4.72	2.98	1.08	1.42	1.18	3.89	1.23
3/31/97	4.34	9.22	4.06	0.65	1.18	0.66	5.87	0.83
4/15/97	2.17	7.24	2.65	0.61	0.72	0.60	4.02	0.64
4/30/97	0.91	2.69	0.83	0.14	0.41	0.24	1.48	0.26
5/15/97	1.07	2.29	1.37	0.69	0.26	0.45	1.58	0.47
5/29/97	1.45	1.77	2.95	2.84	2.31	2.88	2.06	2.68
6/16/97	0.65	1.00	2.41	1.43	2.03	1.97	1.35	1.81
6/30/97	2.82	19.10	2.18	0.44	0.52	1.89	8.03	0.95
7/14/97	2.06	0.52	3.6	1.57	1.68	2.44	2.06	1.90
						Average	25.69	0.97

Nitrate-N (mg NO3-N/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	423.96	392.96	525.95				447.62	
9/27/96	419.00	230.00	446.00	468.00	107.00	74.70	365.00	216.57
10/8/96	25.70	5.20	153.60			337.40	61.50	337.40
10/19/96	0.00	0.00	0.00				0.00	
10/23/96	0.00	0.00	0.00	439.77	425.28	436.54	0.00	433.86
10/24/96			0.00		439.70		0.00	439.70
10/27/96	0.00	0.00	0.00	371.51	428.23	426.95	0.00	408.90
10/28/96	0.00	0.00	0.00	249.19	325.41	332.88	0.00	302.49
10/30/96	0.00	0.00	0.00	202.42	292.09	284.61	0.00	259.71
10/31/96								
11/3/96	0.00	0.00	0.00	118.70	207.59	191.36	0.00	172.55
11/7/96								
11/10/96								
11/17/96								
11/20/96	0.00	0.00	0.00	30.72	53.86	32.93	0.00	39.17
11/24/96		0.00					0.00	
12/3/96	0.00	0.00	0.00	5.30	18.95	8.04	0.00	10.76
12/16/96	0.00	0.00	0.00	2.55	11.51	3.13	0.00	5.73
12/31/96	0.00	0.00	0.00	0.26	3.48	0.44	0.00	1.39
1/13/97	0.00	0.00	0.00	0.00	0.35	0.36	0.00	0.24
1/29/97	4.28	9.06	5.36	0.00	0.00	0.00	6.23	0.00
2/13/97	11.40	1.12	3.40	0.00	0.00	0.00	5.31	0.00
2/27/97	14.82	7.66	11.75	0.00	0.00	0.00	11.41	0.00
3/13/97	0.00	0.00	1.18	0.00	0.00	0.00	0.39	0.00
3/31/97	4.70	0.00	11.89	0.48	0.21	0.60	5.53	0.43
4/15/97	9.52	3.59	33.90	0.29	0.62	0.93	15.67	0.61
4/30/97	4.52	2.86	6.75	1.33	1.06	1.33	4.71	1.24
5/15/97	0.22	0.80	2.21	1.10	1.38	1.39	1.08	1.29
5/29/97	0.63	3.45	4.28	24.88	31.09	3.76	2.79	19.91
6/16/97	0.29	0.00	0.00	16.41	12.09	2.98	0.10	10.49
6/30/97	0.68	0.00	1.83	2.42	2.22	2.32	0.84	2.32
7/14/97	0.00	0.00	0.00	0.76	0.61	1.03	0.00	0.80
						Average	33.15	106.62

TKN (mg N/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	187.20	278.13	192.96				219.4	
9/27/96	237.00	107.00	129.00	36.30	11.50	12.40	157.7	20.07
10/8/96	571.80	533.80	668.00			4.67	591.2	4.67
10/19/96	613.80	568.40	677.00				619.7	
10/23/96	606.00	576.40	671.40	4.70	9.44	3.91	617.9	6.02
10/24/96			660.60		4.74		660.6	4.74
10/27/96	581.60	566.00	632.00	11.71	13.49	8.44	593.2	11.21
10/28/96	621.00	542.00	712.20	7.07	6.26	3.75	625.1	5.69
10/30/96	650.60	601.40	553.20	10.89	13.02	11.45	601.7	11.79
10/31/96								
11/3/96	320.40	378.80	394.00	10.09	11.57	10.37	364.4	10.68
11/7/96								
11/10/96								
11/17/96								
11/20/96	308.40	294.80	221.60	6.65	7.00	6.60	274.9	6.75
11/24/96		243.80					243.8	
12/3/96	198.40	183.40	103.80	3.85	5.20	5.27	161.9	4.77
12/16/96	160.60	113.40	65.20	3.95	4.48	4.04	113.1	4.16
12/31/96	49.60	77.90	89.60	3.33	4.07	4.74	72.4	4.05
1/13/97	82.10	76.60	41.60	3.60	4.03	4.74	66.8	4.12
1/29/97	73.00	59.40	54.00	3.88	4.51	4.95	62.1	4.45
2/13/97	71.10	67.90	72.70	4.12	4.72	5.07	70.6	4.64
2/27/97	45.50	49.84	37.03	3.88	4.36	4.71	44.1	4.32
3/13/97	29.02	32.64	21.42	3.71	4.61	4.39	27.7	4.24
3/31/97	35.42	37.98	41.50	3.75	4.56	4.06	38.3	4.12
4/15/97	37.62	38.42	45.48	3.38	3.87	3.59	40.5	3.61
4/30/97	23.68	24.10	27.58	3.00	3.64	3.28	25.1	3.31
5/15/97	16.95	18.91	21.89	2.90	3.83	3.29	19.3	3.34
5/29/97	49.32	43.71	51.48	5.66	5.11	6.62	48.2	5.80
6/16/97	24.40	15.00	30.10	4.17	4.33	4.75	23.2	4.42
6/30/97	40.90	44.60	36.80	3.58	3.52	4.79	40.8	3.96
7/14/97	24.80	17.40	31.20	3.64	4.08	5.28	24.5	4.33
						Average	230.3	5.97

PO4 (mg PO4/P/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	56.60	50.30	41.90				49.60	
9/27/96	71.80	59.30	58.10	1.19	2.29	2.25	63.07	1.91
10/8/96	74.60	58.90	72.80			1.67	68.77	1.67
10/19/96	71.09	60.62	68.16				66.62	
10/23/96	74.37	68.32	69.68	1.55	2.03	1.95	70.79	1.84
10/24/96			72.44		1.97		72.44	1.97
10/27/96	73.61	74.64	71.98	1.66	1.89	1.89	73.41	1.81
10/28/96	76.74	74.38	72.25	2.44	5.30	4.14	74.46	3.96
10/30/96	87.67	81.58	83.00	2.42	2.56	2.56	84.08	2.51
10/31/96								
11/3/96	82.83	82.49	90.53	2.52	2.33	2.45	85.28	2.43
11/7/96								
11/10/96								
11/17/96								
11/20/96	104.05	106.10	131.22	2.87	2.09	2.43	113.79	2.46
11/24/96		102.20					102.20	
12/3/96	108.46	114.11	104.82	2.45	1.69	1.84	109.13	1.99
12/16/96	113.80	101.80	79.40	4.69	1.61	1.62	98.33	2.64
12/31/96	44.52	81.84	85.93	1.35	1.19	1.21	70.76	1.25
1/13/97	62.80	62.50	36.92	0.68	0.94	0.52	54.07	0.71
1/29/97	39.68	35.79	23.32	0.53	0.79	0.36	32.93	0.56
2/13/97	35.60	35.10	25.30	0.62	0.75	0.52	32.00	0.63
2/27/97	31.18	33.23	18.61	0.46	0.72	0.50	27.67	0.56
3/13/97	26.30	29.30	19.86	0.25	0.51	0.37	25.15	0.38
3/31/97	25.15	31.36	18.34	0.34	0.32	0.28	24.95	0.31
4/15/97	19.24	19.94	15.80	0.44	0.39	0.30	18.33	0.38
4/30/97	16.11	18.17	15.24	0.14	0.27	0.12	16.51	0.18
5/15/97	16.13	22.43	20.57	0.46	0.23	0.17	19.71	0.29
5/29/97	19.78	16.97	18.55	0.12	0.13	0.08	18.43	0.11
6/16/97	24.00	26.40	31.70	0.07	0.10	0.05	27.37	0.07
6/30/97	25.00	29.50	26.90	0.16	0.18	0.00	27.13	0.11
7/14/97	14.90	25.10	14.30	0.00	0.00	0.00	18.10	0.00
						Average	55.18	1.23

Total Organic C (mg/L)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	3612	3513	3863				3663	
9/27/96	4020	2800	4040	198.0	220.0	123.0	3620	180.3
10/8/96	3749	3684	4307			182.0	3913	182.0
10/19/96	4074	3969	4661				4235	
10/23/96	3955	3629	4484	175.9	160.6	185.4	4023	174.0
10/24/96			4278		213.4		4278	213.4
10/27/96								
10/28/96								
10/30/96		3651					3651	
10/31/96								
11/3/96	2062	2329	2376	244.8	188.1	180.7	2256	204.5
11/7/96								
11/10/96								
11/17/96								
11/20/96	1851	1883	1271	143.7	116.1	94.8	1668	118.2
11/24/96		1645					1645	
12/3/96	1244	1194	710.8	30.3	40.9	43.5	1050	38.2
12/16/96	926.4	796.8	398.0	87.4	76.6	100.7	707	88.2
12/31/96	585.9	359.4	475.8	66.5	52.2	70.2	474	63.0
1/13/97	550.3	471.4	259.1	33.6	36.5	41.1	427	37.1
1/29/97	380.5	313.7	262.3	23.7	32.8	30.9	319	29.1
2/13/97	391.8	377.6	377.8	27.1	31.4	33.8	382	30.8
2/27/97	310.7	353.0	240.0	25.95	29.74	32.63	301	29.4
3/13/97	165.4	191.1	129.5	27.0	31.3	32.9	162	30.4
3/31/97	224.3	230.4	236.6	27.5	29.0	30.4	230	29.0
4/15/97	307.5	232.5	493.2	26.8	28.2	28.5	344	27.8
4/30/97	312.2	190.4	244.6	61.3	30.0	27.8	249	39.7
5/15/97	176.7	167.7	345.8	71.3	78.1	89.8	230	79.7
5/29/97	471.6	639.5	411.9	25.6	22.7	30.6	508	26.3
6/16/97	249.1	262.6	141.0	19.5	19.7	26.3	218	21.8
6/30/97	216.9	161.6	251.8	20.7	21.9	27.3	210	23.3
7/14/97	308.8	180.9	247.2	27.5	28.1	31.8	246	29.1
						Average	1500	77.1

Electrical Conductivity (μmhos/cm)								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	26400		28000				27200	
9/27/96		17970	28800	4440	1327	1001	23385	2256
10/8/96	24000	23400	27300			3940	24900	3940
10/19/96	25400	24200	27600				25733	
10/23/96	25600	24800	26900	4650	4730	4910	25767	4763
10/24/96			27200		4910		27200	4910
10/27/96	24700	24000	26800	4150	4820	4780	25167	4583
10/28/96	24400	22300	27000	3040	3860	3960	24567	3620
10/30/96	25000	24100	20700	2620	3590	3510	23267	3240
10/31/96	19550	16810	18170		3460	3360	18177	3410
11/3/96	13090	14750	13950	1849	2870	2750	13930	2490
11/7/96	15430	13220	11560	1207	2230	2100	13403	1846
11/10/96	13340	11510	7980	1066	1790	1655	10943	1504
11/17/96	14170	10270	6560	976	1450	1305	10333	1244
11/20/96	11500	9020	5500	938	1302	1132	8673	1124
11/24/96	10310	7360	4670	873	1127	982	7447	994
12/3/96	5810	5310	3180	652	878	794	4767	775
12/16/96	4220	3220	2100	557	767	753	3180	692
12/31/96	2030	1794	1155	523	597	735	1660	618
1/13/97	1969	1818	1455	530	571	693	1747	598
1/29/97	1486	1458	1475	579	523	728	1473	610
2/13/97	1859	2120	2440	664	571	761	2140	665
2/27/97	1824	2110	1994	638	585	780	1976	668
3/13/97	1160	1470	1400	729	682	832	1343	748
3/31/97	2050	2060	2440	863	802	902	2183	856
4/15/97	1974	2300	2740	981	933	1006	2338	973
4/30/97	1430	1788	1916	1090	1023	1084	1711	1066
5/15/97	1260	1656	1763	1118	1094	1172	1560	1128
5/29/97	2400	2750	3200	1205	1065	1278	2783	1183
6/16/97	1755	1502	2260	900	823	1052	1839	925
6/30/97	1778	2100	1995	714	720	1014	1958	816
7/14/97	1419	3170	1255	882	943	1144	1948	990
						Average	10772	1774

pH								
Date	Sample No.						Average for Compost Only	Average for Compost/Soil Mixture
	Compost Only			Compost/Soil Mixture				
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
9/22/96	8.23		8.38				8.31	
9/27/96		8.03	8.16	7.35	7.41	7.30	8.10	7.35
10/8/96	7.92	8.08	8.37			7.49	8.12	7.49
10/19/96	7.64	7.74	7.58				7.65	
10/23/96	7.71	7.70	7.61	6.88	7.44	7.13	7.67	7.15
10/24/96			7.88		7.57		7.88	7.57
10/27/96	7.82	7.70	7.66	7.21	7.44	7.26	7.73	7.30
10/28/96	8.00	7.78	7.92	7.09	7.04	7.00	7.90	7.04
10/30/96	7.62	7.51	7.53	7.33	7.04	7.19	7.55	7.19
10/31/96	7.38	7.41	7.42		7.14	7.11	7.40	7.13
11/3/96	7.40	7.36	7.46	6.89	6.89	7.03	7.41	6.94
11/7/96	7.63	7.69	7.68	7.04	7.10	7.16	7.67	7.10
11/10/96	7.71	7.81	7.81	7.27	7.31	7.46	7.78	7.35
11/17/96	7.56	7.63	7.80	7.50	7.32	7.27	7.66	7.36
11/20/96	7.51	7.64	7.74	7.10	7.09	7.14	7.63	7.11
11/24/96	7.89	8.09	7.86	7.18	7.66	8.02	7.95	7.62
12/3/96	7.55	7.58	7.55	7.19	7.27	7.39	7.56	7.28
12/16/96	7.57	7.67	7.67	7.52	7.52	7.68	7.64	7.57
12/31/96	7.55	7.56	7.45	7.24	7.18	7.39	7.52	7.27
1/13/97	7.69	7.67	7.66	8.12	7.70	7.59	7.67	7.80
1/29/97	7.20	7.76	7.75	7.52	7.52	7.53	7.57	7.52
2/13/97	8.14	8.29	8.34	7.96	7.89	7.96	8.26	7.94
2/27/97	8.11	8.07	8.13	8.00	7.93	7.94	8.10	7.96
3/13/97	7.84	7.85	7.71	7.93	7.83	7.81	7.80	7.86
3/31/97	8.29	8.13	7.90	7.81	7.85	7.83	8.11	7.83
4/15/97	8.20	8.22	8.12	7.82	7.83	7.93	8.18	7.86
4/30/97	7.78	7.95	7.62	8.02	7.98	7.89	7.78	7.96
5/15/97	8.05	8.28	8.07	7.99	8.02	7.95	8.13	7.99
5/29/97	7.61	7.75	7.64	7.75	7.76	7.73	7.67	7.75
6/16/97	7.51	7.56	7.53	7.74	7.77	7.68	7.53	7.73
6/30/97	7.47	7.94	7.87	7.45	7.55	7.41	7.76	7.47
7/14/97	7.91	7.92	8.16	7.75	7.75	7.65	8.00	7.72
						Average	7.80	7.51