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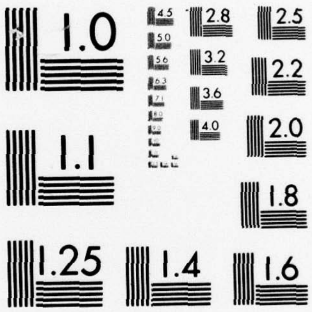

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METHODOLOGY DEVELOPMENT FOR THE IDENTIFICATION AND ANALYSIS OF TRACE CONTAMINANTS FOUND ON ARMY INSTALLATIONS

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I. INTRODUCTION

The concepts of modern warfare and associated weaponry requirements have developed primarily during the past four decades. A variety of wastes was produced in association with weapons production. All too frequently, the composition of these wastes was undefined and little was known regarding their composition, toxicities, persistence, and mobility. Then accepted procedures for waste disposal consisted mainly of land filling with little or no consideration given to managing these wastes to prevent their distribution into the environment.

With time, the recognition of external adverse environment effects lead to the realization that these wastes in many cases were highly persistent and were migrating into the ecosystem.

As a result of these circumstances, the Secretary of the Army directed the development and implementation of a comprehensive project to identify the problems associated with these earlier waste disposal practices. In August 1975, the program manager for Chemical Demilitarization was selected to provide program management leadership for this interservice project and was designated as the Project Manager for Chemical Demilitarization and Installation Restoration. Installation restoration technology providing for the containment or elimination of migrating wastes from these numerous land disposal sites is being developed.

The project manager established the Analytical Systems Working Group (ASWG), composed primarily of army scientists with expertise in environmental chemistry. This group, as one of its tasks, reviews the analytical systems research and development program. Also the group provides the project manager advice and

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recommendations on current environmental problems relating to Installation Restoration programs. The group oversees a quality control program under which all analytical data is generated. The program employs an onsite Quality Control (QC) coordinator at each participating laboratory and an overall Quality Control coordinator who develops all QC plans, monitors regional QC activities, and reports directly to the working group.

Installations selected for a restoration project are screened initially by a records research team for potential waste migration problems. This screening is accomplished by a multidisciplinary professional team which reviews existing historical records for the installation. This team assesses the potential for migration of contaminants from the installation. If their assessment indicates a potential waste migration problem, a limited sampling and analysis study is scheduled for the installation. This preliminary survey provides sufficient information to either support or refute waste migration. If migration is confirmed, the installation is scheduled for a comprehensive survey which determines the extent and level of waste migration and the sources of the migrating wastes. Based on the results of the comprehensive survey, a restoration program may be developed. The methodology described in this paper is used in the preliminary survey, the comprehensive survey, and during the restoration program.

II. TECHNIQUES FOR THE IDENTIFICATION AND SELECTION OF CONTAMINANTS

During the preliminary and comprehensive surveys, efforts are specifically designed to uncover and identify contaminants. Samples taken from installations are screened for contaminants by several techniques. The most common screening techniques used for water are determinations of the water quality parameters, organic extractables, and the common inorganics. Screening techniques commonly used for soil include organic extractables, water extractable inorganics, and total inorganics.

In the preliminary survey, a major effort is placed on screening water and soil. The sampling locations are based on the geohydrology of the area and other information gained from historical records. The sampling points are selected to provide definitive information on potential or actual migration of contaminated plumes.

Screening during the comprehensive monitoring survey is less intense and is only performed on an as required basis. Most newly identified contaminants in this phase of the project are discovered as interferences to the survey analyses. The intent of the comprehensive survey is the identification and description of sources of contaminants and contamination plumes.

Screening techniques for water soluble inorganics and volatile, extractable organic impurities (1) are well defined, and provide satisfactory data. However, screening techniques for water soluble, unextracted nonvolatile and thermally unstable organics are not well developed. Useful screening techniques for these classes of organics is being actively sought.

III. METHODOLOGY DEVELOPMENT

A systematic method for the development of monitoring techniques for contaminants distributed in the environment has long been needed. In the past, when a method was desired, one or more laboratories would work on parts of it. The end result revealed several well-developed parts of a method but with many unanswered questions. Recognizing this, any comprehensive program for defining environmental contamination must be based on a firm well-tested analytical systems approach. A twelve-step development procedure was devised, tested, and implemented. The stepped procedure and a typical development schedule are represented in the figure.

A. Literature Review

A literature review is conducted to obtain available techniques used for detection, identification, and estimation of quantities of the selected contaminants and related environmental degradation products. The reviews are intended primarily for use by the ASWG and the project methodology developers.

During the literature review, special attention is given to the following subjects: extraction procedure, cleanup procedure, analytical methods, environmental degradation products, and special analytical procedures.

B. Development of Standard Analytical Reference Materials (SARMS)

All of the chemical analyses conducted in support of this program are based on SARMS. These materials are either National Bureau of Standards (NBS) Standard Reference Materials or are traceable to one of these materials. Although NBS offers only a limited selection of standards, it is possible to trace any substance through a series of comparisons or titration to an oxidimetric, basemetric, or some other standard reference material.

Candidate high-purity analyses for SARMS are selected and evaluated on a preliminary basis using known materials. Sufficient analyses are run to document the random and systematic errors in the analyses. The most appropriate high-purity analysis is selected for evaluation of the analytical standard. Those design parameters of the standard which are critical to the survey analysis are identified.

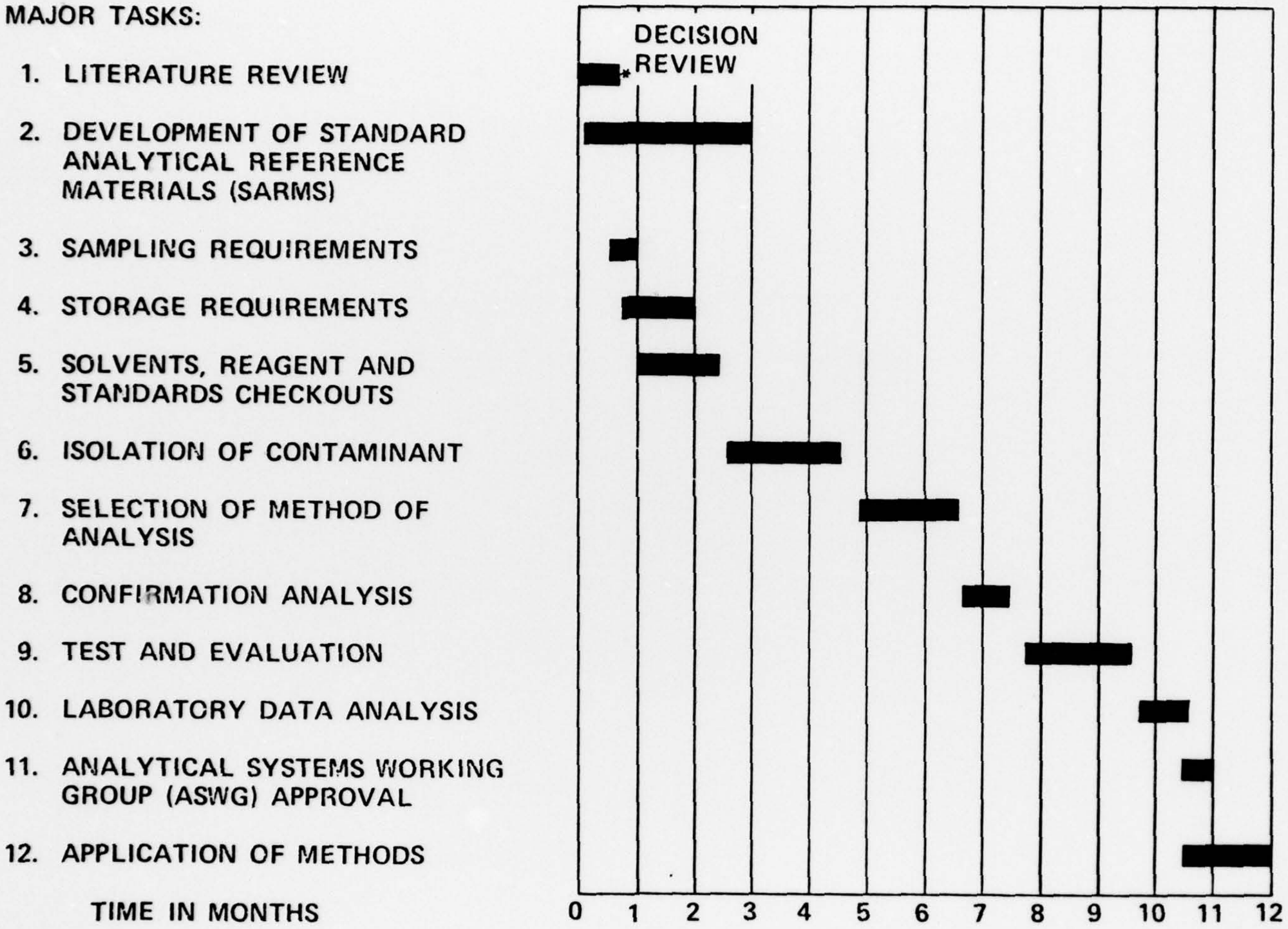

Figure. METHODS DEVELOPMENT PROGRAM

The development of a SARM begins with the synthesis or procurement of the raw material and purification to greater than 98-mole-percent purity. Chromatographic, spectrophotometric, and NMR examinations are routinely used to ensure that each material of certified high purity is indeed the correct compound.

Each SARM is subjected to an aggravated storage period to estimate its stability. Materials showing a propensity for decomposition are repurified and stabilized, if practical. Where not practical an alternate standard is selected. SARMS must emerge from aggravated storage with purities in excess of 98 mole percent.

The SARMS are prepared in sufficient quantity to ensure that enough standard is available for the aggravated storage test, surveillance tests (every six months), and the laboratory QC programs envisioned for two years. The test results are reported to the ASWG. This group approves the suitability of each material and all its supporting data prior to distribution as a SARM. NBS standard reference materials are accepted at face value for use as SARMS; however, care is taken to be sure the standard is being used for the purpose for which it was intended. Commercially available standards may be accepted as SARMS if sufficient supporting data can be obtained from the vendor.

When it is necessary to run preliminary analyses before a SARM is available, the following precautions will be taken.

a. Interim standards are stored at 0°C and a portion retained for a comparison with the approved SARM when available.

b. The following data are recorded as a minimum description of the material.

(1) Infrared spectrum

(2) Melting point, decomposition point, or boiling point

(3) NMR spectrum

(4) Elemental analysis

(5) Gas chromatographic [by difference] analysis

C. Sampling Requirements

The purpose of the sampling requirement task is to ensure that the sample is valid. To accomplish this goal, samples must represent the environmental component being tested. The sampling location, technique, frequencies, duration, and size should be such that the analytical results can be evaluated statistically (2). Special attention is paid to sample integrity and possible cross contamination. Additionally, subsampling is controlled to ensure that samples retain their integrity, and properly represent the initial sample. Analytical results are only as valid as the samples from which they are determined.

D. Storage Requirements

Each contaminant is tested to determine if it is stable in storage. An analysis is made to determine if the sample is degraded by oxidation, visible or ultraviolet radiation, or elevated temperatures. In addition, samples in storage are tested to determine whether contamination occurs by such factors as other sample containers, container seals, or other samples (i.e., through cross contamination). To avoid extensive storage testing, samples are analyzed, as soon as possible, to limit degradation.

E. Solvents, Reagents, and Standards Requirements

Solvents and reagents must be free of substances that interfere with analysis or degrade the sample. To obtain low-background levels and avoid spurious peaks arising from solvent impurities, it is usually necessary to employ specially purified solvents. Solvents and reagents are checked by using them in the specific analytical system. Special methods for uniformly dispersing the standards in soil are studied, tested, and evaluated.

F. Contaminant Isolation Techniques

In order to effectively determine a specific contaminant, it must be isolated from other moieties which could interfere with the determination. Although many methods of contaminant isolation exist, extraction technology is probably the most advanced and is given primary consideration.

Soil extractions are grouped into three classes: batch, column, and continuous. The selection of the method of extraction depends upon the equilibrium constant for partitioning of contaminant between the extraction solvent and the soil. Batch extraction works best when the contaminants strongly partition in the extraction solvent. Continuous extraction works best for all equilibrium conditions and is ordinarily performed when the partition coefficient is unfavorable. Column extraction works with systems having a wide range of partition coefficients. Also, column extraction affords the analyst use of a mixture of solvents to remove the suspect undesirable substance.

The cleanup procedure should be tested to see that it enhances the detection and determination of the suspect contaminant:

At the desired sensitivity or limit of detection

With reasonable recovery (preferably 85% or better)

With reasonable reduction of background interferences

With adequate separation of the substance sought from interfering substances.

Even though some types of samples are analyzed with little or no cleanup, it may still be advisable to use established cleanup procedures in order to enhance the specificity of the analysis. In any case, details of the cleanup procedures are specified fully by the developers of analytical methods. Any changes or modifications are described explicitly.

An extraction procedure is usually efficient and easily controlled; however, it requires extensive preparation and consumes time. Where less time-consuming procedures have been developed or are feasible, they are pursued and evaluated as alternate methods. The focus of this program is to quantitatively and qualitatively identify environmental contaminants rather than to develop varied methodology for similar environmental systems. Therefore, extensive R&D programs are not funded under this task unless specific guidance from the ASWG is first given.

G. Selection of Methods of Analysis

The quantitative measurement step in determining the analyte, i.e., the substance determined analytically, is the most important step of the analytical system. The method selected for assaying the analyte defines the ultimate sensitivity, precision, accuracy, and detection limit possible. When methods are comparable, the one requiring the least amount of operator skills and time is the most desirable.

H. Confirmation Analysis

Confirmatory tests must support the identity of contaminants. A number of factors dictate the actions needed to confirm the identity of a contaminant.

Essentially all methods and tests regularly employed provide qualitative information which is presumptive in nature, i.e., the behavior of an unknown is compared to that of a known standard material. It is possible in any single test to find one material that masquerades as another. When the behavior of an unknown and standard is the same in a number of tests that measure different chemical or physical properties, the certainty of identification is increased.

Analytical methods are most useful when backed by a bank of data on the behavior of many contaminants, of their metabolites and degradation products when subjected to the various operations that make up the method. The analyst should be familiar with the contaminant's use and the chemistry and metabolism of its residues. The analyst should be aware of available information on the behavior of pesticides and other potential residues when subjected to a specific analytical method, and should consider the possible presence of chemicals that interfere with the analysis. Most importantly, the analyst must use common sense and accepted quality control procedures when drawing analytical conclusions.

I. Test and Evaluation of Trace Analysis

Before any analytical system is employed in the comprehensive survey, the following work is conducted. Sufficient standards and blanks are run to statistically establish the limits of detection. An established confidence level for detection must be met. The methods of Hubaux and Vos (3) are suitable. The percent recoveries of all analytes are determined on control soils of each type encountered in the sample load.

A list of potential interferences is prepared for each analysis. The functional relationship between the concentration of the interference and systematic error caused by this interference is estimated at the detection limit and the upper concentration limit specified for the analyte. An interfering substance is defined as one that causes systematic error in the analytical results for at least one concentration of the analyte within the range of the method.

The bounds of uncertainty due to systematic errors are estimated and reported with the analytical results. This estimate includes the errors which are empirically determined and such additional uncertainties as are known to be inherent in the standard.

J. Laboratory Data Analysis

Upon completion of the methods development and during the test and evaluation subtask, techniques for acquiring raw data are examined. The total amount of raw data per day and the frequency with which the method is required in the comprehensive survey is the deciding factor in the technique employed to acquire the data. When the data are produced at a high rate and frequently, automatic data acquisition should be considered.

After the data have been acquired, they are used to calculate the results and the QC parameters. Calculation of the results is studied to obtain the best possible results within the allowable limits. The calculated results are validated by an agreed-upon procedure and reported to all appropriate agencies in specified format.

K. ASWG Approval

All the data generated during the development of the specific method are compiled and a summary of results along with the detailed procedure is presented to the ASWG for approval. At the recommendation of the ASWG, the method is either returned for future work, approved or disapproved. All approved methods are cast into a publishable form and submitted to a suitable journal for publication.

L. Application of Methods

Upon approval of the method by the ASWG, it is released to the users, and its application in their laboratories is carefully monitored. If a user has a problem in establishing the procedure, the developer aids in resolving the problem.

IV. RESULTS AND DISCUSSION

A. Contaminant Identification Tasks

During the screening operations conducted at several installations, well over one hundred contaminants in the ground water and surface water have been identified. In addition, two new screening techniques have been developed; one for volatile organics and the other for determination of organic extractables from sediments.

B. Water Methods

Methods for the analysis of ten contaminants in water have been developed and used in field tests. These contaminants are arsenic, thiodiglycol, elemental phosphorus, acetylcholinesterase inhibitors, diisopropyl methylphosphonate, dicyclopentadiene, p-chlorophenyl methyl sulfide, p-chlorophenyl methyl sulfone, p-dithiane, and p-oxathiane. Even though arsenic has been analyzed by many techniques, the method developed under this task has been shown to be free of interferences which have hampered other techniques. The other methods represent one-of-a-kind procedures unavailable in the open or classified literature. For these methods eight new standard analytical reference materials were developed. These methods have found wide application in both the Government and the private sector.

C. Soil Methods

Analytical methods for five contaminants in soil have been developed. These methods are for the contaminants diisopropyl methylphosphonate, dicyclopentadiene, p-chlorophenyl methyl sulfide, p-chlorophenyl methyl sulfone, and p-dithiane. Since soil is such a complex matrix, a special study to determine the error associated with subsampling was undertaken. Results to date indicate that extremely large errors can occur when soil is improperly subsampled.

V. SUMMARY

This procedure for the development of methodology will allow the user to develop an analytical system with quantitatively defined precision, accuracy, and limits of detection. Treatment of environmental hazards is extremely expensive relative to methodology development and data generation; therefore, the final decision regarding treatment must be founded on data of the highest quality. It should be very clear that any shortcuts in cost or time in the development of methodology or data are not likely to be cost effective. Attention to the generation of quality control parameters in each step is required to meet these stringent conditions. Methodology development for analytical systems is a dynamic process resulting in continuous analytical method modification and validation for varying environmental conditions.

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