Second Annual

United States
Environmental Protection Agency
Symposium
On

Solid Waste Testing and Quality Assurance

PROCEEDINGS

July 15 – 18, 1986
Washington, D.C.
Vista International Hotel

Symposium managed by
The American Public Works Association

SECOND ANNUAL

United States
Environmental Protection Agency

SYMPOSIUM

on

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1313 East 60th Street
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SYMPOSIUM PROGRAM COMMITTEE

David Friedman (Chairman)
Manager, Methods Program
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PROCEEDINGS INTRODUCTION

One of the major environmental problems facing the United States, as well as other nations, is the need for safe handling and disposal of hazardous waste. A fundamental component of all programs relating to waste management is the need to perform measurements. These measurements include waste composition and properties; effectiveness of management processes; engineering properties of materials used in constructing management units; and, last but not least, long term performance of such management units. Thus the pivotal roles played by the measurement methodology and, its attendent, quality assurance.

The analysis of complex waste matrices presents the environmental community with demanding analytical problems for which solutions are being developed at a rapid rate. This annual symposium series, presented by the EPA's Office of Solid Waste, is designed to focus on recent developments in testing methods and quality assurance of importance to both the RCRA and CERCLA programs.

The symposium highlights developing requirements for quality assurance as well as new analytical procedures intedned to be used in EPA's national RCRA and CERCLA hazardous waste management programs. Our purpose in holding these symposia is several fold. First, is as a means of communicating what EPA is doing regarding the activities EPA has already initiated to upgrade the state-of-the-art as reflected in the regulations and in SW-846. Second, to describe the direction EPA's program is taking with respect to testing and quality assurance issues. Third, as a forum for discussion between Agency personnel and representatives from public and private laboratories involved in waste sampling and evaluation.

The presentations describe work in progress. Current plans are that ASTM will publish the complete proceedings in the near future and that prior to publication, the material presented during the symposium wil be updated.

DAVID FRIEDMAN
CHIEF, METHODS SECTION
OFFICE OF SOLID WASTE

Second Annual
United States Environmental Protection Agency

SYMPOSIUM
SOLID WASTE TESTING AND QUALITY ASSURANCE

Vista International Hotel Washington, D.C.

July 15-18, 1986

PROGRAM

Tuesday, July 15, 1986

11:00 am - 1:00 pm REGISTRATION

1:00 pm - 1:20 pm OPENING SESSION

Opening Remarks:

Marcia Williams, Director, Office of Solid Waste, USEPA, Washington, D.C.

Henry Longest, Director, Office of Emergency and Remedial Response, USEPA, Washington, D.C.

1:20 pm - 1:45 pm CONFERENCE OVERVIEW

Overview presented by David Friedman, Manager, Methods Program, Office of Solid Waste, USEPA, Washington, D.C.

1:45 pm - 5:00 pm SESSION I

CHAIRPERSON:

Agnes M. Ortiz, Chemical Engineer, Office of Solid Waste, USEPA, Washington, D.C. 20460

TESTING THE COMPATIBILITY OF SOIL LINERS AND WASTE LEACHATE

Robert S. Truesdale, Research Triangle Institute, P. O. Box 12194, Research Triangle Park, NC 27709

ROUND-ROBIN STUDY OF LEACHING METHODS AS APPLIED TO SOLID WASTES FROM COAL-FIRED POWER PLANTS

Ishwar P. Muraka, Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94303

COFFEE BREAK

COLLABORATIVE STUDY OF THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) FOR METALS, PESTICIDES, AND SEMI-VOLATILE ORGANIC COMPOUNDS

W. Burton Blackburn, S-Cubed, P.O. Box 1620, La Jolla, CA 92038

COMPARISON STUDY OF PREPARATIVE AND ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF SELENIUM IN WATER, SEDIMENT AND VEGETATION MATRICES

Milad Iskander, California State Department of Health Services, 2151 Berkeley Way, Berkeley, CA 94704

Wednesday, July 16, 1986

7:00 am - 8:00 am	CONTINENTAL BREAKFAST
8:00 am - 12:00 pm	SESSION II

CHAIRPERSON:

Ronald Mitchum, Director, Quality Assurance Division, Environmental Monitoring and Support Laboratory, USEPA, Las Vegas, NV 89114

DEVELOPMENT AND VALIDATION OF RCRA METHOD 8280 FOR DIOXINS AND FURANS

Steve Billets, Environmental Monitoring and Support Laboratory, USEPA, Las Vegas, NV 89114

SINGLE LABORATORY EVALUATION OF METHOD 8080 FOR ORGANOCHLORINE PESTICIDES AND PCB's

Werner Beckert, Environmental Monitoring and Support Laboratory, USEPA, Las Vegas, NV 89114

INNOVATIVE TECHNOLOGIES FOR HAZARDOUS WASTE ANALYSIS

Ronald Mitchum, Environmental Monitoring and Support Laboratory, USEPA, Las Vegas, NV 89114

COFFEE BREAK

APPENDIX VIII ANALYSES IN GROUNDWATER

Robert W. April, Office of Solid Waste, USEPA, 401 M Street S.W., Washington, D.C. 10460

COMPARISON OF THE TOX (EPA) AND AOX (DIN) METHODS FOR THE DETERMINATION OF ORGANIC HALOGEN COMPOUNDS IN WATER AND SOLID WASTE

Raimund Roehl, California State Department of Health Services, 2151 Berkeley Way, Berkeley, CA 94704

EVALUATION OF GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) METHOD 8240 AND 8270 FOR APPLICATION TO APPENDIX VIII COMPOUNDS

James Longbottom, Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, OH 45268

Noon - 1:30 pm LUNCH

1:30 pm - 5:00 pm SESSION III

CHAIRPERSON:

Gail A. Hansen, Chemist, Office of Solid Waste, USEPA, Washington, D.C. 20460

HYDRIDE GENERATION METHODS FOR DETERMINATION OF ARSENIC AND SELENIUM

Steve Callio, Region VIII, USEPA, 999 18th Street, Denver, CO 80202-2413

THE RATIONALE FOR FILTRATION OF GROUNDWATER SAMPLES

Olin C. Braids, Geraghty and Miller, Inc., 6800 Jericho Turnpike, Syosset, NY 11791

METHODS FOR THE ANALYSIS OF ORGANOMETALLIC COMPOUNDS IN WASTES

Gregory J. Olson, National Bureau of Standards, Building 223, Gaithersburg, MD 20899

COFFEE BREAK

MICROWAVE PROCEDURE FOR THE DETERMINATION OF METALS IN OILY WASTE

Thomas Copeland, ERCO, 205 Alewife Brook Parkway, Cambridge, MA 02138

INTER-LABORATORY EVALUATION OF ICP METHOD 6010

Thomas Hinners, Environmental Monitoring and Support Laboratory, USEPA, Las Vegas, NV 84114

METHODS FOR EVALUATING SOLIDIFIED WASTE

Albert Liem, Alberta Environmental Centre, Bag 4000, Vegreville, AB, Canada

6:00 pm - 7:30 pm RECEPTION FOR SPEAKERS AND ATTENDEES

Thursday, July 17, 1986

7:00 am - 8:00 am CONTINENTAL BREAKFAST

8:00 am - Noon SESSION IV

CHAIRPERSON:

Duane Geuder, Chemist, Office of Emergency Response and Remediation, USEPA, Washington, D.C. 20460

DYNAMIC VALIDATION OF SUPERFUND/RCRA ANALYTICAL METHODS

Gareth Pearson, Environmental Monitoring and Support Laboratory, USEPA, P.O. Box 15027, Las Vegas, NV 84114

THE SUFFICIENCY, REDUNDANCY, AND APPROPRIATENESS OF SURROGATE AND MATRIX SPIKE COMPOUNDS IN ORGANIC ANALYSIS

Forrest O. Gardner, Lockheed Corporation, 1050 E. Flamingo Road, Las Vegas, NV 89119

STATISTICAL APPROACH TO MULTI-ANALYTIC DATA QUALITY

Ivan T. Show, S-Cubed P.O. Box 1620, La Jolla, CA 92038

COFFEE BREAK

QUALITY ASSURANCE IN THE GROUNDWATER MONITORING TASK FORCE FACILITY ASSESSMENT PROGRAM

Michael Kangas, ICAIR Life Systems, Inc., 24755 Highpoint Road, Cleveland, OH 44122

ANALYSIS FOR CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN ENVIRONMENTAL SAMPLES AND EMISSIONS FROM CONBUSTION AND INCINERATION PROCESSES

Robert Harless, Environmental Monitoring and Support Laboratory, USEPA, Research Triangle Park, NC 27711

SAMPLING AND ANALYSIS FOR DELISTING DATA VERIFICATION/DELISTING SPOT CHECKS

Joan Warren, ORD, USEPA, Washington, D.C. 20460

Noon - 1:30 pm LUNCH

1:30 pm - 5:00 pm SESSION V

CHAIRPERSON:

Denise Zabinski, Chemist, Office of Solid Waste, USEPA, Washington, D.C.

DEVELOPMENT OF PERFORMANCE EVALUATION SAMPLE SERIES FOR THE GROUNDWATER MONITORING SURVEY AT DUMP SITES

Edward Berg, Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, OH 45268

OSWER LABORATORY EVALUATION PROGRAM - A PROGRESS REPORT

Florence M. Richardson, Office of Solid Waste, USEPA, Washington, D.C. 20460

IMPACTS AND INTERFACE OF CERCLA MONITORING REQUIREMENTS WITH OTHER STATE AND FEDERAL PROGRAMS

Kathe Stauer, New Jersey Department of Environmental Pollution, Trenton, NJ 08625

COFFEE BREAK

ANALYSIS OF NON-HOMOGENOUS MIXTURES

Robert L. Fisher, New Jersey Department of Environmental Pollution, Trenton, NJ 08625

HAZARDOUS WASTE ANALYSIS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) AND LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS)

James A. Poppiti, Finnegan Corporation, 1383 Piccard Drive, Rockville, MD 20850

UPDATE ON COOPERATIVE INVESTIGATION OF TEST METHODS FOR SOLIDIFIED WASTE CHARACTERIZATION

Julia Stegemann, Waste Water Technology Centre, Environment Canada, 867 Lake Shore Road, Burlington, ON, Canada

7:30 pm - 9:30 pm SESSION VI (Will be held in Sherwood Room)
(For USEPA and State Agency Attendees Only)

CHAIRPERSON:

Kenneth Jennings, Environmental Scientist, Office of Waste Program Enforcement, USEPA, Washington, D.C. 20460

CORRECTIVE ACTIONS UNDER RCRA, INTERIM MEASURES

Jackeline Moya and Staff, Office of Waste Program Enforcement, USEPA, Washington, D.C.

Friday, July 18, 1986

7:00 am - 8:00 am CONTINENTAL BREAKFAST

8:00 am - Noon SESSION VII

CHAIRPERSON:

J. Howard Beard, Chief, Physical Science Section, Office of Waste Program Enforcement, USEPA, Washington, D.C. 20460

ISSUES AND PROBLEMS RELATED TO CERTIFICATION AND PERFORMANCE EVALUATION OF HAZARDOUS WASTE LABORATORIES

Robert L. Stephens, California State Department of Health Services, 2151 Berkeley Way, Berkeley, CA 94704

SAMPLING HOLDING TIME, A PROGRESS REPORT

Michael Maskarinec, Oak Ridge National Laboratory, P.O. Box 10, Oak Ridge, TN 37830

HAZARDOUS WASTE REGULATIONS IN CANADA

Nancy P. Cathcart, Environment Canada, 351 Saint Joseph Boulevard, Hull, PQ, Canada K1A 2C8

COFFEE BREAK

OVERVIEW OF RCRA ENFORCEMENT

Kenneth Jennings, Office of Waste Program Enforcement, Washington, D.C. 20460

SW-846 UPDATE

Paul Friedman, Office of Solid Waste, USEPA, Washington, D.C. 20460

TECHNICAL ISSUES RELATED TO THE TOXICITY CHARACTERISTICS AND LAND DISPOSAL RESTRICTIONS

David Friedman, Office of Solid Waste, USEPA, Washington, D.C. 20460

POSTER SESSION

Liquid Releast Test (LRT) for Liquid Loaded Sorbents	Benjamin Carpenter Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709
Evaluation of Methods for Determining Chlorine in Waste Oils	Alvia Gaskill, Jr. Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709
Evaluation of Selected Digestion Methods for Determining Hexavalent Chromium in Solid Waste Matrices	Jerry Messman Battelle Columbus Laboratories 505 King Avenue COlumbus, OH 43201
Development of Field Test for Monitoring Organic Hallides	Ray Tarrer College of Engineering Auburn University 230 Ross Hall Auburn, AL 36849-3500
RCRA Laboratory Certification	Robert Hirst Department of Environmental Protection Office of Science and Research CN 402 Trenton, NJ 08625
USEPA Reference Standard and Quality Assurance Materials for Analysis of Environmental Contaminants	R. E. Thompson/P. A. Wylie Northrop Services, Inc. P.O. Box 12313 Research Triangle Park, NC 27709
The Quantitation of PCB's, PCDF's, and PCDD's by Electron Impact GC/MS Using Response Factor Estimation	Andrew D. Sauter A. D. Sauter Consulting 2356 Aqua Vista Henderson, NV 89015
Demonstration of the Toxicity Characteristic Leaching Procedure	Nancy Rothman Energy Resources, Inc. ENSCO 185 Alewife Parkway Cambridge, MA 02138
Demonstration of the Solid Ignitability Procedures	David Binstock Research Triangle Institute P.O. Box 12194 Research Triangle, NC 27709

POSTER SESSION

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Video Tapes

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Demonstration of the Solid Ignitability Procedures	David Binstock Research Triangle Institute P.O. Box 12194 Research Triangle, NC 27709

FIRST SESSION

Tuesday, July 15, 1986
1:45 p.m. - 5:00 p.m.

Chairperson:
Agnes M. Ortiz
Chemical Engineer
Office of Solid Waste
U.S. Environmental
Protection Agency
Washington, D.C.

TESTING THE COMPATIBILITY OF SOIL LINERS AND WASTE LEACHATE

ROBERT TRUESDALE, L. J. GOLDMAN, RESEARCH TRIANGLE INSTITUTE, RESEARCH TRIANGLE PARK, NORTH CAROLINA

ABSTRACT

In order to satisfy RCRA requirements, a soil liner must have a permeability of 10E-07 cm/s or less and must be compatible with the wastes or waste leachate it is meant to contain. The objective of this research effort is to develop and evaluate SW-846 test procedures for measuring the permeability and chemical compatibility of soil liner materials so that adherance to this requirement may be demonstrated. Procedures were developed for fixed-wall and flexible-wall permeameters. Two test devices were chosen because each device has its advantages and disadvantages and best area of application. Fixed-wall tests may be best for chemical compatibility testing because the confining pressure in flexible-wall may prevent desiccation cracks from forming. Flexible-wall tests are better for determining the permeability of core samples from the field because of reduced probability of side-wall leakage. Compatibility tests are to be conducted in tandem on identical laboratory-compacted soil samples, with baseline permeability measurements conducted with construction-site water on one sample and chemical permeability measurements conducted on the other sample.

Ruggedness testing results showed that for both test methods, molding water content and the application of back-pressure were the most important variables influencing permeability measurements. Evaluation of both test methods involved a collaborative testing program with sixteen laboratories, one chemical, and one soil. Triplicate testing of each test method by each laboratory enabled inter-and intralaboratory precision to be determined.

INTRODUCTION

The current Resource Conservation and Recovery Act (RCRA) double liner guidance, developed in response to the Hazardous and Solid Waste Amendments (HSWA) of 1984, recommends the use of a liner composed of inorganic materials (e.g., compacted soil) as the lowest component in the liner system of a hazardous waste storage or disposal facility. To satisfy RCRA requirements, this liner "must be constructed of materials that have appropriate chemical properties...to prevent failure (due to) physical contact with the waste or leachate to which they are exposed" (40 CFR Part 264, 221, 264, 251, 264, 301). It has been recognized for many years that the permeability of clay soils may be altered by the presence of certain chemicals in the permeating fluid. The use of these materials as hazardous waste facility liners creates the dilemma of how to predict and/or measure any permeability changes that might occur in them from contact with waste chemicals; i.e., to test the compatibility of liner materials with the chemicals to be contained by the liner.

Clay-chemical compatibility testing is necessary to select suitable liner material during facility design. In addition to meeting chemical compatibility requirements, RCRA requires that the inorganic liner must have a compacted hydraulic conductivity (permeability) less than or equal to 1×10^{-7} cm/sec. It is necessary, therefore, to measure the hydraulic conductivity of laboratory-compacted samples of liner material to select a suitable liner material. The hydraulic conductivity of undisturbed samples of field compacted liner materials also must be measured to demonstrate that the hydraulic conductivity achieved in laboratory-compacted samples can be achieved in the field and for construction quality assurance to ensure that the constructed liner will perform as designed.

Currently, there are several tests for determing the hydraulic conductivity of inorganic materials used to line waste facilities (e.g., see SW-846 Method 9100). Most of these tests also have been used to measure the chemical compatibility of liner materials. However, none of these tests have been adopted as standard procedures for low-permeability materials. Selection of the test method and procedure can have a profound effect on the test results. In addition, specific test methods may be suitable for determining hydraulic conductivity but unsuitable for compatibility tests. For these reasons, the Research Triangle Institute (RTI), under contract to EPA's Office of Solid Waste (OSW), has developed and evaluated standard test procedures for determining the hydraulic conductivity of inorganic liner materials and for determining the effects of liquid wastes or waste leachates on the fluid conductivity of these materials.

The objective of this research effort was to develop and evalute procedures for measuring hydraulic conductivity and chemical compatibility. To accomplish this objective, the following approach was used:

- Review available literature on permeability and compatibility test methods.
- Select the most suitable test devices.
- Develop procedures for the selected test devices.
- Evaluate these procedures for ruggedness and variability through a collaborative testing program.

This paper summarizes the results of this research effort, except for results of the colloborative testing program which were not available at the time of its preparation.

DEFINITIONS

The following definitions are used in this paper:

- Hydraulic conductivity or permeability testing, is a method for determining volumetric flux, per unit cross-sectional area, of water through a sample of inorganic liner material.
- Compatibility testing is method for determining the difference in permeability of a sample of inorganic liner material to water versus a liquid waste or waste leachate.

BACKGROUND

The procedure most commonly used for measuring the hydraulic conductivity of a compacted soil is to enclose the sample tightly in a cylinder (permeameter), saturate the sample, and then pass a liquid (permeant) through the sample. The pressure differential across the sample is expressed in terms of hydraulic gradient (a dimensionless quantity), which is the change in pressure head across the sample divided by the height of the sample. The gradient can be controlled by superimposing air pressure above the permeant supplied to the influent end of the sample and by regulating the backpressure applied at the effluent end of the sample. The flow of water through the sample is measured, and the hydraulic conductivity is calculated using Darcy's law:

$$K = \frac{Q/A}{dh/dl} \qquad (1)$$

where:

K = hydraulic conductivity (permeability) (cm/s)

Q = volumetric flow rate (cm^3/s)

A = cross-sectional area of flow (cm^3)

dh/dl = hydraulic gradient (dimensionless)

In clay-chemical compatibility testing, the permeability (K) of a clay soil permeated by a certain chemical is measured. A change or lack of change in the volume of K (when compared to K for water) may be due to a combination of two factors:

- Difference in the permeant fluid viscosity and density (compared to water or other baseline permeant fluid).
- Change in porous medium characteristics as a result of clay-chemical interactions.

To separate these effects, it is necessary to report the results of compatability tests in terms of <u>intrinsic</u>

permeability (k), which is a property of the porous medium alone, both for the tests with the baseline permeant fluid and for the tests with the chemical permeant fluid in question.

Intrinsic permeability has units of length squared (e.g., cm^2) and is related to hydraulic conductivity, K, by Equation 2:

$$K = \frac{kpg}{\mu} \quad \text{or} \quad k = \frac{K\mu}{pg}$$

where:

p = density of the fluid

μ = dynamic viscosity of the fluid

g = acceleration due to gravity

In practice, most researchers report and discuss their test results in terms of hydraulic conductivity or permeability (K) rather than intrinsic permeability (k). Provided that the density and viscosity of the test fluid (at the test temperature) are known, one can calculate the k value to correspond to each K value reported.

Permeameter Types

Three types of permeameters have been used to measure hydraulic conductivity of fine-grained soils. The fixed-wall permeameter (Figure 1) consists of a rigid cylinder of plastic or metal, often 4 inches in diameter, which has been modified to contain a soil sample and to allow a permeant to flow through it. A soil sample is usually compacted directly in the cylinder.

In a flexible-wall permeameter, (Figure 2) a cylindrical column of soil is encased laterally in a flexible membrane (often latex rubber) and enclosed at the ends with porous stones. The enclosed soil sample is placed in a fluid-filled cell that is pressurized to provide a confining pressure on the sides of the sample (Figure 2-3). The confining fluid and the permeant are contained in two entirely separate systems which do not allow the two fluids to mix. The sample to be tested may be prepared in a compaction mold and extruded for testing in the flexible-wall cell or may be samples taken from the field using a shelby tube or other coring device.

Consolidation cells are commonly used in the field of geotechnical engineering to determine the compressibility and rate of settlement of soils. Consolidation occurs when water is squeezed out of the soil and is therefore a function of permeability. With proper modification, a fixed-ring consolidation cell can be used to measure permea-

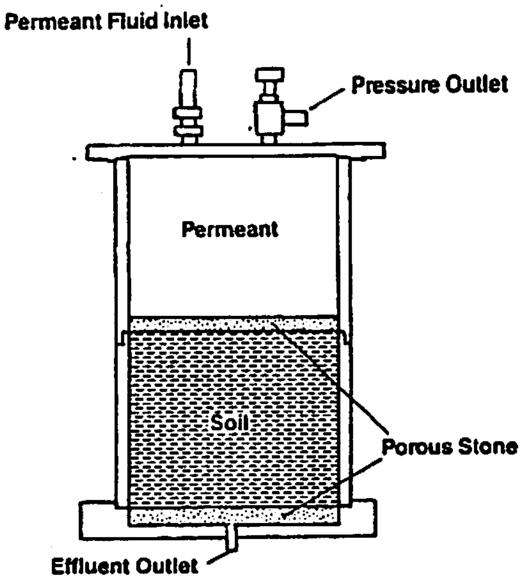

Figure 1. Fixed-Wall Permeameter

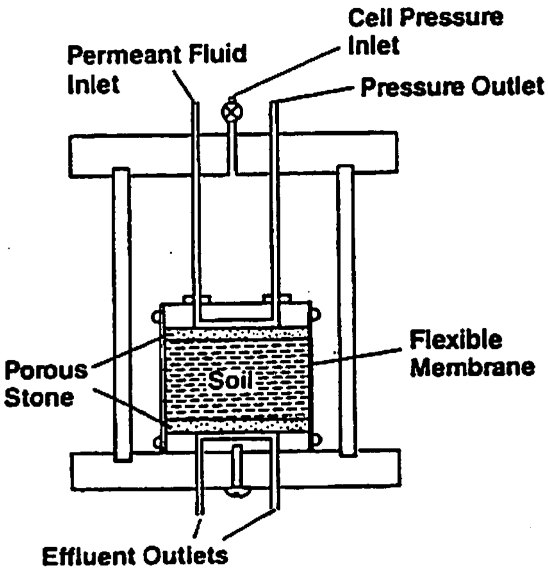

Figure 2. Flexible-Wall Permeameter

bility and is commonly used for applications such as earth dams, retaining walls, and slurry trenches. This device has not been used widely in the evaluation of the chemical compatibility of clay liner materials or for the measurement of hydraulic conductivity. For this reason, test procedures using this device were not evaluated.

Boynton and Daniel (1985) used compaction-mold, consolidation-cell, and flexible-wall permeameters to measure the hydraulic conductivity of kaolinite and fire clay. While there were differences in conductivities measured with the three devices, the type of permeameter did not seem to have a large effect on the results. Differences in measured permeabilities between devices were substantially less than one order of magnitude.

In a series of permeability tests performed on three types of clay, Peirce (1984a,b) found that fixed-wall, flexible-wall, and consolidation permeameters gave essentially the same results.

Factors Influencing Testing Results

Important factors that influence permeability measurements include sample characteristics and preparation, permeant properties, design of the test apparatus, and selection and control of variables during performance of the test. Some of the more important factors are discussed below.

Maintenance of Field Moisture Content--

In preparing soils for permeability tests, some laboratories air dry soil, while others maintain the soil at or near the field moisture content during sample preparation. Drying facilitates breaking up clods, sieving the soil, and obtaining a homogeneous soil mass for testing. With some soils, however, rehydrated dried soil has different properties than soil maintained at field moisture. Sangrey et al. (1976) found that drying and rewetting significantly altered the liquid limits of several clays from field conditions. In spite of rehydration times of several weeks (a 24 hour curing period is commonly used for laboratory tests), the properties of some clays were irreversibly altered by drying. However, Daniel and Liljestrant (1984) tested the permeability of a Gulf Coast clay prepared with and without air drying. This clay did not show any appreciable difference in permeability as a result of the different sample preparation regimes. This suggests that although the properties of some clays may be irreversibly changed by drying, some clays are not appreciably affected.

Clod Size Control--

"Clod" is the term used to described lumps of clay. Daniel (1981) demonstrated that clod size can significantly affect laboratory permeability measurements. For a single clay, samples compacted from 3/8 inch clods had a permeability of 2.5 x 10^{-7} cm/sec; samples compacted from 3/16 inch clods had a permeability of 1.7 x 10^{-8} cm/sec; and samples compacted from 1/16 inch clods had a permeability of 8.5 x 10^{-9} cm/sec. This illustrates the importance of controlling clod size to obtaining consistent laboratory permeability measurements.

Compaction Methods--

Several techniques have been developed for preparing laboratory compacted clay samples for permeability testing. For a fix-wall permeability test the clay is compacted directly in the permeameter, which in this case serves as the compaction mold. For flexible wall tests, the clay is compacted in a separate compaction mold, extruded and then trimmed to fit the permeameter. When samples are trimmed to length, care must be exercised to avoid forming smear zones from the cutting tool sliding against the clay. These smear zones can decrease the permeability of the sample by as much as 20 percent (Carpenter, 1982).

There are three methods that are commonly used to compact test samples in the laboratory. These are:

- static compaction using a hydraulic or mechanical press;
- impact compaction using a drop hammer; and
- kneading compaction using the Harvard Miniature Compactor.

Recently Dunn and Mitchell (1984) reported that when otherwise identical samples were compacted by different methods to 90 and 95 percent of their maximum dry density, there were notable differences in their hydraulic conductivities. At both dry densities, static compaction produced samples with the highest hydraulic conductivities, impact was second highest, and kneading the lowest.

Sample Size--

Boynton and Daniel (1985) compacted test samples with various diameters ranging between 1.5 and 6 inches. The measured hydraulic conductivities showed an increase with sample diameter; the smallest diameter having the lowest conductivity. However, the highest and lowest conductivities differed by only a factor of 2, which was not considered by the authors to be of any practical significance.

Carpenter and Stephenson (in press) used a flexible-wall permeameter to determine the influence of sample length-to-diameter ratio on permeability. All the samples were tested at a gradient of 200. For samples with 2.8-inch and 4-inch diameters, they observed a slight decrease in permeability as the length-to-diameter ratio increased.

Anderson and Bouma (1973) experimented with a series of undisturbed core samples of different lengths to determine the effect of sample size on permeability. They found that permeabilities of cores 17 cm in length were lower by half an order of magnitude than were the permeabilities of 5-cm length cores.

Sample Saturation--

A soil sample, even when compacted, has some degree of porosity. The pores are filled with either gas (usually air) or liquid. Because water cannot flow through a gas bubble, entrapped air within the interconnected pores blocks flow channels causing a reduction in permeant flow and a correspondingly low apparent permeability. Soaking the sample from the bottom with the top open to the atmosphere (a technique used by some in an attempt to saturate the samples) may not result in complete saturation. Smith and Browning (1942) found that in 200 specimens soaked from the bottom, the degree of saturation averaged 91 percent with the lowest value at 78 percent.

The extent of the error in permeability measurement attributable to entrapped gas bubbles has been studied by several investigators. Decreases in permeability by factors ranging from 2 to 5 have been reported by Johnson (1954). Olsen and Daniel (1979) presented evidence that the coefficient of permeability may increase by about four orders of magnitude as the degree of saturation increases from around 20 to 100 percent.

The application of backpressure to a soil sample is the most effective method for achieving saturation (Matyas, 1967; Daniel et al., 1984). Backpressure is pressure applied to the pore fluid within a sample for the purpose of compressing entrapped air bubbles and causing the gas to go into solution in the permeant. This is accomplished by simultaneously applying pressure to both the inflow and outflow ends of the soil sample.

Hydraulic Gradient--

To measure the permeability of compacted clay within a reasonably short period of time, it is necessary to conduct the tests at hydraulic gradients that are substantially greater than those encountered in the field. The two implied conditions in the Darcy equation are: the flow rate is directly poportional to the hydraulic gradient and the relationship between flow rate and hydraulic gradient is linear through the origin. There is no single accepted hydraulic gradient for use in permeability testing.

Gradients of 5 to 20 are recommended by some (Zimmie, 1981) and gradients as high as 362 have been used by others (Brown and Anderson, 1982).

Over the past several decades, there have been several studies aimed at evaluating the validity of Darcy's law by measuring the dependence of permeability on hydraulic gradient. Oakes (1960), Mitchell and Younger (1967), and others have published data that indicate a departure from linearity at low hydraulic gradients. Bowles (1979) observes that in clays a threshold gradient of 2 to 4 may be necessary to produce any flow.

Since Darcy's law indicates a linear relationship between flow rate and hydraulic gradient, many workers have used elevated hydraulic gradients to reduce testing time. However, if hydraulic gradients are excessive, piping (opening flow channels and increasing hydraulic conductivity) or particle migration (blocking flow channels and reducing hydraulic conductivity) may occur, and this can significantly influence permeability measurement. Although such effects can occur and have been reported (Daniel, 1981; Mitchell and Younger, 1967), studies have been conducted at elevated gradients with no evidence of piping or particle migration (e.g., Brown and Anderson, 1982).

Zimmie et al. (1981) have recommended use of hydraulic gradients between 5 and 20 for laboratory studies. Research performed at Louisiana State University concluded that tests conducted under hydraulic gradients as high as 100 are "acceptable for testing, reducing testing times to realistic and practical duration" (Acar and Field, 1983). Dunn and Mitchell (1984) reported that increasing the gradient in steps from 20 to 200 caused an irreversible decrease in hydraulic conductivity.

Confining Pressure--

In flexible-wall cells the membrane-encased sample is subjected to a confining pressure that is greater than the pore pressure within the sample. There is an ongoing controversy about whether flexible-wall cells are appropriate for compatibility testing of permeant fluids that may cause the soil sample to shrink and crack. Because of the confining cell pressure, shrinkage cracks that might occur in the field and that might appear in fixed-wall devices may not form in the flexible-wall cell. Not all researchers are in agreement on this issue, since the effect has not been demonstrated clearly in comparative tests. However, Boynton and Daniel (1985) allowed desiccation cracks to form in soil samples which were then tested with confining pressures of 2, 4, 8, and 15 psi. They found that the permeability decreased markedly as the effective stress increased. Confining pressures in the range of 4 to 8 psi were sufficient to begin closing the cracks, and confining pressures in excess of 8 psi closed the cracks and greatly decreased permeability.

Current Practices in Commercial Laboratories

Peirce (1984a), examined the permeability testing procedures of three commercial laboratories. These procedures are presented in Table 1. For this study, seven other laboratories were contacted and questioned about various aspects of their flexible-wall permeameter testing protocols. The information gathered is presented in Table 2.

In reviewing both Peirce's and our findings, it becomes evident that no two laboratories are using the same test protocol for flexible-wall permeameter permeability testing. The influence on permeability of factors such as material handling, sample preparation, and sample size, makes it questionable whether permeability test results reported by differenct laboratories are comparable.

TEST PROCEDURES DEVELOPMENT

Test procedures for the test cells are detailed in Truesdale et al. (1985). Two test devices were selected for test procedure development and evaluation: fixed-wall permeameters and flexible-wall permeameters. Advantages and disadvantages of these devices are summarized in Table 3. Detailed test procedures for each of these devices were developed (Truesdale et. al., 1985). The test procedures developed for fixed- and flexible-wall test methods are very similar; they differ only in sample dimensions and in the application of confining pressures to the sample in the flexible-wall tests. Rationale for the selection of several key test parameters common to both test devices is presented in this section.

Sample Preparation

The physical properties of some clay change irreversibly upon drying. For this reason it is important to maintain as much moisture in the sample as is practicable. However, it is necessary to dry the clay to the point that clods can be reduced easily to the specified size and homogenized (4 mesh); poor preparation will introduce variability in the test results. The procedures described in ASTM -D 698 (Section 4.1, Method A) were selected for preparing samples for laboratory compaction, because the method is proven and is designed for this purpose.

Sample Compaction

Impact compaction, a modified form of ASTM-D 698, was selected for situations where laboratory compacted samples

TABLE 1. COMMERCIAL LABORATORY PREPARATION OF CLAY SAMPLES FOR PERMEABILITY TESTING

	Clay	Commercial Lab #1	Commercial Lab #2	Commercial Lab #3
Clay	Type	Field clays, mostly kaolinite and illite	Field clays	Field clays (CH)
	Excavation Procedure	Test pits with backhoe	Obtained from client	Backhoe-bulk sample from stockpile
	Handling and Storage	Double wrap of plastic and burlap	Airtight plastic bags	Bulk samples as received
Processing	Size Control	Hand pick or break lumps >¾"	No. 4 sieve	Hand pick
	Organic Control	Hand pick	Hand pick weeds and roots	Hand pick
	Moisture Control	Immediately test for moisture content	Prevent drying	Prevent drying
	Homogenity	Visual inspection—cut and quarter large samples	Use representative sample from bulk	Representative sample from bulk
	Additives	None	None	None
Preparation	Wetting Substance	By priority 1. Site water 2. Tap water 3. Distilled water	As received	Deionized water
	Wetting Procedure	Mist bottle and mixing	As received	Added in small increments—Allow to absorb over night
	Percent Moisture	Optimum moisture plus 1-2%	As received	Optimum
	Size Control	¼-inch sieve	As received	No. 4 sieve
Compaction	Test Vessel Dimensions	2.8" diameter, 3-5" height	4" mold	Shelby tube, 2.8" diameter
	Compaction Procedures	Standard Proctor Modified Proctor	Standard or modified Proctor	Standard or modified Proctor
	Lift Depth	Varies Varies	Approximately 1 inch	2½ inches
	No. of Lifts	3 5	3 or 5	3
	Scarify Lift	Yes	Yes	Yes
Testing	Preflush Substance	Depends on project: site, tap, distilled water	Demineralized water	Deionized water
	Head	50-100 gradient	100 psi	Variable
	Preflush Time (Pore Volumes)	1 pore volume	No set number	3 runs—until constant K achieved
	Chemical Permeants Tested	Organic and inorganic	1.5 pH H_2SO_4 Brine, boiler wastewater	N.A.

From: Peirce et. al. (1984a)

TABLE 2. SOME ASPECTS OF FLEXIBLE-WALL TEST PROCEDURES AT SEVEN COMMERCIAL LABORATORIES (A-G)

Maintenance of Mositure Content	Clod Size Reduction	Mositure Addition	Compaction Method
A. Air dry	A. —	A. Tap water	A. Static compaction—5 lifts—scarify between lifts.
B. Maintain close to field mosture	B. Manually break up to pass #4 sieve	B. Tap water—hand knead—cure for 24 h	B. Hand-tamp with 0.75-inch-diameter rod—1.5-cm lifts—scarify between lifts to depths of 1/8 inch.
C. Dry to just below plastic limit if clumps are larger than #4 sieve	C. Use rubber mallet to large clods	C. Tap water—spray on—hand knead—cure for 24 h	C. Hand-tamp with 0.75-inch-diameter tamper moved in diagonal pattern across sample—5 lifts—scarify between lifts.
D. Maintain close to field moisture	D. —	D. Tap water—hand knead	D. Harvard Miniature Compactor—10 lifts—scarify between lifts
E. Maintain field moisture	E. Manually break up clods—sometimes force through #4 sieve	E. Site water or tap water	E. Hand-tamp known weight of soil to predetermined volume
F. Maintain field moisture	F. Vegetable mixer-shredder produces fine strands of clay (1/10 x 1/16) inch cross section	F. Deionized water—spray on—hand knead	F. Hand-tamp known weight of soil to predetermined volume
G. Oven-dry most clays	G. Manually break up clods	G. Tap water or site water if required	G. Harvard Miniature Compactor with "40-lb" spring—compact in 6 lifts to specified volume—scarify between lifts

TABLE 2. (Continued)

Sample Size	Sample Saturation	Test Conditions
A. 2.85-inch diameter length-to-diameter ratio of 2	A. Backpressure 70-100 psi—maintain until 95% saturation is achieved	A. Permeability to water—gradient of 20-30 for 1 day. Permeability to leachates—gradient of 70-100 for 3 pore volumes
B. 2.9-inch diameter length-to-diameter ratio of 1-1.5	B. Backpressure 70-100 psi—maintain until 95% saturation is achieved	B. Gradient of 10 Test is run until approximately 1 week of consistent readings are obtained.
C. 2-inch diameter	C. Backpressure— maintain effective stress of 1 psi and increase pressures until 95% saturation is achieved	C. Permeability to leachates—head of 45 psi—can vary greatly depending on job requirements.
D. 2-inch diameter length-to-diameter ratio of 1	D. Backpressure 90 psi—gradient under 10	D. Gradient under 10 if possible Water tests run until stable flow obtained. Leachate tests run for 2 pore volumes.
E. 2.8-inch diameter 6-7-inch height	E. Backpressure in small increments (maintain effective stress of 5 psi) until 95% saturation is achieved.	E. Permeability to water—maximum gradient of 25. Tests run until inflow and outflow are equal Permeability to leachates—higher gradients. Tests run until inflow and outflow are equal after 2 pore volumes.
F. 2.8-inch diameter 4-inch height	F. Backpressure	F. Gradients between 6.5 and 9.
G. 2-inch diameter	G. Backpressure 1 hour to overnight at 9.5 psi pore pressure (0.5 psi differential between top and bottom) and 10 psi cell pressure—increase to 15-20 psi cell and 14.5-19.5 pore pressure and check saturation. Increase pressures by 0.5 psi until 95% saturation is achieved.	G. Pressure drop across specimen maintained between 0.5 psi and 15 psi depending on sample characteristics.

TABLE 3. ADVANTAGES AND DISADVANTAGES OF SELECTED TEST METHODS

FIXED-WALL PERMEAMETERS

Advantages

- Shrinkage cracks can form (rigid walls, no confining pressure)
- Simplest device
- Easily made compatible with most chemicals

Disadvantages

- Sidewall leakage can occur
- Cannot measure degree of saturation
- Cannot easily measure sample consolidation or swelling
- More difficult to use undisturbed samples
- Sample diameter is fixed

FLEXIBLE-WALL PERMEAMETERS

Advantages

- Eliminates sidewall leakage
- Can simulate field stresses on sample
- Can use a variety of sample sizes
- Easy to test undisturbed samples
- Can measure degree of saturation
- Can measure vertical and volumetric deformations

Disadvantages

- Confining pressure may prevent shrinkage cracks from forming
- Permeant fluid may be incompatible with membrane
- Cells are more expensive than fixed-wall cells

are to be tested, because it is a reporoducible method that has proven successful in a variety of permeability and compatibility tests. This method was not selected on the basis of what is most representative of field conditions; there is insufficient information currently available to indicate which laboratory compaction method most closely generates permeabilities that are achieved in the field with full-scale compaction equipment.

Sample Thickness

Peirce (1984a,b) proved that a 2-in. thick sample is adequate for reproducible testing in a reasonable amount of time.

Sample Diameter

Boynton and Daniel (1985) demonstrated that sample diameters from 1.5 to 6 in. do not affect testing results significantly. A 4-in. fixed-wall cell was chosen because it is dimensionally the same as a standard compaction mold (ASTM-D 698). A 2.8-in. sample was chosen for flexible-wall tests to accommodate the most common sampling tube (Shelby tube) size. Other sample diameters (from 1.5 to 6 in.) probably can be substituted without a significant change in test results.

Sample Saturation

It is necessary to saturate the sample fully to ensure accurate test results. Backpressure saturation has been proven effective by a variety of researchers and is specified in this procedure.

Gradient

Gradients of 2 to 200 have proven acceptable to researchers. High gradients can promote consolidation of certain types of soil. Low gradients result in excessively long testing times. A gradient of 100 was selected as a compromise between the two extremes.

Termination Criteria

As there is no standard protocol for performing a permeability test, there also is no standard method for determining when a test should be ended. The problem is not so great when water is the permeant since eventually (usually within several days or weeks) a steady state will be reached as evidenced by a constant value of K measured over a period of several days. With chemicals or leachates as permeants, the situation may be quite different, since chemical interactions between the permeant and the clay that could affect the permeability could continue over a long period of time.

In several laboratories the criterion for ending a test is based on the number of pore volumes of permeant that have passed throught the sample. Sometimes the criterion is that a steady-state flow has been established. Often , these two requirements are combined with termination being based on a steady-state flow in conjunction with a certain minimum number of pore volumes having been passed through the sample. Pierce (1984a) has refined this procedure as follows:

> Readings of column level and time are taken at certain intervals throughout the test. The hydraulic conductivity is computed for each time interval. From this set of data, the first ten points are taken and a linear regression analysis is performed to determine the slope of the hydraulic conductivity vs. time curve. The first point is then dropped and another value is added on the other end. The slope is calculated again, and so on. In the beginning of the test, this slope will be fairly large, but as the test progresses it will decrease and approach zero when steady-state is obtained.

Two criteria must be met for a test to be terminated for these procedures.

- o the slope of the curve does not significantly vary from zero at the 95 percent confidence level; and
- o at least one pore-volume of the liquid has passed through the sample.

APPLICATIONS OF TEST PROCEDURES

This section briefly discusses important aspects of the application of the fixed-wall test and flexible-wall procedures.

Permeability Testing--Compacted Samples

Boynton and Daniel (1985) and Peirce (1984a and b) has demonstrated that for permeability measurements on laboratory-compacted samples, the two devices are practically equivalent. For situations requiring this kind of permeability measurement (e.g., preliminary liner material selection), selection of the test device type probably will not influence test results if the test procedures are equivalent. Other than the test cells and a few aspects of their operation (e.g., a cell pressure system for the flexible-wall cell) the procedures for both test devices developed during this study are identical.

Permeability Testing--Undisturbed Samples

Permeability testing of undisturbed samples from the field is necessary for confirming laboratory-derived permeability/density/moisture relationships in a field-compacted test fill and for quality control of liner construction. The samples are collected in sampling tubes (e.g., ASTM D 1587) and placed directly into the permeameters. For this loading the sample into the test cell and because of the reduced probability of sidewall leakage. Because of their reliability, control of sidewall leakage, and ease of teting undisturbed samples, flexible-wall cells were preferred by most of the commerical laboratories contacted during this study.

Compatibility Testing--Compacted Samples

The purpose of compatibility testing of inorganic liner materials is to quantify the change, or lack of change, in permeability of the materials when they are exposed to a liquid waste or waste and leachate, and thus determine the suitability of a liner material for use for hazardous waste containment. Although tests such as Atterberg limits and hydrometer particle size analysis have been suggested as useful and simple index tests that may be used to determine compatibility, permeameter tests are the only methods that are adequately developed for use as standards.

Compatibility testing involves measuring the permeability of a representative sample of liner material to a baseline test fluid and comparing this result with the permeability of the same material to the waste fluid in question. An increase in permeability, after correcting for density and viscosity differences between the same fluids, may be defined as incompatibility.

The test method presented in this document requires baseline and chemical testing to be conducted on separate representative samples of the liner material. Although many researchers follow baseline testing with chemical testing on the same sample, for some low-strength soils, the gradient applied during baseline testing could consolidate the sample so that the sample is changed for the chemical test. In addition, testing separate samples allows the soil to be saturated with the chemical to be tested, ensuring better contact of the chemical with the soil. However, with side-by-side testing it is critical that the samples be the same; they should be taken from the same homogeneous sample and compacted in exactly the same manner.

The choice of test cell device may influence test results more for compatibility testing than for regular permeability testing, although no controlled studies have been conducted that postively demonstrate this. Fixed-wall tests may produce more variable results, because sample shrinkage from chemical attack may cause sidewall leakage or blowout in some samples and not in others. On the other hand, fixed-wall tests may provide more conservative measures of permeability, because they allow the sample to shrink and crack. Boynton and Daniel (1985) have demonstrated that confining pressures of 4 to 8 psi in flexible-wall cells can begin to close previously formed desiccation cracks and that this effect becomes more pronounced at higher cell pressures. The collaborative testing program will demonstrate the differences between the two methods because tests will be conducted with a clay-chemical combination that will definitely produce desiccation cracks in the clay.

Construction-site water is specified as baseline testing fluid in the test procedures. This allows the baseline tests to be used to aid in liner soil selection, and ensures that any interactions of the soil with the baseline fluid are the same as those that may occur in the field. Tap water may be used only if it can be shown that results will be comparable to those with site water. Atterberg limit tests and hydrometer grain size distribution tests without dispersing agents may be rapid and reliable means for establishing comparability.

All materials to be used for constructing compatibility test devices (e.g., valves, tubing, and cell walls) must be compatible with the chemicals tested. Chemically resistant materials such as Teflon and stainless steel are commonly used. If there is doubt about chemical/material compatibility, a sample of the material in question can be soaked in the chemical and then checked for any sign of distortion, swelling, dissolution, corrosion, or other degradation. It is especially important that the tubing and buretts used in the permeant measuring system are not subject to chemical attack or creep, because tubing creeps under pressure and distortion can affect the calibration of flow measurement devices. Some guideines for tubing material selection are:

- Nylon tubing is the stiffest and least susceptible to expansion under pressure or creep. It may, however, be affected adversely by some chemicals (e.g. carbon tetrachloride).
- Teflon tubing is more resistant; however, it may creep under sustained pressure, and it is hard to see through.
- Glass is the best material for flow measuring devices because of its stiffness and resistance to most chemicals. However, it must be thick enough to withstand testing pressures and handled carefully to avoid breakage.

TEST METHOD EVALUATION

As discussed above, two test methods, fixed-wall and flexible-wall, were selected for evaluation. Each appears to satisfy the required measurement objectives and is compatible with existing equipment in commerical laboratories. Current literature on labratory testing of soil/chemical compatibility does not provide sufficient information to allow the selection of the best technique or to demonstate the equivalency of the two procedures. Our own testing of the procedures suggests that they may be comparable; however, further data are needed for a definitive conclusion.

The criteria suggested for comparison of the tests are precision, sensitivity, and ruggedness. Precision can be measured if defined in terms of the random error associated with the measurement process (i.e., the reproducibility of the measurement). Precision is commonly measured by the standard deviation associated with repeated measurements of the same quantity.

In addition to being precise, the test procedure must also be sensitive to differences in hydraulic conductivity. As an extreme example, a test procedure that always gives the measurement "2" would be 100 percent precise but completely insensitive to variations in hydraulic conductivity. Sensitivity can be determined by testing various clay-permeant combinations with the two test procedures and observing the magnitude of the differences in the compatibility measurements. Each measurement would involve running parallel permeability measurements for tap water and chemical and defining compatibility as the increase in permeability of the chemical vs. tap water.

Finally, the test procedures should be rugged, that is, relatively insensitive to minor variations in the operations, equipment, and materials used in testing. The ruggedness of a test procedure is generally assessed by varying in a controlled manner the conditions under which testing occurs.

A two-phase approach to test evaluation was followed: first, a ruggedness test was conducted to refine both procedures for standard use in clay-permeant compatibility measurement and then collaborative testing was carried out to determine the between- and within-laboratory variability of the procedures.

Ruggedness Testing

Ruggedness testing of a procedure should always precede determination of its precision in a collaborative testing program (Youden and Steiner, 1975; ASTM, 1964). The purpose of ruggedness testing is to determine a procedure's sensitivity to minor reasonable variations in the method's variables by deliberately changing these variables in a planned group of tests. This is necessary so that test procedures may be specified and closely controlled as necessary to avoid excessive variation among the collaborative test cooperators, as this may lead to misleading or inconclusive results.

Ruggedness testing of the two test procedures involved repeated measurements of a "standard" clay-permeant combination made by a single laboratory with procedures and parameters varied systematically. The test design that was used for ruggedness testing is a multifactorial design developed by Plackett and Burman (1946) and used for ruggedness testing by Youden and Steiner (1975). The design determines the effect of varying seven factors (test variables) in eight tests for each procedure. The test matrix is pictured in Table 4. Table 5 is a list of the conditions altered and their assigned values.

Table 6 and Table 7 present ruggedness testing results for flexible-wall and fixed-wall devices, respectively. These tables present the differences for each condition; these differences are calculated for each condition from the average of the four high value test runs (capital letters) minus the average of the four low value test runs (lower case letters). The conditions are ranked in each table according to the size of the differences.

Several observations may be made from these tables. First, the flexible-wall test procedure is more rugged than the fixed-wall procedure. This is not surprising because of the confining pressure in the flexible-wall device reduces the probability of sidewall leakage. Inspection of the signs in the tables also is instructive. A negative sign indicates that the high value condition results in a lower permeability than the low value condition. These signs are consistent between fixed-wall and flexible-wall tests for the four highest-ranking conditions, suggesting that changes in these conditions have real effects on the results. The change in signs between devices for the latter three differences suggests that these effects are not significant (Youden and Steiner, 1975).

Collaborative Testing

Following ruggedness testing and refinement of the test procedure, a collaborative study was carried out to determine the variability -- both between and within laboratories -- that can be expected from the normal useage of the test procedures and to compare the two test procedures to see which is more precise. Although it would have been desirable to test multiple clay-permeant combinations, this was much too costly and time-consuming to implement. Instead, for each test procedure, each laboratory made repeated permeability measurements in parallel on a single clay soil using a standard water (0.005 N $CaSO_4$) and a chemical (methanol) previously shown to cause a measurable change in the permeability of the soil. The average compatibility measurements for the tests are compared to determine if the difference between the two average compatibility measurements is explained by the measurement error of

TABLE 4. RUGGEDNESS TEST DESIGN

Experimental Conditions	Combination or Determination No.							
	1	2	3	4	5	6	7	8
1	A	A	A	A	a	a	a	a
2	B	B	b	b	B	B	b	b
3	C	c	C	c	C	c	C	c
4	D	D	d	d	d	d	D	D
5	E	e	E	e	e	E	e	E
6	F	f	f	F	F	f	f	F
7	G	g	g	G	g	G	G	g

TABLE 5. LIST OF ALTERED CONDITIONS AND VALUES FOR RUGGEDNESS TESTING OF PERMEABILITY/COMPATIBILITY TEST METHODS

Condition	Letter	High value (capital letter)	Low value (lower case letter)
1. Sample preparation	A,a	Air drying and grinding	Limited drying and manual size reduction
2. Scarification	B,b	Yes	No
3. Moisture content	C,c	2-3% above optimum	2-3% below optimum
4. Lift thickness	D,d	1.5 inch	0.75 inch
5. Compactive energy	E,e	110% std. proctor	90% std. proctor
6. Hydraulic gradient	F,f	200	100
7. Backpressure	G,g	Yes	No

TABLE 6. TABLE OF DIFFERENCES--FLEXIBLE-WALL

Parameter		Difference (cm/sec)
Moisture Content		-2.30 E-7
Lift Height		-1.81 E-7
Back Pressure		1.78 E-7
Compactive Energy		-9.23 E-8
Drying Procedure		8.37 E-8
Scarification		-4.66 E-8
Hydraulic Gradient		4.54 E-8
Mean (cm/sec)	1.28 E-7	
Std. Dev. (cm/sec)	1.98 E-7	

TABLE 7. TABLE OF DIFFERENCES--FIXED-WALL

Parameter		Difference (cm/sec)
Compactive Energy		-5.36 E-7
Moisture Content		-4.90 E-7
Lift Height		-4.31 E-7
Back Pressure		4.20 E-7
Hydraulic Gradient		-9.94 E-8
Drying Procedure		-9.19 E-8
Scarification		8.69 E-8
Mean (cm/sec)	2.61 E-7	
Std. dev. (cm/sec)	4.27 E-7	

the two procedures. This is a crude measure of sensitivity. More accurate measures would require much more testing than was possible in this study.

To measure the precision of the compatibility tests, each laboratory in the collaborative study made repeated measurements with each test procedure of the change in permeability of the standard clay between the standard water and the standard chemical permeant. The measurements with standard water also will be used to determine the precision of the test procedures for measuring permeability.

To initiate the study, a sufficient quantity of the standard clay soil was obtained for all repetitions of the test procedures. The clay soil was thoroughly homgenized and then split into samples, with each sample randomly assigned to a laboratory/test procedure/repetition combination. The homogenization ensured that the samples of clay are were similar as possible. The randomization of samples provided additional protection should systematic differences in the clay remain after homogenization.

To determine the number of measurements necessary to adequately determine the precision of the tests, it was decided to set , the probability of determining that there is a difference in the two test procedures when there is none, at 0.05, and , the probability of determining that the tests are the same when they are different, at 0.05, for a standard error ratio of 2 (i.e., a standard error ratio of 2 must be detected without error 95 percent of the time). To meet these requirements it was determined that 30 repetitions of each test procedure were needed. This is in basic agreement with ASTM D2777 (Determination of Precision and Bias of Methods of Committee D-19 on Water) which suggests that a total of 31 replicates be used in testing.

In this testing program, sixteen laboratories agreed to conduct each procedure in triplicate, for a total of 48 replications for each test procedure. This ensures that the minimum requirements discussed above will be met and that interlaboratory precision and total variability can be determined with an adequate degree of confidence even if all laboratories do not complete the full testing program. The long testing times and expense of conducting these tests makes incomplete results a real possibility.

CONCLUSION

1. The most commonly used laboratory methods for determining the permeability of soil liner materials to water or waste leachates involves the use of permeameter cells in which a permeant fluid is forced through a saturated soil layer at an elevated gradient.

2. No standard test procedures for determining the chemical compatibility of soil liner materials currently

exist. The literature reveals large variability in the test methods and procedures used by various researchers. However, two types of permeability cells predominate: fixed-wall, in which the sample is contained by a rigid-walled container, and flexible-wall, in which the sample is contained by flexible membrane. Both methods have distinct advantages and disadvantages. However, several studies have demonstrated that these two test methods produce comparable results when used to test a clay soil's permeability to water.

3. Surveys of commercial laboratories reveal considerable variation in test procedures. The most commonly used permeameter cell is the flexible-wall device, with ease of testing undisturbed samples and no sidewall leakage being cited as the reasons for this preference. Fixed-wall cells are also used is some laboratories.

4. Review of the literature has revealed that permeability and compatibility test results are influenced by test methods and procedures. The variability in methods and procedures that prevails among testing organizations thus makes it difficult to compare test results from laboratory to laboratory.

5. Two test cells, fixed-wall and flexible-wall, were selected to be evaluated for ruggedness and interlaboratory precision. These test cells were selected based on their technical suitability and widespread acceptance and use. Test procedures have been developed for each cell type, based on information gathered from the literature and investigators' experience with permeability testing.

6. A ruggedness test was conducted to determine the methods' sensitivity to minor changes in procedures. Test procedures and parameters evaluated included sample preparation technique, clod size, moisture content, compactive energy, sample thickness, gradient, and saturation method. Results of the ruggedness testing were used to refine the test procedures prior to collaborative testing.

7. A collaborative testing program was designed to determine the interlaboratory precision of the two methods. A total of 60 tests, 30 for each method, were conducted to estimate and compare the variability of the two test methods. The tests were conducted using a single clay soil, a standard baseline permeant (0.005 N $CaSo_4$), and a waste permeant (methanol) that will change the clay soil's permeability.

REFERENCES

Acar, Y. B. and S. D. Field. 1982. Organic Leachate Effects to Hydraulic Conductivity in Fine-Grained Soils. Report GE-82-01, Hazardous Waste Research Center, Louisiana State University. Baton Rouge, LA.

Anderson, J. L., and J. Bouma. 1973. Relationships Between Saturated Hydraulic Conductivity and Morphometric Data of an Argillic Horizon. Soil Science Society American Proceedings. 37:408-413.

Bowles, J. E. 1979. Physical and Geotechnical Properties of Soils. McGraw-Hill Book Company. New York. 478 pp.

Boynton, S. S., and D. E. Daniel. 1985. Hydraulic Conductivity Tests on Compacted Clay. J. of Geotechnical Engineering. 111(4):465-478.

Brown, K. W. and D. Anderson. 1982. Effects of Organic Solvents on the Permeability of Clay Soils. Draft Report. Texas A&M University. Texas Agricultural Experiment Station. College Station, TX. 153 pp.

Carpenter, G. W. 1982. Assessment of the Triaxial Falling Head Permeability Testing Technique. PhD. Dissertation. University of Missouri. Rolla, MO.

Daniel, D. E. 1981. Problems in Predicting the Permeability of Compacted Clay Liners. In: Symposium on Uranium Mill Tailings Management, Fort Collins, CO. pp. 665-675.

Daniel, D. E. and H. M. Liljestrand. 1984. Effects of Landfill Leachates on Natural Systems. A Report to Chemical Manufacturers Association.

Dunn, R. J., and J. K. Mitchell. 1984. Fluid Conductivity Testing of Fine Grained Soils. J. of Geotechnical Engineering. 110(11):1648-1665.

Johnson, A. I. 1954. Symposium on Soil Permeability. ASTM STP 163, American Society for Testing and Materials. Philadelphia, PA. pp. 98-114.

Mitchell, J. K., and J. S. Younger. 1967. Abnormalities in Hydraulic Flow through Fine-Grained Soil. ASTM STP 417. pp. 106-139.

Oakes, D. J. 1960. Solids Concentration on Effects in Bentonite Drilling Fluids. Clay and Clay Minerals. 8:252-273.

Olson, R. E., and D. E. Daniel. 1979. Field and Laboratory Measurements of the Permeability of Saturated and Partially Saturated Fine-Grained Soils. In: ASTM Symposium on Permeability and Groundwater Contaminant Transport. Philadelphia, PA. 67 pp.

Peirce, J. J. 1984a. Effects of Inorganic Leachates on Clay Liner Permeability. Report of U. S. Environmental Protection Agency. MERL-SHWRD. Cincinnati, OH.

Peirce, J. J. 1984b. Soil Preparation and Permeability Testing with Consolidation Cell Apparatus. Final Report. EPA Contract No. 68-03-3149-24-2. Cincinnati, OH.

Plackett, R. L. and J. P. Burman. 1946. The Design of Optimum Multifactorial Experiments. Biometrika. 33:305.

Sangrey, D. A., D. K. Noonan, and G. S. Webb. 1976. Variation in Atterberg Limits of Soil Due to Hydration History and Specimen Preparation. Soil Specimen Preparation for Laboratory Testing. ASTM STP 599. American Society for Testing and Materials. pp. 158-168.

Smith, R. M., and D. R. Browning. 1942. Persistent Water-Unsaturation of Natural Soil in Relation to Various Soil and Plant Factors. Soil Science Society of American Proceedings. 4:114-119.

Truesdale, R. S., et al. 1985. Laboratory Methods for Testing the Permeability and Chemical Compatibility of Inorganic Liner Materials. Final Report. EPA Contract 68-03-3149-10-6. U. S. Environmental Protection Agency. Washington, D.C.

Youden, W. S. and E. H. Steiner. 1975. Statistical Manual of the Association of Official Analytical Chemists. AOAC. Washington, D.C.

Zimmie, T. F., J. S. Doynow, and J. T. Wardell. 1981. Permeability Testing of Soils for Hazardous Waste Disposal Sites. In: Proceeding of the Tenth International Conference on Soil Mechanics and Foundation Engineering, Vol. 2. Stockholm, Sweden. pp. 403-406.

ROUND-ROBIN STUDY OF LEACHING METHODS AS APPLIED TO SOLID WASTES FROM COAL FIRED POWER PLANTS

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ABSTRACT

In 1979, the Electric Power Research Institute (EPRI) sponsored a multiple laboratory investigation of the variability and reproducibility of the U.S. EPA Extraction Procedure (EP) used for classifying wastes. Four laboratories extracted five utility solid wastes (two fly ashes, two bottom ashes, and one scrubber sludge) and analyzed the concentrations of eight elements (As, Ba, Cd, Cr, Pb, Hg, Ag and Se) in the extracts. In late 1985 and early 1986, EPRI sponsored another round-robin study to compare the results of EPA's new Toxicity Characteristics Leaching Procedure (TCLP) with the EP method. In this latest study, three laboratories were used to extract and analyze the concentrations of fourteen constituents (Ag, As, B, Ba, Cd, Cr, F, Hg, Mn, Pb, Se, SO_4, V and Zn) from seven utility wastes (3 fly ashes, 2 bottom ashes, and 2 scrubber sludges). The results were evaluated to determine the reproducibility of the two methods, the factors contributing to the variability of the EP and TCLP extracts, and the differences in mean concentrations between the two extract types for the selected wastes. The results show that reproducibility differs by constituent, waste type, and between the two extraction methods. Generally, the concentrations measured in the TCLP extracts are higher than those obtained by the EP method. It also appears that the reproducibility of the TCLP results (as measured by the coefficient of variation) are equal to or better than the EP method (e.g., for As, B, Cd, Cr, Mn and V). Differences in the extractions between laboratories accounted for at least 25 percent of the total variability more frequently for the EP method than the TCLP method. For the TCLP, the analytical variability components (i.e., differences in analyses between laboratories and differences in analyses of duplicate splits by the same laboratory) accounted for at least 25 percent of the total variability more frequently.

INTRODUCTION

In 1978, the U.S. Environmental Protection Agency (U.S. EPA) proposed a laboratory method to be used in the classification of solid waste as hazardous or non-hazardous. The method, which came to be called the EP method, was based upon a dilute acetic extraction of the waste, followed by analysis of the extraction liquid for the eight inorganic chemicals included in the National Interim Primary Drinking Water Standards. The EP test was subsequently promulgated as the method for use in regulations stemming from the

Resource Conservation and Recovery Act (RCRA). The Electric Power Research Institute (EPRI) sponsored a round-robin study in 1979 to evaluate the reproducibility and variability of extract concentrations obtained using the EP test on utility industry solid wastes. The results of this study are summarized in this paper. Detailed discussions of the study and conclusions are presented in two EPRI reports, Rose et al, 1981 and Eynon and Switzer, 1983.

In late 1985, the U.S. EPA issued a draft description of a new laboratory method, the Toxicity Characteristics Leaching Procedure (TCLP), as a candidate for replacing the EP method for the classification of solid wastes as hazardous or non-hazardous. It is expected that the TCLP will soon be published in the Federal Register for public comment prior to its final promulgation (slated for mid-1986). With the cooperation of U.S. EPA staff, EPRI sponsored a round-robin study in late 1985 and early 1986 to evaluate the reproducibility of the new TCLP, to identify factors contributing to variability in the TCLP and EP results, and, to quantify the differences in extract concentrations obtained by the two methods. The results of both the 1979 and 1985-1986 EPRI studies are presented below. A detailed discussion of the latter study will be presented in an EPRI report by Mason and Carlile, to be published in the fall of 1986.

1979 EP ROUND-ROBIN STUDIES

In 1979, EPRI selected five wastes (two fly ashes, two bottom ashes, and one scrubber sludge) and four laboratories (Radian Corporation, Camp Dresser & McKee, Acurex Corporation, and Systems, Science & Software) to evaluate the EP test. Each of the five waste samples was homogenized and split into 16 subsamples. Each laboratory then received four of these subsamples on which quadruplicate EP extracts were produced. In turn, each extract liquid was split into eight aliquots. Each laboratory retained two of the resulting aliquots and exchanged two aliqouts with each of the other three participating laboratories. Each laboratory analyzed all the aliquots for eight elements (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag), using both flame and graphite furnace atomic absorption spectroscopy.

The measured concentrations were then analyzed statistically using a nested analysis of variance (ANOVA) model. This type of model allows total variability to be determined and quantifies the relative contribution of individual sources to this variability. This method relies on the grouping of components and is sometimes referred to as a hierarchic ANOVA. This type of approach can be used to analyze both fixed effects (e.g., use of two different extraction procedures) and random effects (e.g., analytical variability of duplicate samples). In the 1979 and the 1985-1986 studies, all the components were considered to be random effects. The variance components model used for the 1979 study is given below:

$$x_{ijkl} = \log Y_{ijkl} = \mu + a_i + b_{ij} + c_k + d_{ijk} + e_{ijkl}$$

where

i = extraction laboratory 1,2,3,4

j = extraction replicate 1,2,3,4

k = analysis laboratory 1,2,3,4

l = analysis replicate 1,2

Y_{ijkl} = measured concentration

μ = the overall mean

a_i = The variance in the average amount extracted at different extraction laboratories (between-laboratory extraction variability)

b_{ij} = The variance in different extracts prepared at the same laboratory (within-laboratory extraction variability)

c_k = The variance in the average analytical results at each laboratory. (between-laboratory analysis variability)

d_{ijk} = The variance in the average analytical results for a given extract at each laboratory. (within-extract, between-laboratory analysis variability)

e_{ijkl} = The variance in replicate analysis of the same extract at the same laboratory (within-laboratory analysis variability)

Table 1 summarizes the results of the variance components analyses for each chemical, waste, and analytical method for which above detection limit concentrations were found in the extracts. The largest component of the variability in most of the waste samples for Ba, Cd, Pb and Se was due to between-laboratory analysis (component c_k in Table 1). The largest contributing component for Hg and for As and Cr in about a third of the wastes was between-laboratory extraction variability (component a_i in Table 1). Variability in chromium concentrations appears to be an exception, as dif-

Table 1

RELATIVE SIZE OF VARIANCE COMPONENTS - 1979 ROUND ROBIN STUDY

				Percent of Total Variance				
Element	Analysis	Prep	Waste*	a_i	b_{ij}	c_k	d_{ijk}	e_{ijkl}
Arsenic	FURNACE AA	EP	DFA-AC	32	2	51	9	6
			DFA-ALK	4	44	31	7	13
			SS	47	12	37	2	2
	FLAME AA	EP	DFA-AC	35	2	14	17	32
			DFA-ALK	10	33	4	36	17
			SS	29	1	10	23	38
Barium	FURNACE AA	EP	DFA-AC	0	0	82	5	12
			DFA-ALK	0	3	73	18	6
			WA-AC	0	7	65	12	15
			WA-ALK	2	0	88	0	11
			SS	1	0	90	0	10
	FLAME AA	EP	WA-ALK	6	0	63	16	15
Cadmium	FURNACE AA	EP	DFA-AC	28	1	45	7	20
			DFA-ALK	0	29	41	2	28
			WA-AC	12	12	56	2	17
			WA-ALK	7	6	65	11	10
			SS	13	5	70	4	8
	FLAME AA	EP	DFA-AC	29	0	32	13	26
Chromium	FURNACE AA	EP	DFA-AC	0	28	4	19	50
			DFA-ALK	11	39	13	13	24
			WA-AC	0	71	9	10	10
			WA-ALK	42	18	2	22	16
			SS	70	24	3	0	3
	FLAME AA	EP	DFA-ALK	3	65	15	13	4
Mercury	FLAME AA	EP	SS	53	4	0	24	19
Lead	FURNACE AA	EP	DFA-AC	12	0	54	7	27
			SS	6	0	32	25	38
Selenium	FURNACE AA	EP	DFA-AC	23	2	34	6	36
			DFA-ALK	16	34	11	22	17
			SS	0	15	13	23	49
	FLAME AA	EP	DFA-AC	4	0	86	3	6
			DFA-ALK	6	15	58	14	7
			SS	2	0	72	4	21

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* DFA-AC = Acidic dry fly ash;
DFA-ALK = Alkaline dry fly ash;
WA-AC = Acidic wet bottom ash;
WA-ALK = Alkaline wet bottom ash;
SS = Flue gas desulfurization sludge

ferences between the results of multiple extracts prepared at the same laboratory accounted for more of the variability (component b_{ij} in Table 1), with a relatively small contribution from between-laboratory analysis variability (component c_k in Table 1).

These results suggested that both the EP test and common laboratory and chemical analysis procedures at the various laboratories contributed to the variability in the reproducibility of extract concentrations. One method to reduce this variability would be to carry out multiple extractions and average the results. This would yield a statistically more precise estimate of chemical concentrations.

1985-86 EP AND TCLP ROUND-ROBIN TESTS

In 1985-86, EPRI selected three laboratories (Battelle, Pacific Northwest Laboratories; Radian Corporation; and Oak Ridge National Laboratory) and seven wastes (three fly ashes, two bottom ashes, and two scrubber sludges) for use in evaluating the TCLP test and for comparing its results with those of the EP test. In this round-robin test, each waste sample was freeze-dried after collection from a power plant, homogenized, and split into 16 subsamples of about 100 g each. The acid-base characteristics of each waste (as required by TCLP) were tested in triplicate by Battelle, PNL to determine which extraction medium (i.e., acetic acid or sodium acetate buffer) should be used. The results are given in Table 2. Sodium acetate buffer was required for all wastes except the two FGD sludge samples and the alkaline fly ash sample.

Two of the participating laboratories received four subsamples of each of the seven waste types, while the third laboratory received the remaining eight subsamples of each waste. The laboratories receiving four subsamples carried out the EP and TCLP extractions using two subsamples for each extraction method and each waste. The third laboratory carried out the EP and TCLP extractions using four subsamples of each waste. Duplicate extracts at each laboratory were split into six aliquots each. Then the laboratories exchanged two aliquots with each of the other two participating laboratories, while retaining two of the aliquots. The laboratory receiving four subsamples carried out quadruplicate extractions and duplicate aliquot analyses on those extracts. Each laboratory analyzed the sample aliquots using graphite furnace atomic absorption (GFAA), flame atomic absorption (FAA), cold vapor atomic absorption, inductively coupled argon plasma spectroscopy (ICAP), ion chromatography (IC), or ion specific electrode (ISE) as appropriate for the fourteen constituents of concern (As, B, Ba, Cd, Cr, Mn, Pb, Hg, Ag, Se, V, Zn, F, SO_4).

Table 2

MEASURED pH VALUES AND THE CORRESPONDING EXTRACTION MEDIUM

Waste*	Initial pH	Final pH	Selected Medium**
W1	12.0 ± 0.3	11.1 ± 0.2	M2
W2	3.9 ± .8	---	M1
W3	11.0 ± 0.4	2.05 ± 0.03	M1
W4	8.0 ± 0.7	1.46 ± 0.01	M1
W5	8.0 ± 0.4	5.9 ± 0.2	M2
W6	10.1 ± 0.6	6.1 ± 0.5	M2
W7	7.7 ± 0.5	1.7 ± 0.1	M1

* W1 - alkaline fly ash
W2 - acidic fly ash
W3 - alkaline bottom ash
W4 - neutral bottom ash
W5 - forced oxidized FGD sludge
W6 - FGD sludge
W7 - neutral fly ash

**M1 is a sodium acetate buffer solution
M2 is an acetic acid solution

The data from this study were analyzed statistically to estimate the variability in extract concentrations and the factors which might account for the estimated variability. Data were analyzed separately for each chemical, each waste, and each extraction method using the following variance components model:

$$Y_{ijkl} = \mu + a_i + b_{ij} + c_k + d_{ijk} + e_{ijkl}$$

where

i = extraction laboratory 1,2,3
j = extraction replicate 1,2 for laboratories 2 and 3 and 1,2,3,4 for laboratory 1
k = analysis laboratory 1,2,3
l = analysis replicate 1,2
μ = the overall mean
a_1 = The variance due to the difference in the average amounts extracted at different extraction laboratories (between-laboratory extraction variability)
b_{ij} = The variance due to the difference in different extracts prepared at the same laboratory (within-laboratory extraction variability)
c_k = The variance due to the difference in average analytical results at each laboratory (between-laboratory analysis variability)
d_{ijk} = The variance due to the difference in average analytical results for a given extract at each laboratory (within-extract, between-laboratory analysis variability)
e_{ijkl} = The variance due to replicate analysis of the same extract at the same laboratory (within-laboratory analysis variability)

This model is similar to the type used in the 1979 study. In the 1985-86 study, the measured concentrations were not log-transformed. The variance components were calculated using a maximum likelihood estimation procedure. Statistical analyses were not conducted if more than 25 percent of the data for a given constituent and waste type were below detection.

Table 3 lists the percent of the total variance assigned to each component by chemical constituent, analytical technique, extraction method, and waste type. These results show that the variance components can be quite different from one waste type to another and for the different constituents. For example, the largest source of

Table 3

RELATIVE SIZE OF VARIANCE COMPONENTS FOR THE 1985-86 ROUND ROBIN STUDY

Element	Analysis Method	Extraction Method	Waste No.	Components of Variance as % of Total Variance				
				a_i	b_{ij}	c_k	d_{ijk}	e_{ijkl}
As	GFAA	EP	W7	50	19	0	28	3
		TCLP	W7	4	0	0	57	39
B	ICAP	TCLP	W1	2	9	47	29	13
			W2	0	12	30	31	27
			W3	56	22	0	11	11
			W5	0	0	17	77	6
			W6	0	1	19	74	6
			W7	0	0	17	56	27
		EP	W1	50	22	0	22	6
			W2	29	0	37	22	12
			W3	6	52	0	0	42
			W5	0	0	0	56	44
			W6	0	0	0	82	18
			W7	0	10	29	30	31
Ba	ICAP	TCLP	W1	2	0	67	9	22
			W3	33	1	1	7	58
			W7	0	82	1	0	17
		EP	W1	50	5	41	3	1
			W3	90	7	1	1	1
			W7	80	14	4	1	1
Cd	GFAA	TCLP	W1	14	4	43	0	40
			W2	0	9	21	32	38
			W4	0	0	0	0	100
			W5	0	0	21	22	57
			W6	0	6	24	15	55
			W7	0	4	20	21	55
		EP	W1	61	7	17	0	15
			W2	0	13	5	27	55
			W4	15	5	12	0	68
			W5	5	2	0	54	40
			W6	69	6	0	21	4
			W7	0	10	0	34	56

Table 3

continued

				Components of Variance as % of Total Variance				
Element	Analysis Method	Extraction Method	Waste No.	a_i	b_{ij}	c_k	d_{ijk}	e_{ijkl}
Cd	ICAP	TCLP	W2	0	0	0	0	100
			W5	0	0	34	28	38
		EP	W2	0	2	18	74	6
			W5	0	0	35	28	37
Cr	GFAA	TCLP	W1	22	1	0	71	6
			W2	71	14	0	14	1
			W3	0	5	0	84	11
			W5	0	0	0	80	20
			W6	0	3	14	81	2
		EP	W1	34	5	3	56	2
			W2	0	1	43	50	6
			W3	13	16	33	26	12
			W5	0	1	46	52	1
			W6	0	0	14	78	8
	ICAP	TCLP	W1	0	18	41	37	4
		EP	W1	33	18	29	15	5
F	ISE	TCLP	W1	5	1	11	67	16
			W2	1	0	71	0	28
			W5	0	0	44	19	37
			W6	7	4	43	26	20
			W7	0	6	42	8	44
		EP	W1	34	0	18	37	11
			W2	15	4	18	0	63
			W5	5	2	0	89	4
			W6	48	2	2	47	1
			W7	54	0	11	15	20
Mn	FAA	TCLP	W1	25	25	0	30	20
			W2	9	1	0	78	12
			W3	0	71	9	0	20
			W5	0	1	29	54	16
			W6	0	7	3	58	32
		EP	W1	46	40	1	12	1
			W2	74	1	0	15	10
			W3	0	94	2	2	2
			W5	39	51	4	0	6
			W6	98	1	1	0	0

Table 3

continued

Element	Analysis Method	Extraction Method	Waste No.	Components of Variance as % of Total Variance				
				a_i	b_{ij}	c_k	d_{ijk}	e_{ijkl}
Mn	ICAP	TCLP	W1	69	24	0	4	3
			W2	11	39	15	9	26
			W3	21	59	16	0	4
			W4	26	47	16	3	8
			W5	8	0	0	66	26
			W6	1	0	6	1	92
			W7	10	0	32	11	47
		EP	W1	58	38	0	3	1
			W2	60	12	3	12	13
			W3	0	79	0	0	21
			W4	0	2	0	3	95
			W5	20	0	0	28	52
			W6	98	1	0	1	0
			W7	37	16	34	6	7
Se	GFAA	TCLP	W7	18	1	0	75	6
		EP	W7	0	13	0	76	11
SO_4	IC	TCLP	W1	0	0	43	57	0
			W2	8	0	69	22	1
			W3	0	0	37	61	2
			W5	4	0	74	22	0
			W6	0	3	0	96	1
			W7	0	0	33	67	0
		EP	W1	9	1	41	50	0
			W2	0	1	59	38	2
			W3	0	1	49	44	6
			W5	0	0	78	21	1
			W6	0	5	0	92	3
			W7	0	0	29	71	0
V	ICAP	TCLP	W1	0	4	59	8	29
			W2	83	15	0	1	1
			W3	0	0	10	17	73
			W4	0	13	0	0	87
			W5	6	0	58	21	15
			W6	0	2	22	70	6
			W7	0	13	9	43	35

Table 3

continued

Element	Analysis Method	Extraction Method	Waste No.	Components of Variance as % of Total Variance				
				a_i	b_{ij}	c_k	d_{ijk}	e_{ijkl}
V	ICAP	EP	W1	14	8	35	19	24
			W2	0	0	56	0	44
			W3	0	0	15	56	29
			W4	1	6	42	16	35
			W5	0	2	57	14	27
			W6	2	0	24	60	12
			W7	0	7	19	49	25
	GFAA	TCLP	W1	72	6	0	16	5
			W7	0	9	0	78	13
		EP	W1	0	59	0	0	41
			W7	7	19	0	60	14
Zn	FAA	TCLP	W1	89	1	0	4	6
			W2	38	6	0	32	24
			W4	74	1	0	10	14
			W5	77	3	0	12	8
			W6	9	1	0	7	83
			W7	49	10	3	2	36
		EP	W1	83	13	0	1	3
			W2	50	4	27	0	19
			W4	83	12	0	4	1
			W5	30	37	0	23	10
			W6	91	5	0	4	0
			W7	83	7	4	6	0
	ICAP	TCLP	W1	83	2	3	5	7
			W2	42	11	7	23	17
			W3	80	0	0	0	20
			W4	70	0	0	12	18
			W5	0	1	0	51	48
			W6	55	7	6	6	26
			W7	51	11	0	0	38
		EP	W1	76	15	0	6	3
			W2	36	0	47	0	17
			W3	69	17	2	0	12
			W4	80	11	0	1	8
			W5	12	0	0	38	50
			W6	43	4	0	50	1
			W7	84	11	0	3	2

variability in the Zn concentration is associated with the extraction by different laboratories (component a_i) in all but two of the wastes. However, the largest source of variability in the SO_4 concentration is associated with differences between analysis laboratories (component c_k and d_{ijk}).

To focus on the overall differences between the EP and TCLP, a summary table has been prepared listing the number of times a particular variance component accounted for more than 25 percent of the total variance (Table 4A) and for more than 75 percent of the total variance (Table 4B). Different analytical techniques for a given constituent and the different waste types have been combined. The following discusses chemical constituents for which the source of variability were the same in three or more cases. The summary table (Table 4) indicates that differences in the amounts extracted by the laboratories (component a_i) accounted for more than 25 percent of the total variability more often in the EP extracts than the TCLP extracts. In the EP extracts, this is true in 3 or more cases for Ba, F, Mn and Zn. In the TCLP extracts, this is true in three or more cases only for Zn. In the case of Zn, the extraction step (a_i) account for over 75 percent of the variability in seven cases in EP extracts and four cases in TCLP extracts. This high variability may be due in part to the presence of higher concentrations of Zn in the blanks from extraction laboratory three (Table 5). The variability in duplicate extracts by the same laboratory (component b_{ij}) exceeded 25 percent in five cases for Mn in both the EP and TCLP extracts. Only once at most did the extraction variability associated with the same laboratory exceed 25 percent for either the EP or the TCLP for any other constituent. This implies that each laboratory was consistent in its extraction method although there must be some actual differences in the implementation of the procedures between labs.

The between-laboratory analytical variability (component c_k) accounted for 25 percent and 75 percent of the total variability approximately the same number of times for the EP and TCLP extracts. This component of variability accounted for at least 25 percent of the total variability in three or more cases for Cr, SO_4 and V in the EP extracts and F and SO_4 in the TCLP extracts. In only one case, for SO_4 in an EP extract, did this component account for 75 percent or more of the total variability. These results imply that there was nothing inherent in either the EP or TCLP extracts which caused higher variability in chemical analyses.

The analytical variability can be further separated into variability associated with analysis of duplicate extracts by the three different laboratories (compoent d_{ijk}) and the variability associated with analysis of duplicate splits by the same laboratory (component e_{ijkl}). Analysis of

Table 4

FREQUENCY DISTRIBUTION BASED ON VARIANCE COMPONENT ACCOUNTING FOR AT LEAST (A) 25% (B) 75% OF TOTAL VARIABILITY

	Variance Component	As	B	Ba	Cd	Cr	F	Mn	Se	SO_4	V	Zn	Total
(A)	EP Method												
	a_i	1	2	3	2	2	3	8	0	0	0	12	33
	b_{ij}	0	1	0	0	0	0	5	0	0	1	1	8
	c_k	0	2	1	1	4	0	1	0	5	4	2	20
	d_{ijk}	1	3	0	5	5	3	1	1	5	4	2	30
	e_{ijkl}	0	3	0	5	0	1	2	0	0	6	1	18
	Total	2	11	4	13	11	7	17	1	10	15	18	109
	TCLP Method												
	a_i	0	1	1	0	1	0	2	0	0	2	11	18
	b_{ij}	0	0	1	0	0	0	5	0	0	0	0	6
	c_k	0	2	1	2	1	4	2	0	5	2	0	19
	d_{ijk}	1	5	0	2	5	2	5	1	4	3	2	30
	e_{ijkl}	1	2	1	8	0	3	5	0	0	4	5	29
	Total	2	10	4	12	7	9	19	1	9	11	18	102
(B)	EP Method												
	a_i		0	2	0	0	0	2	0	0	0	7	11
	b_{ij}		0	0	0	0	0	2	0	0	0	0	2
	c_k		0	0	0	0	0	0	0	1	0	0	1
	d_{ijk}		1	0	0	1	1	0	1	1	0	0	5
	e_{ijkl}		0	0	0	0	0	1	0	0	0	0	1
	Total		1	2	0	1	1	5	1	2	0	7	20
	TCLP Method												
	a_i		0	0	0	0	0	0	0	0	1	4	5
	b_{ij}		0	1	0	0	0	0	0	0	0	0	1
	c_k		0	0	0	0	0	0	0	0	0	0	0
	d_{ijk}		1	0	0	3	0	1	1	1	1	0	8
	e_{ijkl}		0	0	2	0	0	1	0	0	1	1	5
	Total		1	1	2	3	0	2	1	1	3	5	19

Table 5

MEASURED MEAN CONCENTRATIONS IN PROCEDURE BLANKS
mg/l

Extraction Lab	Analysis Lab		
Ba ICAP EP	1	2	3
1	.013	.02	<.02
2	<.004	.005	<.02
3	.447	.14	.43
Ba ICAP TCLP			
1	.032	.07	.045
2	.125	.045	.067
3	.574	.53	.59
Zn FAA EP			
1	<.02	.01	.01
2	.04	<.01	.01
3	.19	.10	.23
Zn FAA TCLP			
1	.025	.04	.031
2	.086	.03	.037
3	.355	.35	.412
Zn ICAP EP			
1	.017	.01	<.02
2	.045	.015	<.02
3	.244	.125	.218
Zn ICAP TCLP			
1	.025	.04	.031
2	.111	.03	.037
3	.433	.35	N/A

duplicate extracts by different laboratories contributed more than 25 percent of the variability in at least three cases for B, Cd, Cr, F, SO_4, and V in EP extracts and for B, Cr, Mn, SO_4 and V in TCLP extracts. For Cr, the variability exceeded 75 percent in three of the TCLP extracts. The total number of times when this component (d_{ijk}) exceeded 25 percent of the total variability is the same for both EP and TCLP extracts (i.e., 30 times). Analysis of duplicate splits by the same laboratory (component e_{ijkl}) contributed more than 25 percent of the variability in at least three cases for B, Cd and V in EP extracts and for Cd, F, Mn, V and Zn in TCLP extracts. The total number of cases with more than 25 percent variability was higher for the TCLP extracts (29 times) than for the EP extracts (18 times). Overall, components associated with the extraction step (a_i and b_{ij}) account for at least 25 percent of the total variance more frequently for the EP method than for the TCLP method. For the TCLP, the analysis step (components, c_k, d_{ijk}, and e_{ijkl}) more frequently account for 25 percent of the total variance.

Table 6 gives the mean concentrations in the EP and TCLP extracts of each waste by extraction laboratory and by analysis laboratory. Values for concentrations near or below detection are not listed in this table. The mean concentrations in the TCLP extracts when compared to EP extracts were higher in most wastes for As, Ba, Cr, F, Mn, Pb, Se, V and Zn. For As, Ba, Cr, Mn, and V differences were large for many of the wastes. Differences were small in those cases where the concentrations in the wastes were high (e.g., B).

The differences in the two extraction methods can also be summarized by waste type. Table 7 lists the mean concentration and coefficient of variation for each extraction method by constituent. These results show that Ag and Hg concentrations are below detection in both the EP and the TCLP extracts for all wastes extracted. Se is present in measurable quantities in only the acidic and neutral fly ash samples. Pb is detectable in only the acidic fly ash sample. V is not detectable in the two bottom ash samples or in one of the scrubber sludge samples.

The coefficient of variation was typically low (i.e., less than 30 percent) for B and Mn (Table 7). Based on the results shown in this table, the reproducibility of the TCLP test is equal to or better than the EP method for As, B, Cd, Cr, Mn and V. Because of the many values below the detection limit, differences between EP and TCLP could not be determined for Ag, Hg, Pb or Se.

Table 8 shows the relative frequency distribution of the ratio of mean TCLP to EP concentrations. Only about 13

Table 6

MEAN CONCENTRATIONS DETERMINED BY THE EXTRACTING LABORATORIES AND BY THE ANALYSIS LABORATORIES

				Extraction Lab			Analysis Lab		
	Analysis	Waste	Extraction	1	2	3	1	2	3
Element	Method	No.	Method		(mg/l)			(mg/l)	
As	GFAA	W1	EP	0.006	0.0232	0.0052	0.0167	0.0074	0.0067
			TCLP	0.0108	0.0053	0.0096	0.01	0.008	0.0079
		W2	EP	0.0062	0.0053	0.0047	0.01	0.0026	0.0023
			TCLP	0.5030	0.1451	0.2403	0.2952	0.4267	0.2358
		W7	EP	0.0401	0.0238	0.092	0.0467	0.047	0.0603
			TCLP	0.1579	0.1476	0.137	0.1389	0.1542	0.1558
Ba	ICAP	W1	EP	0.2962	0.5950	0.3623	0.4285	0.5267	0.2542
			TCLP	0.2989	0.3604	0.3318	0.4049	0.4075	0.1433
		W2	EP	0.0658	0.0855	0.0836	0.0769	0.1125	0.0420
			TCLP	0.0783	0.1154	0.106	0.1025	0.1333	0.0558
		W3	EP	0.2708	0.3243	0.7468	0.3692	0.4833	0.4567
			TCLP	0.6816	0.6785	1.1418	0.7074	0.9292	0.8567
		W4	EP	0.0574	0.0219	0.4713	0.1317	0.2092	0.1850
			TCLP	0.696	0.2031	0.6597	0.2725	0.2867	0.3056
		W5	EP	0.0678	0.0705	0.1106	0.0948	0.105	0.0400
			TCLP	0.0896	0.1090	0.1759	0.1464	0.1292	0.0800
		W6	EP	0.1827	0.1518	0.1498	0.1852	0.205	0.0933
			TCLP	0.1959	0.2286	0.206	0.2613	0.2675	0.0800
		W7	EP	0.1284	0.1593	0.2582	0.1597	0.1975	0.1783
			TCLP	0.3742	0.4453	0.5513	0.4276	0.4375	0.447
B	ICAP	W1	EP	17.3	14.6	19.4	17.4	17.4	16.5
			TCLP	17.8	18.2	17.2	18.9	17.2	16.5
		W2	EP	43.6	47.1	46.2	46.3	46.7	43.1
			TCLP	45.2	43.9	45.2	46.1	45.7	42.3
		W3	EP	1.31	1.39	1.61	1.45	1.46	1.37
			TCLP	1.50	1.42	1.88	1.66	1.56	1.53
		W4	EP	0.22	0.15	0.29	0.16	0.32	0.20
			TCLP	0.31	0.19	0.30	0.23	0.30	0.30
		W5	EP	0.76	0.78	1.01	0.96	0.85	0.67
			TCLP	0.99	0.79	0.95	1.02	1.05	0.66

Table 6 continued

Element	Analysis Method	Waste No.	Extraction Method	Extraction Lab 1 (mg/l)	Extraction Lab 2 (mg/l)	Extraction Lab 3 (mg/l)	Analysis Lab 1 (mg/l)	Analysis Lab 2 (mg/l)	Analysis Lab 3 (mg/l)
B	ICAP	W6	EP	1.82	1.63	1.57	1.73	2.05	1.27
			TCLP	2.19	1.70	1.68	1.95	2.32	1.38
		W7	EP	1.19	1.22	1.18	1.16	1.42	1.04
			TCLP	1.24	1.24	1.22	1.21	1.36	1.14
Cd	GFAA	W1	EP	0.0149	0.0083	0.0157	0.0152	0.0109	0.0128
			TCLP	0.185	0.014	0.0159	0.0198	0.0132	0.0152
		W2	EP	0.2237	0.2592	0.2606	0.2398	0.275	0.2233
			TCLP	0.2369	0.2460	0.2526	0.2459	0.2725	0.2142
		W4	EP	0.0014	0.0022	0.0014	0.0014	0.0022	0.0014
			TCLP	0.0017	0.0062	0.0011	0.0018	0.0074	0.0018
		W5	EP	0.0371	0.0320	0.0295	0.0306	0.0375	0.0327
			TCLP	0.0281	0.0271	0.0288	0.0312	0.0255	0.0262
		W6	EP	0.0063	0.0020	0.0073	0.0055	0.0046	0.0058
			TCLP	0.0044	0.0045	0.0040	0.0053	0.0080	0.0041
		W7	EP	0.0050	0.0058	0.0060	0.0051	0.0059	0.0058
			TCLP	0.0062	0.0058	0.0062	0.0069	0.0044	0.0064
	ICAP	W1	EP	0.0238	0.0226	0.0209	0.0256	0.0112	0.03
			TCLP	0.0224	0.0208	0.0219	0.0297	0.0104	0.0226
		W2	EP	0.2313	0.2102	0.2288	0.248	0.1858	0.2308
			TCLP	0.2298	0.242	0.2279	0.2366	0.2367	0.2242
		W5	EP	0.0289	0.0277	0.0323	0.0388	0.0195	0.0273
			TCLP	0.0346	0.0256	0.0245	0.0345	0.0177	0.0326
Cr	GFAA	W1	EP	0.38	0.26	0.42	0.35	0.41	0.31
			TCLP	0.42	0.32	0.29	0.37	0.34	0.34
		W2	EP	0.014	0.008	0.025	0.0046	0.0425	0.0038
			TCLP	1.33	0.53	0.56	0.94	0.89	0.73
		W3	EP	0.005	0.0078	0.013	0.0056	0.0142	0.0058
			TCLP	0.0123	0.0081	0.0087	0.0119	0.0078	0.0096
		W4	EP	0.0015	0.0015	0.0022	0.0015	0.0017	0.002
			TCLP	0.0064	0.0027	0.0030	0.0042	0.0044	0.0043
		W5	EP	0.0355	0.0239	0.0302	0.0187	0.0617	0.0148
			TCLP	0.0373	0.0634	0.0251	0.0337	0.0675	0.0258

Table 6 continued

Element	Analysis Method	Waste No.	Extraction Method	Extraction Lab			Analysis Lab		
				1	2 (mg/l)	3	1	2 (mg/l)	3
Cr	GFAA	W6	EP	0.0511	0.0023	0.0246	0.0024	0.0894	0.0024
			TCLP	0.011	0.0226	0.0056	0.0087	0.0267	0.0047
		W7	EP	0.0027	0.0022	0.0025	0.0016	0.0041	0.002
			TCLP	0.0666	0.0578	0.0502	0.0604	0.0575	0.0588
	ICAP	W1	EP	0.4419	0.3592	0.4743	0.4827	0.3725	0.4067
			TCLP	0.5089	0.4304	0.5564	0.529	0.405	0.455
		W2	EP	0.0671	0.07	0.0609	0.765	0.0383	0.08
			TCLP	1.3513	0.5705	0.6967	1.1341	0.7992	0.7575
		W3	EP	0.0325	0.0389	0.0379	0.0183	0.0158	0.08
			TCLP	0.0388	0.0417	0.0406	0.0287	0.0158	0.08
		W5	EP	0.0524	0.0764	0.0627	0.0586	0.0508	0.08
			TCLP	0.1250	0.0729	0.0927	0.0810	0.0642	0.16
		W6	EP	0.1097	0.1032	0.0483	0.0414	0.0558	0.1867
			TCLP	0.1207	0.0539	0.0762	0.0445	0.0717	0.160
		W7	EP	0.0419	0.0337	0.0333	0.0084	0.0317	0.08
			TCLP	0.1136	0.0654	0.075	0.0725	0.0758	0.1192
F	ISE	W1	EP	0.1697	0.4683	0.2182	0.145	0.3758	0.3375
			TCLP	0.3636	0.1833	0.3817	0.1443	0.4492	0.4083
		W2	EP	1.675	1.6958	1.3525	1.39	1.76	1.67
			TCLP	1.432	1.4367	1.6492	0.82	2.07	1.87
		W3	EP	0.0425	0.0631	0.094	0.0297	0.1183	0.0558
			TCLP	0.0488	0.092	0.150	0.0371	0.1283	0.1292
		W4	EP	0.0438	0.504	0.0634	0.0235	0.105	0.0358
			TCLP	0.0425	0.0828	0.1702	0.0429	0.1125	0.14
		W5	EP	5.85	9.09	7.53	6.11	8.75	7.52
			TCLP	7.94	9.34	7.84	6.59	11.29	7.69
		W6	EP	1.45	3.18	1.93	1.86	2.60	1.82
			TCLP	1.94	2.24	1.91	1.83	2.38	1.89
		W7	EP	0.47	1.26	0.97	0.89	1.02	0.66
			TCLP	1.44	1.54	1.48	1.44	1.68	1.33
Mn	FAA	W1	EP	3.84	2.78	3.54	3.72	3.20	3.28
			TCLP	4.62	4.45	5.40	4.83	4.82	4.75

Table 6 continued

				Extraction Lab (mg/l)			Analysis Lab (mg/l)		
Element	Analysis Method	Waste No.	Extraction Method	1	2	3	1	2	3
Mn	FAA	W2	EP	3.26	3.81	3.61	3.46	3.59	3.56
			TCLP	3.75	4.24	4.09	3.81	4.16	4.10
		W3	EP	0.41	0.40	0.56	0.45	0.45	0.47
			TCLP	0.61	0.59	0.67	0.61	0.61	0.65
		W5	EP	1.2777	1.6188	1.3707	1.3811	1.3833	1.4683
			TCLP	1.5046	1.5188	1.4989	1.5328	1.425	1.555
		W6	EP	1.81	0.76	0.18	1.16	0.85	0.96
			TCLP	1.93	1.98	1.90	1.99	1.85	1.94
		W7	EP	0.14	0.15	0.13	0.15	0.09	0.16
			TCLP	0.17	0.18	0.12	0.19	0.10	0.19
	ICAP	W1	EP	3.78	2.52	3.22	3.51	3.05	3.04
			TCLP	4.49	4.00	5.08	4.60	4.42	4.52
		W2	EP	3.24	3.55	3.42	3.39	3.43	3.34
			TCLP	3.69	3.91	3.82	3.80	3.87	3.71
		W3	EP	0.45	0.41	0.58	0.50	0.47	0.46
			TCLP	0.57	0.61	0.67	0.63	0.62	0.59
		W4	EP	0.0478	0.0255	0.0273	0.0267	0.0583	0.0226
			TCLP	0.0374	0.0293	0.0288	0.0344	0.0333	0.0288
		W5	EP	1.13	1.57	1.34	1.39	1.22	1.34
			TCLP	1.45	1.50	1.62	1.56	1.49	1.48
		W6	EP	1.87	0.78	0.20	1.18	0.97	0.92
			TCLP	1.98	1.90	1.88	1.97	1.84	1.95
		W7	EP	0.1403	0.1603	0.1616	0.1592	0.1558	0.1408
			TCLP	0.1674	0.1747	0.1674	0.1764	0.1683	0.1625
Pb	GFAA	W2	EP	0.0193	0.0111	0.0222	0.0219	0.0082	0.0217
			TCLP	0.3143	0.0787	0.1066	0.2282	0.1417	0.1583
Se	GFAA	W7	EP	0.0623	0.047	0.0727	0.0566	0.0517	0.0756
			TCLP	0.1524	0.1484	0.0991	0.1361	0.1283	0.1408
SO_4^{2-}	IC	W1	EP	996	354	1144	502	1710	447
			TCLP	933	529	1139	490	1759	500
		W2	EP	2794	2552	3169	2189	4052	2475
			TCLP	3304	2970	3945	2691	4898	2833

Table 6 continued

Element	Analysis Method	Waste No.	Extraction Method	Extraction Lab			Analysis Lab		
				1	2	3	1	2	3
					(mg/l)			(mg/l)	
SO_4^{2-}	IC	W3	EP	370	114	502	52	992	49
			TCLP	404	50	543	52	1017	45
		W4	EP	51	15	150	12	208	10
			TCLP	181	16	195	16	416	15
		W5	EP	1415	1278	1661	996	2444	1053
			TCLP	1458	1169	1722	971	2574	967
		W6	EP	1627	1626	1241	1292	1856	1459
			TCLP	1671	1198	1204	1205	1789	1233
		W7	EP	561	191	454	186	972	174
			TCLP	589	228	411	197	970	191
V	ICAP	W1	EP	.0529	.1123	.0412	.0212	.1158	.08
			TCLP	.0687	.0709	.0764	.0373	.1492	.04
		W2	EP	.0344	.0325	.0358	.02	.0633	.0242
			TCLP	1.0495	.1135	.3023	.6638	.51	.42
		W3	EP	.0154	.0129	.0098	.0069	.0225	.02
			TCLP	.0136	.0156	.0145	.0104	.0197	.02
		W4	EP	.0118	.0102	.0093	.0061	.0135	.02
			TCLP	.0364	.0078	.0087	.0223	.0053	.03
		W5	EP	.0203	.0392	.0417	.0091	.0758	.02
			TCLP	.0428	.0317	.0342	.0097	.07	.04
		W6	EP	.1129	.0613	.0537	.0398	.16	.525
			TCLP	.1683	.1183	.0811	.0916	.235	.0667
		W7	EP	.0874	.0444	.0783	.0563	.1217	.0425
			TCLP	.2142	.2153	.1981	.2033	.2258	.2025
	GFAA	W1	EP	.0356	.0561	.0369	.0482	.0293	.0470
			TCLP	.0842	.0424	.0764	.0751	.0550	.0620
		W2	EP	.0115	.0087	.0087	.0200	.0020	.0040
			TCLP	1.1006	.2130	.3220	.7369	.4542	.5658
		W3	EP	.0142	.0092	.0087	.0200	.0038	.0063
			TCLP	.0151	.0116	.0126	.0206	.0069	.0098
		W4	EP	.0015	.0088	.0087	.0200	.0021	.0040
			TCLP	.0091	.0087	.0087	.0175	.0021	.0040

Table 6 continued

				Extraction Lab			Analysis Lab		
Element	Analysis Method	Waste No.	Extraction Method	1	2 (mg/l)	3	1	2 (mg/l)	3
V	GFAA	W5	EP	.0015	.0090	.0087	.0200	.0023	.0040
			TCLP	.0116	.0053	.0091	.0175	.0021	.0044
		W6	EP	.0707	.0311	.0327	.0549	.0198	.0651
			TCLP	.1027	.1039	.0663	.1082	.0446	.1183
		W7	EP	.0612	.0487	.0762	.0559	.0605	.0713
			TCLP	.1971	.2135	.2108	.1996	.2058	.2150
Zn	FAA	W1	EP	0.0928	0.0743	0.372	0.16	0.17	0.185
			TCLP	0.1298	0.1351	0.4843	0.2349	0.2383	0.2408
		W2	EP	4.86	5.35	5.34	4.95	5.32	5.25
			TCLP	5.06	5.48	5.67	5.32	5.48	5.32
		W3	EP	0.022	0.017	0.262	0.082	0.097	0.103
			TCLP	0.037	0.100	0.398	0.135	0.166	0.202
		W4	EP	0.035	0.023	0.141	0.060	0.063	0.068
			TCLP	0.55	0.112	0.399	0.165	0.182	0.183
		W5	EP	1.38	1.56	1.54	1.45	1.51	1.50
			TCLP	1.39	1.62	1.88	1.57	1.63	1.64
		W6	EP	0.13	BDL	0.22	0.12	0.12	0.13
			TCLP	0.17	0.35	0.44	0.26	0.41	0.26
		W7	EP	0.078	0.107	0.231	0.109	0.148	0.149
			TCLP	0.134	0.216	0.385	0.192	0.239	0.284
	ICAP	W1	EP	0.109	0.076	0.332	0.165	0.153	0.179
			TCLP	0.129	0.109	0.479	0.252	0.201	0.223
		W2	EP	5.14	5.49	5.52	5.60	5.32	5.08
			TCLP	5.16	5.26	5.73	5.45	5.35	5.26
		W3	EP	0.027	0.040	0.281	0.091	0.108	0.123
			TCLP	0.045	0.111	0.415	0.166	0.162	0.204
		W4	EP	0.048	0.034	0.152	0.071	0.072	0.082
			TCLP	0.079	0.137	0.427	0.210	0.184	0.206
		W5	EP	1.175	1.501	1.505	1.484	1.252	1.342
			TCLP	1.438	1.555	1.465	1.365	1.533	1.583
		W6	EP	0.127	0.048	0.186	0.112	0.127	0.126
			TCLP	0.181	0.184	0.425	0.271	0.282	0.206

Table 6 continued

Element	Analysis Method	Waste No.	Extraction Method	Extraction Lab 1 (mg/l)	Extraction Lab 2 (mg/l)	Extraction Lab 3 (mg/l)	Analysis Lab 1 (mg/l)	Analysis Lab 2 (mg/l)	Analysis Lab 3 (mg/l)
Zn	ICAP	W7	EP	0.096	0.123	0.253	0.143	0.165	0.149
			TCLP	0.156	0.240	0.438	0.250	0.246	0.292

BDL = below detection limit.

Table 7

MEAN CONCENTRATIONS AND COEFFICIENT OF VARIATION (CV) MEASURED IN THE EP-TCLP EXTRACTS

ELEMENT/ CHEMICAL TECH.	EXTRACT. METHOD	ALKALINE FLY ASH mean (mg/l)	CV (%)	ACIDIC FLY ASH mean (mg/l)	CV (%)	BOTTOM ASH mean (mg/l)	CV (%)	BOTTOM ASH mean (mg/l)	CV (%)	SCRUBBER SLUDGE mean (mg/l)	CV (%)	SCRUBBER SLUDGE mean (mg/l)	CV (%)	NEUTRAL FLY ASH mean (mg/l)	CV (%)
Ag	EP	BDL		BDL		BDL		BDL		BDL		BDL		BDL	
GFAA	TCLP	BDL		BDL		BDL		BDL		BDL		BDL		BDL	
As	EP	0.0109	101	0.0054	72	0.0053	74	0.0054	72	0.0066	88	0.0083	39	0.0509	67
GFAA	TCLP	0.0088	38	0.3168	72	0.0053	75	0.0053	74	0.0056	69	0.0104	20	0.1486	14
Ba	EP	0.4057	44	0.0771	42	0.4297	51	0.1709	121	0.0814	53	0.1636	34	0.1766	34
ICAP	TCLP	0.3272	45	0.0977	43	0.8187	41	0.2867	105	0.1213	57	0.2088	54	0.4460	31
B	EP	17.14	14	45.45	6	1.43	20	0.22	96	0.84	34	1.69	24	1.20	20
ICAP	TCLP	17.72	8	44.85	6	1.59	18	0.27	45	0.92	29	1.89	29	1.23	12
Cd	EP	0.0131	31	0.2454	21	0.0020	194	0.0017	52	0.0333	25	0.0053	48	0.0055	18
GFAA	TCLP	0.0195	25	0.2444	16	0.0007	35	0.0035	358	0.0280	17	0.0043	38	0.0060	32
Cd	EP	0.0226	41	0.2242	17	0.0081	63	0.0076	49	0.0296	39	0.018	64	0.0096	67
ICAP	TCLP	0.0218	46	0.2329	43	0.0076	49	0.0091	77	0.0289	41	0.015	84	0.0099	73
Cr	EP	0.3572	26	0.0157	145	0.0082	75	0.0017	38	0.0304	85	0.0285	219	0.0025	54
GFAA	TCLP	0.3518	27	0.8602	50	0.01	46	0.0043	55	0.0415	86	0.0129	116	0.0590	30
Cr	EP	0.4268	18	0.0661	30	0.0361	82	0.0294	115	0.0627	35	0.0893	91	0.0369	97
ICAP	TCLP	0.4696	15	0.9207	44	0.0402	68	0.0435	146	0.0997	61	0.0873	87	0.0879	39
F	EP	0.28	69	1.58	24	0.06	67	0.05	72	7.33	30	2.07	41	0.86	51
ISE	TCLP	0.32	72	1.50	45	0.09	92	0.09	131	8.33	33	2.02	17	1.48	14
Hg	EP	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Cold Vapor	TCLP	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Pb	EP	BDL		0.018	54	BDL		BDL		BDL		BDL		BDL	
GFAA	TCLP	BDL		0.18	67	BDL		BDL		BDL		BDL		BDL	
Mn	EP	3.43	17	3.53	7	0.46	25	0.03	33	1.41	12	1.01	70	0.14	32
FAA	TCLP	4.8	12	4	8	0.62	12	0.03	47	1.51	5	1.93	6	0.16	32
Mn	EP	3.23	20	3.39	5	0.48	24	0.035	157	1.33	26	1.04	70	0.15	10
ICAP	TCLP	4.52	10	3.79	4	0.61	11	0.032	17	1.52	8	1.93	8	0.17	6
Se	EP	BDL		BDL		BDL		BDL		BDL		BDL		0.06	39
GFAA	TCLP	BDL		0.0249	65	BDL		BDL		BDL		BDL		0.14	27
SO4	EP	848	90	2834	34	333	163	70	202	1448	49	1511	33	418	120
IC	TCLP	874	84	3396	33	340	173	136	233	1451	57	1389	36	427	113
V	EP	0.04	47	0.01	86	BDL		BDL		BDL		0.05	61	0.06	25
GFAA	TCLP	0.07	28	0.60	74	BDL		BDL		BDL		0.09	43	0.21	11
V	EP	0.0672	92	0.0343	74	0.0131	86	0.0106	76	0.0324	113	0.08	100	0.07	78
ICAP	TCLP	0.0717	91	0.5445	81	0.0144	68	0.0203	275	0.0369	83	0.127	84	0.21	10
Zn	EP	0.17	83	5.15	6	0.09	140	0.06	86	1.48	8	0.12	66	0.13	53
FAA	TCLP	0.24	72	5.37	7	0.16	106	0.18	96	1.61	14	0.31	91	0.23	60
Zn	EP	0.17	74	5.36	6	0.11	125	0.07	74	1.37	25	0.12	57	0.15	48
ICAP	TCLP	0.23	79	5.36	6	0.18	101	0.2	87	1.48	23	0.26	56	0.26	59

BDL = below detection limit

Table 8

RELATIVE FREQUENCY DISTRIBUTION OF RATIO OF MEAN TCLP CONCENTRATIONS TO MEAN EP CONCENTRATIONS

Ratio Range	Frequency*	Relative Frequency (% value)
<0.5	2	1.5
0.8- <1.0	16	12.0
1.0- <1.20	62	46.6
1.20-<1.50	17	12.8
1.50-<2.00	16	12.1
2.00- 5.00	12	9.0
>5.00	8	6.0
TOTAL	133	100%

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* When both TCLP and EP concentrations are below detection limit, the ratio has been assigned a value of 1.0.

percent of the ratio values are less than 1, with 12 percent falling in the range of 0.8 to 1. Forty-seven percent of the ratios fell between 1.0 and 1.2, another 25 percent were between 1.2 and 2.0, and the remaining 15 percent exceeded 2.0. Overall, mean TCLP concentrations exceeded the EP concentrations 86 percent of the time.

SUMMARY AND CONCLUSIONS

The two EPRI sponsored round-robin studies have produced data on the reproducibility and variability of extract concentrations produced by the EP and the TCLP tests when applied to electric utility industry solid wastes. Both these studies show that reproducibility differs for the various constituents, waste types, extraction methods, laboratories carrying out the extractions, and laboratories analyzing the extracts. The TCLP and EP tests do differ with respect to the relative size of the components of variance. It appears that generally the reproducibility of the TCLP is equal to or better than the EP method for As, B, Cd, Cr, Mn and V. In the 1979 study the largest variability in measured concentrations in extracts from the EP method appeared to be due to differences in between-laboratory analyses (the C_k component), while in the 1985-86 study of the EP test it appears to be mostly due to differences in the amount extracted at different extraction laboratories (component a_i) and to a lesser extent the analytical variability associated with analysis of duplicate extracts by different laboratories (component d_{ijk}). The most frequently encountered source of variability in the TCLP extracts appears to be due to this same component (d_{ijk}). In general, higher concentrations are measured in the TCLP extracts compared to the EP extracts for a given constituent and waste type. This is thought to be due to differences in the extraction fluids (e.g., acetic acid for the EP test and either acetic acid or sodium acetate buffer for the TCLP test), and lack of pH adjustment during extraction in the TCLP test.

REFERENCES

1. Rose, S.J., J. Dane, B. Eynon and P. Switzer. Extraction Procedure and Utility Industry Solid Waste. Electric Power Research Institute, Report No. EA-1667, 1981.
2. Eynon, B. and P. Switzer. A Statistical Comparison of Two Studies on Trace Element Composition of Coal Ash Leachates. Electric Power Research Institute, Report No. EA-3181, 1983.
3. Mason, B. and D. Carlile. Round Robin Evaluation for Selected Elements and Anionic Species from TCLP and EP Extractions. Electric Power Research Institute, Draft Report, 1986.

COLLABORATIVE STUDY OF THE TOXICITY CHARACTERISTICS LEACHING PROCEDURE (TCLP) FOR METALS, PESTICIDES, AND SEMIVOLATILE ORGANIC COMPOUNDS

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ABSTRACT

The United States Environmental Protection Agency has developed a new procedure, the Toxicity Characteristic Leaching Procedure (TCLP), to more effectively simulate the leaching of hazardous waste in a landfill environment. The procedure involves an 18-hour extraction of a sample with either an acid or sodium acetate solution, and subsequent analysis of the leachate for metals, pesticides, and semi-volatile organic compounds. To validate the method, three waste samples at two different pH levels were sent to 23 different volunteer government and commercial laboratories for extraction and analysis. The results and statistical analysis of this collaborative test are presented and discussed. The results of the collaborative study indicate that the TCLP can be applied consistently by a diverse group of organizations for the analyses considered in this study.

DISCLAIMER

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1.0 INTRODUCTION

As part of its effort to improve the Extraction Procedure (EP) protocol and to expand its applicability to all toxic constituents that could leach from hazardous wastes in landfills, the U.S. Environmental Protection Agency (EPA) recently proposed the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP was published as a draft protocol on December 20, 1985. It was officially published in the Federal Register on January 14, 1986, as part of the Land Disposal Restrictions Rule and again for public comment on June 13, 1986, as part of EPA's efforts to expand its Toxicity Characteristic. The protocol calls for the extraction of semi-volatile organic compounds, metals and pesticides using a bottle or jar similar to the EP procedure. For the extraction of volatile organic compounds (VOCs), a new device known as a Zero Headspace Extractor (ZHE) is used.

The purpose of this study was to assess the interlaboratory precision of the TCLP for the determination of metals, pesticides, base-neutral/acid extractable organic compounds, and volatile organic compounds. As the volatile organic compounds portion of this study is ongoing, this paper reports on the results of the study for metals, pesticides and base-neutral/acid extractable organic compounds. In addition, while this paper incorporates the majority of the data from the participating laboratories, we anticipate receiving additional data at a later date which will be incorporated into a final analysis.

TABLE 1.1. Participating Laboratories

ALBERTA ENVIRONMENTAL CENTRE
CHEMICAL WASTE MANAGEMENT
COMPUCHEM LABORATORIES
EG&G IDAHO
ENSECO
ENVIRODYNE
ENVIRONMENTAL SCIENCE & ENGINEERING
ENVIRONMENTAL TESTING & CERTIFICATION
INDUSTRIAL & ENVIRONMENTAL ANALYSTS
IT CORPORATION
LANGSTON LABS
LEMSCO
MICROBAC LABS
NUS
OAK RIDGE NATIONAL LABORATORY
PEI ASSOCIATES
RADIAN CORPORATION
ROCKY MOUNTAIN ANALYTICAL
S-CUBED
THERMAL-ANALYTICAL LABS
U.S. DEPT. OF ENERGY-MORGANTOWN
WESTERN RESEARCH INSTITUTE
WILSON LABS

2.0 METHODS

2.1 Collaborative Study Design

A total of 23 laboratories participated in the analytical aspects of the study. These laboratories are shown in Table 1.1.

Each of the laboratories agreeing to participate were invited to a meeting at S-CUBED in San Diego, California. This meeting was held to discuss with the participants the details of the collaborative study and to familiarize them with the TCLP procedure. Familiarization samples were distributed to the participants for return to their laboratories and subsequent TCLP analysis for semi-volatile organic compounds and metals.

A flowchart outlining the structure of the collaborative study is given in Figure 2.1. After analysis of familiarization samples (consisting of spiked sludges), the participating laboratories showing outlier values were contacted to identify and rectify possible analytical problems before proceeding with the collaborative study samples. In addition, statistical methods were refined after evaluation of familiarization sample data.

The collaborative study samples consisted of three different matrices; (1) an ammonia lime still bottom, (2) an API separator sludge, and (3) a fossil fuel fly ash. Each of these wastes was identified throughout the study as *Waste A, Waste B, and Waste C*, respectively. The pH was adjusted on split portions of each waste so that one portion would require the use of Extraction Fluid 1; the other portion requiring the use of Extraction Fluid 2 as defined in TCLP protocol. A total of six different samples were created: three different sample matrices each with two different pH's.

The samples were distributed among the participating laboratories such that each laboratory received two portions from a sample waste type, each portion having a different pH, thus requiring a different extraction fluid. In addition, a single sample at one pH level of another waste type was received by each laboratory, for a total of three samples for leaching and analysis. Samples were shipped to the participating laboratories via overnight courier in glass containers with Teflon-lined caps. Samples were packaged with ice packs to ensure the samples remained cold during transit.

2.2 Analytical Methods

Toxicity Characteristic Leaching Procedure

The TCLP is a second generation extraction procedure which improves upon the existing EP technique and allows for the inclusion of an expanded list of volatile and semi-volatile organic compounds. A new ZHE has been developed for a separate leaching of wastes to be analyzed for volatile organic compounds. Existing EP apparatus, with few modifications, may be employed for leaching of wastes to be analyzed for metals and semi-volatile organic compounds (including pesticides).

An outline of the TCLP procedure is shown in Figure 2.2. As with the EP, an initial liquid/solid separation is made. Glass fiber filters (0.6-0.8 μm pore size) are used for all filtrations in the TCLP rather than the membrane filters used in EP. After the initial separation, a pH measurement is made of the solid phase for determination of the appropriate extraction fluid to be used in the leaching procedure. The waste and extraction fluid are loaded into the extraction vessel and rotated at 30 ± 2 RPM for 18 hours.

No pH adjustments are made during this leaching period. A final liquid/solid separation is made at the conclusion of the 18-hour leaching. The solid phase is discarded and the final filtrate is either combined physically with the initial filtrate and analyzed, or the initial and final leachates are analyzed separately and the results are mathematically combined.

Chemical Analysis Procedure

For the purpose of comparability, all participating laboratories were requested to adhere to SW-846[1] analytical protocol. A summary of these methods is given in Figure 2.3.

SAMPLE (LEACHATE) PREPARATION METHODS

Analyte Group	Technique	Reference[1]
Semi-Volatile Organic Compounds	Solvent Extraction	3510
Metals	Acid Digestion	Series 30xx
Pesticides	Solvent Extraction	3510

ANALYTICAL PROCEDURES

Analyte Group	Technique	Reference
Semi-Volatile Organic Compounds	Gas Chromatography/Mass Spectroscopy	8270
Metals}	Atomic Absorption Inductively Coupled Plasma	Series 70xx 6010
Pesticides	Gas Chromatography/Electron Capture Detection	8270

Figure 2.3. Chemical Analysis Methods

3.0 STATISTICAL DESIGN

From a statistical point of view, the purpose of the study was to determine the efficacy of the TCLP. Efficacy was judged by the precision of the method measured among replicates conducted under the same conditions by a group of collaborating laboratories. Precision was determined by appropriate variance estimates derived from a designed statistical experiment and the subsequent analysis of variance (ANOVA)[2]. Since there was no direct knowledge of the exact contents of the test samples, bias was not measured directly. However, the relative distribution of bias among collaborating laboratories was considered.

The following discussion presents a step-by-step outline of the statistical aspects of the program and details the statistical procedures used. In several instances, hypothetical numbers are used to demonstrate various aspects of the analyses. Relevant tables and graphs are presented, where appropriate, in idealized form.

Raw data were submitted by each collaborating laboratory in the following form (Table 3.1). A separate submission was made for each type of sample (semi-volatile organic compounds, metals, and pesticides). For all submittals, a careful distinction was made between zero results and missing values.

TABLE 3.1. Raw Data Submittal Form

			Laboratory Test Sample No.					
	Familiarization Sample		One		Two		Three	
List of Materials	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1	#	#	#	#	#	#	#	#
2	#	#	#	#	#	#	#	#
3	#	#	#	#	#	#	#	#
•	•	•	•	•	•	•	•	•
•	•	•	•	•	•	•	•	•
•	•	•	•	•	•	•	•	•
m	#	#	#	#	#	#	#	#

However, the statistical analysis began using procedures similar to those outlined in the AOAC Manual[3] (Pages 74 and 75). First, the data were tabularized as shown in Table 3.2.

TABLE 3.2. Tabularized and Ranked Data

	Sample 1			Sample 2			Sample 3			
Lab	Rep	Sum	Rank	Rep	Sum	Rank	Rep	Sum	Rank	Total Rank
1	# #	#	#	# #	#	#	# #	#	#	#
2	# #	#	#	# #	#	#	# #	#	#	#
3	# #	#	#	# #	#	#	# #	#	#	#
•	• •	•	•	• •	•	•	• •	•	•	•
•	• •	•	•	• •	•	•	• •	•	•	•
•	• •	•	•	• •	•	•	• •	•	•	•
c	# #	#	#	# #	#	#	# #	#	#	#

The information in Table 3.2 was used for two separate, but related, purposes:

(1) The identification of outlying laboratories, and

(2) The identification of outlying individual samples results.

The *Rep* column in Table 3.2 represents the sum of all concentrations of the appropriate analytes, herein called *total recovery*. This particular univariate treatment of the data was somewhat artificial. However, there was at least some justification based on the following: at the time that the study was designed, it was felt that if a laboratory's measurements were consistently high (or low) on a given sample, then the measurements for all or most of the materials list would also be consistently high (or low). Therefore, dependencies among materials would tend to emphasize measurement differences among laboratories, but would not greatly influence the ranking of the laboratories.

Computational procedures for outlying laboratories in Table 3.2 were as follows. The *Sum* column was calculated separately for each sample as the sum of the two corresponding *Rep* values. The *Rank* column for each sample was then calculated based on the *Sum* column. If two or more laboratories tied for a given rank, each was given the mean rank of all tied ranks. For example, if three laboratories tied for rank *k*, then each was given the rank of [k + (k + 1) + (k + 2)]/3. Finally, the three *Rank* columns were summed to obtain the *Total Rank* column.

Each *Total Rank* was compared with the upper and lower 95 percent rank limits given in Appendix Table B (AOAC Manual) for the appropriate number of collaborating laboratories. The rank limits are based on the fact that any laboratory that is consistently high or low on all samples will have a *Total Rank* that is inordinately high or low, respectively. Laboratories having a *Total Rank* outside the tabulated limits were identified as outliers.

Individual outliers were identified using data from all laboratories, including those identified as outliers in Table 3.2. Each sample was considered independently. First, *Sum* values for the sample were arranged in ascending order and designated as S(1) through S(n), where S(1) had the lowest rank and S(n) the highest. The following ratios were computed for the *Sum* column values designated S(1) and S(n) (i.e., the two with the most extreme ranks):

$$S(n)\ \text{highest:}\quad \frac{(S)n - S(n-2)}{S(n) - S(3)}$$

$$S(1)\ \text{lowest:}\quad \frac{S(3) - S(1)}{S(n-2) - S(1)}$$

If either ratio exceeded the tabulated value (Appendix Table C.1, AOAC Manual) for *n* measurements, then that value was identified as an outlier. After the removal of outliers, the data were reranked and the entire procedure repeated.

The experiment design was defined by the following independent variables and relevant characteristics:

C - Collaborating Laboratories	c = 23
S - Samples (test samples of Table 2.1)	s = 3
B - Batches (sample lots)	b = 2
R - Replicates (duplicate analyses)	r = 2

Each independent variable was considered as a random variable, meaning that it can be interpreted as a sample of a larger population. The dependent variable was total recovery.

The resultant ANOVA is shown in Table 3.3. In the source of variation (SV) column, the notation CS indicates an interaction (i.e., the synergistic effect of C and S); the notation B/CS indicates that B is nested within CS (i.e., B might be different in each C and S combination). The numbers in parenthesis in the degrees of freedom (DF) column are based on the above definitions. A significant F-ratio indicates a failure of the extraction method on the indicated independent variable. For example, the significant F-ratio on C would indicate that the variability among collaborating laboratories was unacceptably high, or alternatively, that the potential for systematic error between laboratories was too great. The exception is that a significant Sample (S) main effect is allowable because the samples were in fact different.

TABLE 3.3. Analysis of Variance (ANOVA)

SV	DF		SS	MS	F-Ratio
Total	csbr	(600)	SS(T)	–	-
Mean	1	(1)	SS(mean)	–	-
C	c-1	(14)	SS(C)	MS(C)	MS(C) / MS(CS)
S	s-1	(1)	SS(S)	MS(S)	MS(S) / MS(CS)
CS	(c-1)(s-1)	(14)	SS(CS)	MS(CS)	MS(CS) / MS(B/CS)
B/CS	cs(b-1)	(270)	SS(B/CS)	MS(B/CS)	MS(B/CS) / MS(R/CSB)
R/CSB	csb(r-1)	(300)	SS(R/CSB)	MS(R/CSB)	-

Following the ANOVA, the following variance and standard deviation estimates were calculated:

Variance Estimates:

Between Replicates: $S_0^2 = MS(R/CSB)$

Batches (Lots): $S_B^2 = [MS(B/CS) - S_0]/r$

CS Interaction: $C_{CS}^2 = [MS(CS) - S_B - rS_0]/rb$

Among Laboratories: $S_C^2 = [MS(C) - S_B - rS_0 - rbS_{CS}]/rbs$

Standard Deviation Estimates:

Repeatability: $S_0 = \sqrt{MS(R/CSB)}$

Reproducibility: $S_R = \sqrt{S_0^2 + S_{CS}^2 + S_C^2}$

A note is in order on the calculation of sums of squares (SS). Because of the prevalence of missing values, a method for unbalanced ANOVA was used. By this method, only the values actually present contribute to the sums of squares; there is no attempt to estimate missing values. The degrees of freedom (DF) reflect the number of valid cases making up each sum of squares. In the *Results* section of this paper (Section 4.0), it will be noted that the degrees of freedom are generally very low in relation to comparable values if all cases were present.

4.0 RESULTS AND DISCUSSION

Tables 4.1 to 4.18 give the results of the collaborative study. Tables 1 to 6 present semi-volatile organic compound results for the 22 target compounds used in the study. Summarized values are in µg/L, the standard deviation, and relative standard deviation (RSD) are given. The RSD generally varied in the range of 20 to 120 percent for these compounds. No discernible trend was observed with respect to either the base/neutral or acid fractions from one sample batch to another.

Tables 4.7 to 4.12 give results for the metals extraction and analyses. The RSD for these results generally vary between 20 and 110 percent, with most values being below 90 percent. The variations of the different metals were not consistent from waste to waste. Thus, the TCLP does not appear to create particular extraction/analysis problems for any particular element. The use of the lower pH extraction system did result in generally higher metal results and less variable data.

Tables 4.13 to 4.18 present pesticide data. Only a limited number of pesticides were spiked in this study, so much of the data reported were detection limits which varied by organization. The RSD values for most compounds, especially dieldrin, 4,4-DDE, and endrin, do not reflect actual analytical results, but only detection limit variability.

Tables 4.19 to 4.27 present the results of the rank order test for the laboratories for semi-volatile organic compounds, metals, and pesticides, respectively. For both the semi-volatile organic compounds and metals, the results were good. No laboratories showed unacceptable total recoveries for organic compounds, and only two of the laboratories had unacceptable metals data. The pesticides data (Table 4.21) again reflect the variable detection limit problem for unspiked pesticides and a number of laboratories were found to be statistically unacceptable.

Tables 4.22, 4.23, and 4.24 report the analysis of variance results for the study. The key factor in these results is found in the last column of each table. The first factor gives the probability that the total recoveries for the different laboratories were statistically different. The values of 0.54, 0.47, and 0.85 for semi-volatile organic compounds, metals and pesticides, respectively, indicate that the performance of the laboratories was essentially the same. This was less true of the pesticides than for the other two types of analyses. The next value, 0.96, 0.93, and 0.65 for the three types of analyses, reflects whether the samples differed significantly from each other. In the case of semi-volatile organic compounds and metals, this was clearly the case. For pesticides, the results suggest this was not true. None of the pesticide samples contained background levels of pesticides, unlike the other materials. The smaller number of variables (six) and lack of background material was undoubtedly contributory to the statistical similarity of the results.

The third probability value of 0.01, 0.06, and 0.02 reflects the probability that the total recovery varies among laboratory sample combinations. These results reflect well on the overall consistency of the study, since they indicate little probability that there was a significant difference in the overall analyte concentration patterns observed among laboratories for different samples.

Finally, the last results from Tables 4.22, 4.23, and 4.24 indicate that the total recoveries did not vary within a batch. Thus, Samples A-1 and A-2, B-1 and B-2, and Samples C-1 and C-2, which were designed to require different TCLP leaching pH solutions, all yield comparable recoveries. As would be expected for the semi-volatile organic compounds and pesticides where water solubility is a critical factor, these probabilities are very low, 0.000 and 0.09, respectively. For metals, not surprisingly, the probability is much higher, 0.69, but it is still not significant at the 95 percent confidence level.

Overall, the statistical design used in this study was successful in providing the answers required. If the design and analysis were in error, they were in error on the conservative side as far as the result required to call the TCLP successful. The sums of squares (SS) and mean square error (MSE) in the ANOVAs were quite large. However, they were artificially so because of the use of total recovery as the dependent variable.

The major weakness in the statistics was the use of total recovery in outlier detection and as the dependent variable in the ANOVA. Its use assumes that the semi-volatile organic compounds, pesticides, and metal samples are independent of one another. This assumption is not necessarily true for all analytes. Multivariate methods to deal with this problem are under development at the present time (see paper by Show, Williams and Taylor in these proceedings). Whether these methods will yield similar results remains to be seen. When the multivariate methods become available, they will be used in addition to the univariate treatment used in this study.

TCLP COLLOBORATIVE STUDY RESULTS

Semi-volatile Organic Compounds

Table 4.1
SAMPLE A-1

Compound	$\bar{x}$	**SD**	**RSD**
Phenol	6950	1650	24
1,2-Dichlorobenzene	117	90.3	77
2-Methylphenol	933	538	58
4-Methylphenol	3540	1910	54
Nitrobenzene	361	223	62
2-Nitrophenol	8.20	6.40	78
1,2,4-Trichlorobenzene	7.31	4.60	63
Naphthalene	774	618	80
Hexachlorobutadiene	8.72	2.41	28
2-Methylnaphthalene	136	79.7	59
2,4,6-Trichlorophenol	363	139	38
2,4,5-Trichlorophenol	1800	1120	62
2-Chloronaphthalene	78.1	58.5	75
4-Nitrophenol	20.0	21.6	108
Hexachlorobenzene	7.14	4.88	68
Pentachlorophpenol	1230	737	60
Phenanthrene	126	70.7	56
Di-*N*-Butylphthalate	8.74	7.05	81
Fluoranthene	25.6	14.9	58
Bis(2-ethylhexyl)Phthalate	9.21	3.71	40
Chrysene	5.97	5.06	85
Di-*N*-Octylphthalate	7.31	3.91	54

TCLP COLLOBORATIVE STUDY RESULTS
Semi-volatile Organic Compounds

Table 4.2
SAMPLE A-2

Compound	$\bar{x}$	SD	RSD
Phenol	15900	8410	53
1,2-Dichlorobenzene	ND	ND	—
2-Methylphenol	1880	856	46
4-Methylphenol	10300	5150	50
Nitrobenzene	6.49	4.88	75
2-Nitrophenol	16.2	15.5	96
1,2,4-Trichlorobenzene	7.11	4.42	62
Naphthalene	1300	1200	92
Hexachlorobutadiene	ND	ND	—
2-Methylnaphthalene	134	106	79
2,4,6-Trichlorophenol	7.10	4.42	62
2,4,5-Trichlorophenol	37.7	31.7	84
2-Chloronaphthalene	ND	ND	—
4-Nitrophenol	28.4	31.0	109
Hexachlorobenzene	ND	ND	—
Pentachlorophpenol	36.3	29.6	82
Phenanthrene	130	82	63
Di-*N*-Butylphthalate	8.80	6.57	75
Fluoranthene	13.9	13.5	97
Bis(2-ethylhexyl)Phthalate	ND	ND	—
Chrysene	6.49	4.88	75
Di-*N*-Octylphthalate	ND	ND	ND

TCLP COLLOBORATIVE STUDY RESULTS

Semi-volatile Organic Compounds

Table 4.3
SAMPLE B-1

Compound	$\bar{x}$	**SD**	**RSD**
Phenol	113	81.0	72
1,2-Dichlorobenzene	19.0	13.8	73
2-Methylphenol	136	92.6	68
4-Methylphenol	158	98	62
Nitrobenzene	164	108	66
2-Nitrophenol	5.92	4.89	83
1,2,4-Trichlorobenzene	6.52	4.76	73
Naphthalene	133	79.5	60
Hexachlorobutadiene	6.98	4.02	58
2-Methylnaphthalene	70.4	45.6	65
2,4,6-Trichlorophenol	88.8	43.9	49
2,4,5-Trichlorophenol	405	251	62
2-Chloronaphthalene	5.89	4.18	71
4-Nitrophenol	20.2	26.0	128
Hexachlorobenzene	5.43	5.02	92
Pentachlorophpenol	174	175	101
Phenanthrene	5.28	4.08	77
Di-*N*-Butylphthalate	6.13	5.35	87
Fluoranthene	5.50	4.71	85
Bis(2-ethylhexyl)Phthalate	16.4	21.4	130
Chrysene	5.08	4.86	96
Di-*N*-Octylphthalate	5.71	5.10	89

TCLP COLLOBORATIVE STUDY RESULTS
Semi-volatile Organic Compounds

Table 4.4
SAMPLE B-2

Compound	$\bar{x}$	SD	RSD
Phenol	74.2	60.1	81
1,2-Dichlorobenzene	20.1	13.5	67
2-Methylphenol	34.0	29.5	87
4-Methylphenol	45.0	29.4	65
Nitrobenzene	110	67.1	61
2-Nitrophenol	18.8	26.3	140
1,2,4-Trichlorobenzene	3.6	4.98	138
Naphthalene	165	32.9	20
Hexachlorobutadiene	3.6	4.98	138
2-Methylnaphthalene	65.3	46.3	71
2,4,6-Trichlorophenol	276	264	96
2,4,5-Trichlorophenol	346	301	87
2-Chloronaphthalene	6.66	4.44	67
4-Nitrophenol	4.90	7.35	150
Hexachlorobenzene	2.92	4.54	156
Pentachlorophpenol	308	173	56
Phenanthrene	3.93	4.32	110
Di-*N*-Butylphthalate	6.47	4.88	75
Fluoranthene	3.20	4.38	137
Bis(2-ethylhexyl)Phthalate	25.3	31.6	125
Chrysene	3.6	4.98	136
Di-*N*-Octylphthalate	3.1	4.25	137

TCLP COLLOBORATIVE STUDY RESULTS
Semi-volatile Organic Compounds

Table 4.5
SAMPLE C-1

Compound	**$\bar{x}$**	**SD**	**RSD**
Phenol	24.7	21.6	87
1,2-Dichlorobenzene	22.4	21.8	97
2-Methylphenol	51.9	55.4	107
4-Methylphenol	26.8	25.1	94
Nitrobenzene	103	68.1	66
2-Nitrophenol	5.33	7.14	134
1,2,4-Trichlorobenzene	4.22	5.04	119
Naphthalene	35.2	34.2	97
Hexachlorobutadiene	4.45	4.83	108
2-Methylnaphthalene	4.22	5.04	119
2,4,6-Trichlorophenol	29.8	28.8	96
2,4,5-Trichlorophenol	176	235	134
2-Chloronaphthalene	39.2	49.6	126
4-Nitrophenol	16.1	23.1	144
Hexachlorobenzene	3.83	4.08	106
Pentachlorophpenol	50.1	53.2	106
Phenanthrene	4.60	4.81	105
Di-*N*-Butylphthalate	7.47	6.47	87
Fluoranthene	22.0	23.0	104
Bis(2-ethylhexyl)Phthalate	259	400	154
Chrysene	4.75	5.12	108
Di-*N*-Octylphthalate	11.2	15.2	136

TCLP COLLOBORATIVE STUDY RESULTS
Semi-volatile Organic Compounds

Table 4.6
SAMPLE C-2

Compound	$\bar{x}$	SD	RSD
Phenol	23.3	8.4	36
1,2-Dichlorobenzene	13.3	13.9	104
2-Methylphenol	31.9	23.1	72
4-Methylphenol	22.0	16.8	76
Nitrobenzene	54.0	30.4	56
2-Nitrophenol	6.3	9.5	150
1,2,4-Trichlorobenzene	ND	ND	—
Naphthalene	36.6	31.6	86
Hexachlorobutadiene	7.38	3.33	45
2-Methylnaphthalene	ND	ND	—
2,4,6-Trichlorophenol	20.3	9.5	47
2,4,5-Trichlorophenol	140	71.6	51
2-Chloronaphthalene	49.5	47.0	95
4-Nitrophenol	ND	ND	—
Hexachlorobenzene	4.50	4.12	92
Pentachlorophpenol	287	51.9	18
Phenanthrene	ND	ND	—
Di-*N*-Butylphthalate	ND	ND	—
Fluoranthene	19.6	10.3	53
Bis(2-ethylhexyl)Phthalate	7.83	12.3	157
Chrysene	ND	ND	—
Di-*N*-Octylphthalate	4.03	4.91	122

TCLP COLLOBORATIVE STUDY RESULTS

Metals

Table 4.7
SAMPLE A-1

Metal	$\bar{x}$	SD	RSD
Aluminum	5.83	3.60	62
Cadmium	52.6	31.4	60
Calcium	19600	8500	43
Chromium	1.54	1.43	93
Cobalt	13.1	7.3	56
Copper	3.10	1.71	55
Iron	2.22	1.36	61
Lead	2.97	2.67	90
Magnesium	2220	446	20
Manganese	131	58	44
Nickel	1.50	1.49	99
Thallium	7.11	5.37	76
Vanadium	0.87	1.12	129

Table 4.8
SAMPLE A-2

Metal	$\bar{x}$	SD	RSD
Aluminum	14.9	13.5	91
Cadmium	27.6	14.8	54
Calcium	19300	1300	7
Chromium	3.79	3.79	100
Cobalt	6.70	3.78	56
Copper	0.53	0.28	53
Iron	8.3	6.9	83
Lead	3.89	2.59	67
Magnesium	2330	598	26
Manganese	9.91	0.32	3
Nickel	1.93	1.82	94
Thallium	2.691	2.90	108
Vanadium	0.98	1.04	106

TCLP COLLOBORATIVE STUDY RESULTS
Metals

Table 4.9
SAMPLE B-1

Metal	$\bar{x}$	SD	RSD
Aluminum	2.60	1.79	69
Cadmium	4.59	2.82	61
Calcium	12000	5590	47
Chromium	56.1	22.7	40
Cobalt	6.84	7.88	115
Copper	2.15	0.58	27
Iron	1.45	1.62	112
Lead	3.12	3.13	100
Magnesium	421	78.3	19
Manganese	1.39	0.50	36
Nickel	0.95	1.00	105
Thallium	41.7	47.3	113
Vanadium	0.76	0.27	35

Table 4.10
SAMPLE B-2

Metal	$\bar{x}$	SD	RSD
Aluminum	20.8	18.1	87
Cadmium	0.48	0.37	77
Calcium	105	41.4	39
Chromium	105	18.0	17
Cobalt	0.50	0.15	30
Copper	8.35	2.33	28
Iron	0.93	0.63	68
Lead	12.4	13.6	110
Magnesium	72.1	61.9	86
Manganese	0.13	0.06	46
Nickel	0.39	0.08	20
Thallium	74.1	40.4	54
Vanadium	11.3	7.03	62

TCLP COLLOBORATIVE STUDY RESULTS
Metals

Table 4.11
SAMPLE C-1

Metal	$\bar{x}$	SD	RSD
Aluminum	521	429	82
Cadmium	87.1	67.4	77
Calcium	10900	2960	27
Chromium	18.5	14.0	76
Cobalt	51.7	40.2	78
Copper	0.35	0.36	103
Iron	31.1	25.8	83
Lead	8.69	7.40	85
Magnesium	1380	960	70
Manganese	19.0	15.4	81
Nickel	0.69	0.42	61
Thallium	40.9	22.3	54
Vanadium	0.52	0.37	71

Table 4.12
SAMPLE C-2

Metal	$\bar{x}$	SD	RSD
Aluminum	2690	937	35
Cadmium	86.7	17.7	26
Calcium	11900	5740	48
Chromium	84.1	23.7	28
Cobalt	89.0	9.23	10
Copper	4.67	1.48	32
Iron	532	294	55
Lead	45.7	8.3	18
Magnesium	2360	164	7
Manganese	65.8	23.1	35
Nickel	1.17	0.66	56
Thallium	41.3	13.2	32
Vanadium	5.99	2.62	44

TCLP COLLOBORATIVE STUDY RESULTS
Pesticides

Table 4.13
SAMPLE A-1

Compound	$\bar{x}$	**SD**	**RSD**
β-BHC	27.6	27.8	99
Γ-BHC (Lindane)	58.9	36.6	161
Aldrin	15.1	28.0	54
Dieldrin	4.16	6.69	62
4,4-DDE	13.2	35.1	38
Endrin	3.05	6.89	44

Table 4.14
SAMPLE A-2

Compound	$\bar{x}$	**SD**	**RSD**
β-BHC	17.4	19.5	71
Γ-BHC (Lindane)	17.8	24.6	72
Aldrin	2.00	1.87	107
Dieldrin	2.63	2.36	111
4,4-DDE	1.50	0.71	211
Endrin	ND	ND	—

TCLP COLLOBORATIVE STUDY RESULTS
Pesticides

Table 4.15
SAMPLE B-1

Compound	$\bar{x}$	SD	RSD
β-BHC	3.90	2.22	176
Γ-BHC (Lindane)	6.61	4.08	162
Aldrin	2.29	2.16	106
Dieldrin	1.88	2.22	85
4,4-DDE	1.71	1.86	92
Endrin	0.70	0.45	156

Table 4.16
SAMPLE B-2

Compound	$\bar{x}$	SD	RSD
β-BHC	3.08	3.01	102
Γ-BHC (Lindane)	15.64	20.18	76
Aldrin	0.98	0.90	109
Dieldrin	2.17	3.33	65
4,4-DDE	0.43	0.40	107
Endrin	0.63	0.48	131

TCLP COLLOBORATIVE STUDY RESULTS
Pesticides

Table 4.17
SAMPLE C-1

Compound	**$\bar{x}$**	**SD**	**RSD**
β-BHC	56.7	48.0	118
Γ-BHC (Lindane)	ND	ND	—
Aldrin	ND	ND	—
Dieldrin	ND	ND	—
4,4-DDE	ND	ND	—
Endrin	ND	ND	—

Table 4.18
SAMPLE C-2

Compound	**$\bar{x}$**	**SD**	**RSD**
β-BHC	ND	ND	—
Γ-BHC (Lindane)	ND	ND	—
Aldrin	ND	ND	—
Dieldrin	ND	ND	—
4,4-DDE	ND	ND	—
Endrin	ND	ND	—

SUMMARY RESULTS
SEMI-VOLATILE ANALYSIS

Table 4.19
SAMPLE A

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	22200.50	6.00	16472.50	2.00	19336.50	4.00	Acceptable
4	12306.25	3.00	12117.45	1.00	12211.85	2.00	Acceptable
5	25888.00	7.00	36529.50	3.00	31208.75	5.00	Acceptable
7	19185.25	5.00	42998.95	4.00	31092.10	4.50	Acceptable
9	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-
18	11094.90	2.00	-	-	11094.90	2.00	Acceptable
19	-	-	-	-	-	-	-
20	10044.65	1.00	-	-	10044.65	1.00	Acceptable
23	-	-	149001.41	5.00	149001.41	5.00	Acceptable
24	18266.00	4.00	-	-	18266.00	4.00	Acceptable

<u>Notes</u>:
1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
SEMI-VOLATILE ANALYSIS

Table 4.20
SAMPLE B

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	1524.00	4.00	-	-	1524.00	4.00	Acceptable
4	739.35	2.00	-	-	739.35	2.00	Acceptable
5	2798.00	9.00	-	-	2798.00	9.00	Acceptable
7	1679.05	5.00	-	-	1679.05	5.00	Acceptable
9	5376.00	10.00	2480.00	6.00	3928.00	8.00	Acceptable
10	1817.20	6.00	1792.95	4.00	1805.07	5.00	Acceptable
12	2688.50	7.00	1984.00	5.00	2336.25	6.00	Acceptable
14	1223.30	3.00	1714.35	3.00	1468.82	3.00	Acceptable
15	97.00	1.00	505.00	1.00	301.00	1.00	Acceptable
17	2797.00	8.00	1266.50	2.00	2031.75	5.00	Acceptable
18	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
23	39292.24	11.00	-	-	39292.34	11.00	Not Acceptable
24	-	-	-	-	-	-	-

Notes:
1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
SEMI-VOLATILE ANALYSIS

Table 4.21
SAMPLE C

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
9	1448.00	8.00	-	-	1448.00	8.00	Not Acceptable
10	742.85	5.00	-	-	742.85	5.00	Acceptable
12	964.00	7.00	-	-	964.00	7.00	Acceptable
14	926.60	6.00	-	-	926.60	6.00	Acceptable
15	-	-	-	-	-	-	-
17	332.00	1.00	-	-	332.00	1.00	Acceptable
18	572.90	2.00	512.35	1.00	542.63	1.50	Acceptable
19	688.00	4.00	742.00	2.00	715.00	3.00	Acceptable
20	2808.00	8.00	1453.00	4.00	2130.50	6.00	Not Acceptable
23	-	-	-	-	-	-	-
24	601.00	3.00	819.00	3.00	710.00	3.00	Acceptable

Notes:
1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
PESTICIDES ANALYSIS

Table 4.22
SAMPLE A

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	133.00	5.00	42.50	4.00	87.50	4.50	Acceptable
2	157.70	7.00	11.30	1.00	84.50	4.00	Acceptable
4	131.00	4.00	82.50	5.00	106.75	4.50	Acceptable
5	146.75	6.00	29.55	3.00	88.15	4.50	Acceptable
7	427.50	8.00	450.00	6.00	438.75	7.00	Not Acceptable
9	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-
18	1153.00	9.00	-	-	1153.00	9.00	Not Acceptable
20	15.74	9.00	18.80	2.00	17.27	2.00	Not Acceptable
21	53.00	3.00	-	-	53.00	3.00	Acceptable
24	0.15	1.00	-	-	0.15	1.00	Not Acceptable

Notes:
1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY REPORTS
PESTICIDES ANALYSIS

Table 4.23
SAMPLE B

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	72.25	6.00	-	-	72.25	6.00	Not Acceptable
2	23.85	4.00	-	-	23.85	4.00	Acceptable
4	13.85	1.00	-	-	13.85	1.00	Acceptable
5	18.55	2.00	-	-	18.55	2.00	Acceptable
7	450.00	9.00	-	-	450.00	9.00	Not Acceptable
9	22.03	3.00	45.33	2.00	33.68	2.50	Acceptable
10	199.00	8.00	199.00	5.00	199.00	6.50	Not Acceptable
12	120.50	6.00	182.25	4.00	151.38	5.00	Not Acceptable
14	0.00	1.00	0.00	1.00	0.00	1.00	Not Acceptable
17	-	-	168.50	3.00	168.50	3.00	Acceptable
18	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-
24	-	-	-	-	-	-	-

Notes:

1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
PESTICIDES ANALYSIS

Table 4.24
SAMPLE C

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
9	53.29	3.00	-	-	53.29	3.00	Acceptable
10	-	-	-	-	-	-	-
12	135.80	6.00	-	-	135.80	6.00	Acceptable
14	78.00	4.00	-	-	78.00	4.00	Acceptable
17	-	-	-	-	-	-	-
18	1129.00	7.00	532.50	4.00	830.75	5.50	Acceptable
20	6.70	2.00	18.80	3.00	12.75	2.50	Not Acceptable
21	96.00	5.00	0.00	1.00	48.00	3.00	Acceptable
24	0.15	1.00	0.15	2.00	0.15	1.50	Not Acceptable

Notes:

1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
METALS ANALYSIS

Table 4.25
SAMPLE A

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	24143.55	5.00	22643.27	4.00	23392.41	4.50	Acceptable
2	29946.54	7.00	29191.73	5.00	29569.14	6.00	Acceptable
4	23380.59	4.00	21899.73	3.00	22640.16	3.50	Acceptable
5	20874.81	2.00	20540.91	1.00	20707.86	1.50	Acceptable
7	21567.46	3.00	20792.69	2.00	21180.07	2.50	Acceptable
8	37458.75	9.00	-	-	37458.75	9.00	Not Acceptable
9	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-
18	4706.57	1.00	-	-	4706.57	1.00	Not Acceptable
20	24283.10	6.00	-	-	24283.10	6.00	Acceptable
21	-	-	-	-	-	-	-
24	18733.10	1.00	-	-	18733.10	1.00	Acceptable

Notes:

1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
METALS ANALYSIS

Table 4.26
SAMPLE B

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	23020.36	10.00	-	-	23020.36	10.00	Acceptable
2	25501.81	11.00	-	-	25501.81	11.00	Acceptable
4	13000.52	7.00	-	-	13000.52	7.00	Acceptable
5	12775.09	6.00	-	-	12775.09	6.00	Acceptable
7	12100.93	4.00	-	-	12100.93	4.00	Acceptable
8	-	-	-	-	-	-	-
9	10570.35	3.00	447.07	2.00	5508.71	2.50	Acceptable
10	8032.94	2.00	328.36	1.00	4180.65	1.50	Acceptable
12	12524.85	5.00	867.67	4.00	6696.26	4.50	Acceptable
14	14369.60	7.00	493.95	3.00	7431.78	5.00	Acceptable
16	13109.94	6.00	3060.35	5.00	8085.14	5.50	Acceptable
17	3956.20	1.00	21178.55	6.00	12567.38	3.50	Acceptable
18	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-
24	-	-	-	-	-	-	-

<u>Notes</u>:

1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

SUMMARY RESULTS
METALS ANALYSIS

Table 4.27
SAMPLE C

	LOT 1		LOT 2		MEAN		
Lab No.	Total	Rank	Total	Rank	Total	Rank	a = 0.05
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
8	29768.75	11.00	28049.75	5.00	28909.25	8.00	Acceptable
9	15447.70	7.00	-	-	15447.70	7.00	Acceptable
10	17285.06	8.00	-	-	17385.06	8.00	Acceptable
12	13543.60	5.00	-	-	13543.60	5.00	Acceptable
14	9684.43	3.00	-	-	9684.43	3.00	Acceptable
16	9163.10	2.00	-	-	9163.10	2.00	Acceptable
17	18762.40	10.00	-	-	18762.40	10.00	Acceptable
18	5771.71	1.00	9058.73	1.00	7415.22	1.00	Acceptable
20	10114.00	4.00	17322.40	3.00	13718.20	3.50	Acceptable
21	17894.81	9.00	20534.51	4.00	19214.66	6.50	Acceptable
24	14988.95	6.00	13382.80	2.00	14185.88	4.00	Acceptable

Notes:
1. Totals represent total recovery for the lab summed over all chemicals and all lots.
2. Ranks are based on total recovery - Rank 1 is given to the lowest total recovery, etc.
3. "Not Acceptable" indicates that total recovery is a statistical outlier.

Table 4.28 ANOVA Semi-Volatile Organic Compounds

SV	DF	SS	MSE	F-Ratio	Prob(F>f)
Total	75	38.3×10^9	-	-	-
Mean	1	9.4×10^9	-	-	-
C	14	3.1×10^9	2.2×10^8	1.02	0.540
S	2	1.6×10^9	8.0×10^8	3.68	0.093*
CS	28	6.1×10^9	2.2×10^8	0.43	0.014
B/CS	28	14.2×10^9	5.1×10^8	0.08	0.0003
R/CSB	2	12.3×10^9	61.7×10^8	-	-

Definitions:

C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

Significance:

* - Indicates significant effect
** - Indicates highly significant effect

Table 4.30 ANOVA Pesticides

SV	DF	SS	MSE	F-Ratio	Prob(F > f)
Total	71	63.4×10^5	-	-	-
Mean	1	2.1×10^5	-	-	-
C	13	10.1×10^5	7.8×10^4	1.61	0.856
S	2	1.1×10^5	5.3×10^4	1.09	0.649
CS	26	12.5×10^5	4.8×10^4	0.43	0.017
B/CS	26	29.3×10^5	11.2×10^4	0.41	0.086
R/CSB	3	8.2×10^5	27.4×10^4	-	-

Definitions:
C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

Significance:
* - Indicates significant effect
** - Indicates highly significant effect

Table 4.29 ANOVA Metals

SV	DF	SS	MSE	F-Ratio	Prob(F>f)
Total	84	$28.7x10^9$	-	-	-
Mean	1	$3.1x10^9$	-	-	-
C	15	$3.3x10^9$	$21.8x10^7$	0.94	0.469
S	2	$1.3x10^9$	$65.4x10^7$	2.83	0.927
CS	30	$6.9x10^9$	$23.1x10^7$	0.56	0.056
B/CS	31	$12.9x10^9$	$41.5x10^7$	1.63	0.693
R/CSB	5	$1.3x10^9$	$25.4x10^7$	-	-

Definitions:

C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

Significance:

`*` - Indicates significant effect
`**` - Indicates highly significant effect

Table 4.31 ANOVA Semi-Volatiles Familiarization

SV	DF	SS	MSE	F-Ratio	Prob(F>f)
Total	38	90.2×10^5	-	-	-
Mean	1	60.6×10^5	-	-	-
C	16	16.2×10^5	10.1×10^4	1.23	0.656
B/C	16	13.2×10^5	8.3×10^4	25.98	0.998
R/BC	5	0.2×10^5	0.3×10^4	-	-

<u>Definitions</u>:

C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

<u>Significance</u>:

* - Indicates significant effect
** - Indicates highly significant effect

Table 4.32 ANOVA Pesticides Familiarization

SV	DF	SS	MSE	F-Ratio	Prob(F>f)
Total	43	19.6×10^5	-	-	-
Mean	1	8.1×10^5	-	-	-
C	17	80.8×10^5	47.5×10^3	2.41	0.961*
B/C	17	33.5×10^5	19.7×10^3	189.51	0.999**
R/BC	8	0.1×10^5	0.1×10^3	-	-

Definitions:

C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

Significance:

* - Indicates significant effect
** - Indicates highly significant effect

Table 4.33 ANOVA Metals Familiarization

SV	DF	SS	MSE	F-Ratio	Prob(F>f)
Total	63	11.8×10^7	-	-	-
Mean	1	9.7×10^7	-	-	-
C	22	12.9×10^7	58.5×10^5	1.85	0.921
B/C	22	7.0×10^7	31.6×10^5	7.07	0.999**
R/BC	18	0.8×10^7	4.5×10^5	-	-

Definitions:

C = Collaborating Labs Main Effect
S = Samples Main Effect
CS = Lab-Sample Interaction
B/CS = Batches (Lots) nested within Lab-Sample Interaction
R/BCS = Replicates nested within B/CS nested Effect

SV = Source of Variation
DF = Degrees of Freedom
SS = Sums of Squares
MSE = Mean Squared Error

Significance:

* - Indicates significant effect
** - Indicates highly significant effect

5.0 CONCLUSIONS

The results of the collaborative study indicate that the TCLP can be applied consistently by a diverse group of organizations. Total recoveries for both semi-volatile organic compounds and metals were sufficiently good to indicate that variability is within reasonable statistical limits (at a 95 percent confidence level) for these two groups of parameters. The pesticide results were distorted by the limited amount of data and the wide range of detection limits reported by the participating laboratories. It is felt that a larger data set would yield comparable results to that for other organic compounds.

6.0 REFERENCES

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(1) *Test Methods for Evaluating Solid Wastes*: U.S. Environmental Protection Agency. Office of Solid Waste. Washington, DC, 1982.

(2) Kempthorne, O. *The Design and Analysis of Experiments*; Robert E. Krieger Publishing Company. Huntington, NY, 1973; pp. 631.

(3) Youden, W. J.; Steiner, E.H. *Statistical Manual of the Association of Official Analytical Chemists*; The Association of Official Analytical Chemists: Arlington, VA, 1975.

COMPARISON STUDY OF PREPARATIVE AND ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF SELENIUM IN WATER, SEDIMENT AND VEGITATION MATRICES

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ABSTRACT

In an effort to develop precise and accurate methodologies for the determination of Se, a potentially toxic and difficult to determine element, in various sample matrices, different approaches of sample preparation and analysis were evaluated. Modification of methods was applied when needed and modified methodologies were assessed.

Nitric acid digestion, with and without H_2O_2 and HCl, was considered. Selenium (total) in various digestates was determined by Inductively-Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Heated Graphite Atomizer-Atomic Absorption (HGA-AA), and Hydride Generation-Atomic Absorption (HG-AA) Spectrometry.

The data generated by this work showed that there is a reasonable agreement among the Se results obtained by ICP-AES and HGA-AA in the sediment and vegetation samples. The HGA-AA technique, however, is preferred for the determination of low levels of Se in water (sub ppm) due to its higher sensitivity relative to that of ICP-AES. Several problems were encountered with the hydride generation technique (HG-AA) and its use required difficult manipulations and extreme care. Generally, Se recoveries of 77% to 108% were attained at levels of 2 ppm and 30 ppm total Se.

This paper describes the various methods of samples preparation considered, and the operating parameters of the different instrumental techniques used. A comparative discussion of these methods and techniques is also reported along with recommendations pertinent to the use of each.

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SECOND SESSION

Wednesday, July 16, 1986
8:00 a.m. - 12:00 p.m.

Chairperson:
Ronald Mitchum
Director
Quality Assurance Division
Environmental Monitoring and Support Laboratory, USEPA,
Las Vegas, NV 89114

DEVELOPMENT AND VALIDATION OF RCRA METHOD 8280 FOR DIOXINS AND FURANS

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ABSTRACT

RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans, as published in the Federal Register in April 1983, revealed the need for several modifications to allow for the determination of the target analytes in complex matrices, such as industrial sludge and still-bottom samples. Details of these modifications and of the subsequent applicaton of the revised method to a limited number of samples which were analyzed in the course of a single laboratory evaluation will be reported.

Further evaluation of RCRA Method 8280 for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans has been performed. The Method has been modified to provide for the quantitation of total tetra-through octa-chlorinated doixins and dibenzofurans and has been applied to sample matrices derived from industrial polychlorophenal sources as well as to fly-ash, still-bottom, and Missouri soil samples. As an additional test of Method performance, an inter-laboratory validation study was conducted in two parts. A two-part study was used becasue the Method had been extensively revised since its publication in the Federal Register, and it was felt that participating laboratories would be unfamiliar with some of the proposed procedures. The first phase was intended to allow the participants to acquire familiarization with the Method by analyzing relatively simple matrices for a few specified analytes which had been spiked into the samples. The second phase required the total quantitation of tetra-through octa-CDD's and CDF's in complex samples containing the analytes at both low (ppt) and extremely high (ppm) levels; no spiking was used for these samples. A method detection limit study using all available $^{13}C^{12}$ - labeled PCDD and PCDF isomers spiked into seven different sample matrices was also performed and the results indicated both matrix and homolog specific differences.

The revised Method 8280 has undergone a period of continual development, new documentation which will be reported includes Method performance data on complex samples from polychlorophenol use processes, results from an inter-laboratory study of the revised method, and method detection limits of selected PCDD's and PCDF's in a variety of environmental and hazardous waste matrices.

INTRODUCTION

On a molecular basis, 2,3,7,8-tetrachlorodibenzo-p dioxin (2,3,7,8-TCDD) is one of the most poisonous synthetic chemicals known. The compound has been shown in animals to possess teratogenic, embryotoxic, carcinogenic, and co-carcinogenic properties in addition to acute toxicity. Because of its chemical stability, lipophilic character, and extreme toxicity, it presents potentially severe health hazards to the human population. Although 2,3,7,8-TCDD is the most toxic of the 75 chlorinated dibenzo-p dioxins (PCDD's), many of the others (as well as the 135 chlorinated dibenzofurans (PCDF's) which have similar genesis, structures, and properties) are known to possess relatively high toxicity to humans and animals. For this reason, the entire spectrum of PCDD's and PCDF's is of environmental concern.

Based on this information, it was concluded that samples containing tetra-, penta-, hexa-, hepta-, and octa-CDD's and -CDF's are likely to exhibit increased toxicity. A method to analyze hazardous wastes for the relevant PCDD's and PCDF's was included in the Resource Conservation and Recovery Act (RCRA) requirements for hazardous waste monitoring. A single-laboratory evaluation of RCRA Method 8280 for the analysis of PCDD's and PCDF's in hazardous waste has been the subject of a previous report prepared for the Office of Solid Waste. That report presented results obtained with sample matrices including pottery clay, a Missouri soil, a fly-ash, a still-bottom from a chlorophenol-based herbicide production process and an industrial process sludge. Major revisions to the Method which was first published in 1983 were necessary to accommodate the analysis of complex samples such as sludge and still-bottom.

The revised Method 8280 has undergone a period of continual development, and this report presents results obtained during the further evolution of the Method. The Method has now been modified to enable the quantitation of total tetra- through octa-chlorinated dioxins and dibenzofurans and has been applied to six different sample matrices derived from industrial polychlorophenol sources and also to fly-ash, still-bottom, and Missouri soil samples. An interlaboratory validation of the Method was conducted in two phases: Phase I required the analysis of spiked and unspiked clay and sludge samples for certain specified PCDD/PCDF analytes, and Phase II required the analysis of soil, sludge, fly-ash, and still-bottom samples for total tetra- through octa-chlorinated dioxins and dibenzofurans. Method detection limits of $^{13}C_{12}$-labeled polychlorinated dioxins and dibenzofurans in seven matrices have also been determined.

RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, as published in the Federal Register in April 1983, revealed the need for several modifications to allow for the determination of the target analytes in complex hazardous waste matrices, such as industrial sludge and stillbottom samples. Subsequently, the Method has been further refined in several important ways as needed for the characterization and assessment aspects of RCRA. A summary of these changes is as follows: In order to improve the accuracy of quantitation of the hepta- and octa-CDD's and -CDF's, a second internal standard ($^{13}C_{12}$-OCDD) is added together with $^{13}C_{12}$-2,3,7,8-TCDD prior to sample workup. Some of the ions specified in the multiple ion detection (MID) descriptors have been changed so as to increase sensitivity by monitoring the most intense ion in the isotopic cluster. To ensure that coeluting polychlorinated diphenyl ethers (PCDE's) are not contributing to the signal response due to PCDF's, the molecular ion of the appropriate PCDE was included in each MID descriptor. In addition, the criteria for the positive identification of PCDD and PCDF isomers were made more explicit. Instrument tune criteria employing PCDD standard reference materials were substituted for those based on the use of decafluorotriphenylphosphine (DFTPP). The section on the calculation of concentrations of the target analytes was expanded to include a procedure for measuring unknown PCDD and PCDF isomers.

This report presents data on the performance of the Method as it was applied to the analysis of a variety of wastes derived from the use of polychlorophenols in the wood-preserving industry. As an additional test of Method performance, an interlaboratory validation study was conducted. This study was divided into two phases because the Method had been extensively revised since its first publication in the Federal Register, and it was felt that participating laboratories would be unfamiliar with some of the proposed procedures. The first phase was intended to allow the participants to acquire familiarization with the Method by analyzing relatively simple matrices for a few specified analytes which had been spiked into the samples. The second phase required the total quantitation of tetra-through octa-CDD's and -CDF's in complex samples containing the analytes at both low and extremely high concentration levels; no spiking was used for these samples. A method detection limit study using all available $^{13}C_{12}$-labeled PCDD and PCDF isomers spiked into seven different sample matrices was also performed and will be reported.

Data obtained from Phase I of the interlaboratory study indicate that the Method is biased high and that the bias appears to decrease as the concentrations of the analytes increase. Data from the method detection limit (MDL) study can also be used as an indicator of intralaboratory precision. For seven replicate determinations of a TCDF and a PeCDD in fly-ash with each at a measured concentration of 2.6 times their final calculated MDL's, the relative standard deviations (RSD's) were 12.3 percent and 12.2 percent, respectively. Similar determinations for a PeCDF and a TCDD which were measured at a level 6.0 and 4.4 times their MDL's gave RSD's of 5.2 percent and 7.2 percent, respectively.

Encouraging results were obtained from Phase I of the interlaboratory study in which specific analytes spiked into clay and sludge samples were quantitated. The good overall recovery (greater than 50 percent) of the internal standard and the small differences between the spiked concentrations and the mean measured values both indicate that the Method can provide acceptable data in a multi-laboratory evaluation. Phase II of the interlaboratory study which required the quantitation of total tetra- through octa-CDD's and -CDF's in 10 aliquots of 4 sample types also provided generally satisfactory results. The internal standards ($^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD) were recovered in overall acceptable yields ranging from 51 to 82 percent. However, quantitation of the analytes was less precise than in Phase I. Two major, probable reasons for this are as follows:

- o the complex samples themselves, some of which contained endogenous amounts of the target analytes at low and at extremely high levels. This required a large dilution effect which minimized the value of the internal standard, and
- o the analysis required the identification, confirmation, and quantitation of unknown peaks for each congener without an authentic reference material which could be used to confirm the identification.

Statistical analysis of the Phase II data revealed that:

- o the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard was a function of sample type whereas that of the $^{13}C_{12}$-OCDD internal standard was not;
- o the laboratories were equivalent in accuracy for all analytes except OCDD; and
- o the laboratories were equivalent in precision for 31 of the 40 possible matrix/analyte combinations.

As a result of the experience gained during the single-and multi-laboratory testing of the Method with a variety of environmental samples, several modifications and areas of further study are recommended as follows:

- The Method should allow for the use of disposable, open carbon columns as an option to the HPLC carbon column cleanup. This would allow for an increase in the rate of sample throughput and would also reduce solvent consumption.
- Gas chromatography (GC) conditions should be modified to improve the resolution between the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) and the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD). If this cannot be readily achieved, then use of an alternative recovery standard should be considered.
- The elution windows (defined by first and last eluting isomers) of the tetra- through octa-CDD and -CDF congeners should be established for the GC conditions used in the Method.
- Method 8280 should be written to require as many GC/MS analyses as necessary by using the appropriate MID descriptors whenever an elution overlap is noted in a sample. The descriptors should include at least one ion for each overlapping homologue.
- Kovats Indices should be determined for available PCDD's and PCDF's. This would aid laboratories in the identification of isomers not known or available and would be useful in a GC screening program.
- The need to monitor for polychlorinated diphenyl ethers (PCDE's) in the final sample extract should be investigated.
- A source of a well-defined GC performance standard should be identified. Column performance guidelines should be established for a variety of columns.

These changes have been incorporated into the final version of the Method.

In order to assess method performance, 10 waste samples derived from the industrial use of pentachlorophenol (PCP) were provided to the EPA. These samples together represent 4 different matrix types, viz. sludge, fuel oil, alcohol fuel oil, and soil. The range of matrix types encompassed is expected to be representative of those to be analyzed under RCRA regulations and is expected to provide varying degrees of sample complexity.

Each sample was analyzed in duplicate for the quantitation of total tetra- through octa-CDD's and -CDF's. Two criteria were applied to confirm that peaks in the extracted ion current profiles (EICP's) of the quantitation ions were due to the targeted analytes and were not due to either interferences or spurious noise signals. These were the following:

- single-to-noise ratio greater than 3 to 1
- the presence of the confirmation ion such that the relative intensity of the quantitation ion and the confirmation ion was within the limits specified in the Method.

Signal responses that did not meet these criteria are reported as "ND" (not detected). Quantitation was usually performed against $^{13}C_{12}$-2,3,7,8-TCDD as the internal standard, and values were corrected for the recovery using this compound as an isotopic diluent. However, due to the extremely high levels of hexa-, hepta-, or octa-CDD's/CDF's present in some samples, these analytes were quantitated against $^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-OCDD added to the extracts after dilution. It is a disadvantage of the quantitation method that multiple GC/MS analyses are therefore required for samples containing both low and high analyte concentration level. To spike the sample with the appropriate $^{13}C_{12}$-standard at the levels found would have caused an unnecessarily large expense. Whenever possible, sample re-run requirements were imposed to lessen the need for quantitation by anything other than the isotopic diluent. Several characteristics are evident in the data presented in Table 1. First is the total absence of detectable levels of TCDD in all of the 10 samples and the occurrence of PeCDD in only 3 samples, second is the very high levels of hepta- and octa-CDD present in the PCP process samples.

For purposes of this study, the method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a given matrix containing the target analyte. The data for this study was obtained using all available $^{13}C_{12}$-labeled analytes spiked into seven different sample types at a concentration of twice the estimated MDL of each analyte. This experimental design was used in order to obtain MDL values in each matrix without spiking with unlabeled PCDD's and PCDF's and without changing the integrity of the sample. In order to establish an appropriate spiking level, the MDL was estimated as that concentration at which the response of the appropriate quantitation ion gave a signal/noise ratio of 3 to 1. Statistical considerations required that a minimum of seven replicates of each sample type should be processed through

TABLE 1. ANALYSIS[a] OF PCP PROCESS SAMPLES USING METHOD 8280

PCDD/ PCDF	Sludge B-6d (ppb)	Fuel oil B-7b (ppb)	Sludge B-8b (ppb)	Sludge B-12h (ppb)	Fuel oil A-2g (ppb)	Alcohol fuel oil A-3g (ppb)	Sludge A-4g (ppb)	Soil A-5g (ppb)	Soil A-6.1g (ppb)	Soil A-6.2g (ppb)
TCDD	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	27	ND
HxCDD	2150	2186	ND	ND	2079	762	726	283	730	396
HpCDD	51520[c]	67176[c]	2166[c]	978[c]	38195[c]	17956[c]	59600[c]	12945[c]	24700[c]	12300[c]
OCDD	72300[c]	154000[c]	2670[c]	2550[c]	59100[c]	24500[c]	106000[c]	16500[c]	26300[c]	15000[c]
TCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDF	ND	154	ND	ND	246	ND	ND	ND	61	ND
HxCDF	68	2933	ND	ND	2852	76	1568	65	252	56
HpCDF	343	1342	ND	ND	1913	1118	1948	533	1695	434
OCDF	4100[c]	7500[c]	ND	76	447	741	3200[c]	900[c]	3080[c]	1690[c]
$^{13}C_{12}$-2,3,7,8-TCDD percent recovery	66.8	69.0	64.3	67.8	69.2	60.0	62.9	77.0	75.4	74.8

[a] Mean of duplicates; concentrations shown are for the total of all isomers within a given homologous series.

[b] ND is below the detection limit for the sample matrix. Detection limits are estimated as 5 ppb for the tetra- through hexa-isomers, and 10 ppb for the hepta- and octa-isomers.

[c] Due to the extremely high levels of HpCDD, OCDD, and OCDF detected in the GC/MS analysis, the extracts were diluted after normal quantitation of the tetra-, penta-, hexa-CDD/CDF and hepta-CDF. HpCDD, OCDD, and OCDF were then quantitated versus $^{13}C_{12}$-1,2,3,4-TCDD added after dilution; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.

the entire analytical method. Two initial replicates were tested to verify the reasonableness of the MDL estimate for each sample type. When a reasonable spiking level had been achieved, five more determinations were made at the same spike concentration. The standard deviation (S) of the mean concentration determined for each analyte was then calculated from the seven replicte measurements for each of the seven matrix types. The MDL was then calculated from the equation:

$$\text{MDL} = t_{(n-1,\ 1-\alpha = 0.99)} \times (S)$$

where $t_{(n-1,\ 1-\alpha = 0.99)}$ is the Student's t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom.

Therefore,

$$\text{MDL} = 3.143(S).$$

The concentration (C_s) of each analyte in each sample was determined with reference to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard, which was spiked after sample workup to give a final concentration of 40 pg/μL.

The eight $^{13}C_{12}$-labeled PCDD's and PCDF's used in this study and their MDL's in the seven sample matrices are listed in Table 2. Several characteristics and trends are apparent in the data: $^{13}C_{12}$-2,3,7,8-TCDD/TCDF usually had the lowest MDL values for each sample type while $^{13}C_{12}$-HpCDD/OCDD usually had the highest; as might be expected, the MDL values for all analytes generally increased in passing from the "clean" sample types (reagent water, fly-ash) to the more complex, organics-containing matrices (still-bottom, industrial sludge). The MDL for $^{13}C_{12}$-2,3,7,8-TCDD in reagent water (0.44 ppt) determined in this study using Method 8280 compares well with the value reported for 2,3,7,8-TCDD in reagent water (2 ppt) which was determined using Method 613 (capillary column GC/MS with selected ion monitoring). The MDL procedure, involving seven replicate determinations of each of the eight analytes in each of seven sample matrices, generated other data (percent recovery, precision) which is of interest in assessing the performance of Method 8280. These data are presented in Tables 3 and 4. It can be seen that good recoveries were obtained and that the precision at low spike levels was acceptable.

Phase I of the interlaboratory study was intended to allow participating laboratories an opportunity to become familiar with the requirements of the revised Method 8280. This phase of the study was considered necessary since extensive revisions had been made to the original version of the Method. These included (1) changes in the procedure for the

TABLE 2. METHOD DETECTION LIMITS OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/ Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

[a] Sample size 1,000 mL
[b] Sample size 10 g
[c] Sample size 2 g
[d] Sample size 1 g
Note: The final sample-extract volume was 100 µL for all samples.

TABLE 3. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM FUEL-OIL

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract Spiked	Measured	RSD Percent	Mean Recovery Percent
2,3,7,8-TCDD	40	29.7	8.0	74.3
1,2,3,7,8-PeCDD	80	56.8	11.7	71.0
1,2,3,6,7,8-HxCDD	120	110.7	14.4	92.3
1,2,3,4,6,7,8-HpCDD	150	118.3	21.9	78.9
OCDD	250	232.8	31.7	93.1
2,3,7,8-TCDF	20	12.9	11.9	64.5
1,2,3,7,8-PeCDF	40	27.7	9.2	69.3
1,2,3,4,7,8-HxCDF	80	57.2	11.7	71.5

TABLE 4. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM INDUSTRIAL SLUDGE

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract Spiked	Measured	RSD Percent	Mean Recovery Percent
2,3,7,8-TCDD	40	25.3	10.2	63.3
1,2,3,7,8-PeCDD	80	56.7	16.5	70.9
1,2,3,6,7,8-HxCDD	80	90.6	15.8	113.3
1,2,3,4,6,7,8-HpCDD	120	128.6	16.7	107.2
OCDD$_a$	175	--	16.2	--
1,2,3,7,8-TCDF	20	15.6	14.6	78.0
1,2,3,7,8-PeCDF	40	26.4	14.1	66.0
1,2,3,4,7,8-HxCDF	80	49.5	14.8	61.9

[a] Peak shape was distorted by very high level of interferent.

extracton of analytes from the sample, (2) modification of the open column alumina chromatography cleanup, (3) deletion of the HPLC cleanup, (4) addition of a carbon column cleanup, and (5) incorporation of internal and recovery standards into the Method.

Five laboratories were selected by the Contract Laboratory Program to participate in the study and were each provided with samples, analytical standards, isotopically labeled internal and recovery standard solutions, and the revised Method, also provided were, detailed supplemental instructions which included guidance on the sample size, the volume of the final extract, typical MID descriptors, typical MID and RIC chromatograms, and the reporting requirements for data and deliverables. Each laboratory was provided with the six samples which had been prepared by personnel of the referee Laboratory who also analyzed these samples.

The results obtained by the referee Laboratories' personnel who were familiar with the Method, although not obtained as part of the blind study, were valuable for comparison and are included in the relevant Tables.

A very simple, qualitative measure of how well the combined extraction, chromatographic cleanup, and GM/MS analysis prescribed in the Method deals with the various analytes may be obtained by noting the number of target analytes for which values were reported by each laboratory. As shown in Table 5, at least one laboratory in addition to referee detected all of the analytes, and two laboratories reported 12 of 13. Relatively lower reporting by Laboratories II and IV is presumed to be due to lack of familiarity with the extraction and cleanup procedures and may be expected to improve with experience.

A more quantitative measure of the extraction and cleanup efficiency is provided by monitoring the percent recovery of the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) which was added to the sample immediately prior to extraction. Table 6 shows that three of the participating laboratories, apart from the referee, obtained acceptable results (mean recovery greater than 40 percent). The two other laboratories reported mean recoveries of less than 30 percent.

A summary of results obtained from the sludge samples is described in Table 7 and the results of the study are summarized as follows:

TABLE 5. INTERLABORATORY TEST OF METHOD 8280, PHASE I:
SUMMARY OF ANALYTES REPORTED BY PARTICIPATING LABORATORIES

Sample	Number of Analytes Spiked	Referee Lab	Number of Analytes Reported by Each Laboratory				
			I	II	III	IV	V
Clay Spike No. 1	13	13	13	8	12	11	12
Clay Spike No. 2	13	13	13	8	12	4	12
Sludge Spike No. 1	6	6	6	3	4	6	4
Sludge Spike No. 2	6	6	6	3	4	6	4

TABLE 6. INTERLABORATORY TEST OF METHOD 8280, PHASE I: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-2,3,7,8-TCDD

Sample	Referee Lab	Participating Laboratories					Mean	RSD Percent
		I	II	III	IV	V		
Clay Blank	66.3	34.3	9.1	54	21	67	42.0	57.7
Clay Spike No. 1	62.8	64.3	13.3	53	26	63	47.1	46.7
Clay Spike No. 2	78.9	132	10.2	60	14	58	58.9	76.4
Sludge Blank	88.4	84.5	28.7	57	34	35	54.6	48.6
Sludge Spike No. 1	66.1	79.0	28.4	12	25	32	40.4	64.6
Sludge Spike No. 2	74.0	96.4	32.9	15	36	44	49.7	60.2

TABLE 7.
INTERLABORATORY TEST OF METHOD 8280, PHASE I: QUANTITATION OF ANALYTES IN SPIKED SLUDGE SAMPLES (PPB)

Analyte	Spike Level	Referee Lab	Participating Laboratories					Mean	RSD Percent
			I	II	III	IV	V		
2,3,7,8-TCDD	125.0	132.1	62.2	156.4	270	150	163.2	152.0	39.4
		127.9	48.9	153.2	220	155	184.8		
1,3,7,8-TCDD	125.0	147.3	50.7	204.2	ND	93	177.9	122.2	47.8
		134.5	29.1	185.1	ND	84	116.1		
1,2,7,8-TCDD	125.0	132.2	85.7	181.6	50	180	ND	116.7	50.8
		128.5	38.3	173.5	37	160	ND		
1,2,8,9-TCDD	125.0	136.4	60.9	ND	160	260	805.2[a]	145.8	47.3
		135.6	33.7	ND	140	180	205.6		
1,2,3,4,7-PeCDD	125.0	113.3	67.2	ND	87	110	ND	93.3	34.9
		118.8	42.4	ND	68	140	ND		
1,2,3,7,8-PeCDF	125.0	115.1	48.2	ND	ND	120	170.9	116.6	44.4
		123.4	33.4	ND	ND	150	171.7		

[a] Not included in calculation of mean and standard deviation.
ND = Not detected.

The mean value for 114 determinations of 11 analytes spiked into clay at the 5 ppb level was 6.02 ± 2.78 ppb.

The mean value for 16 determinations of 2 analytes spiked into clay at the 2.5 ppb level was 3.56 ± 2.35 ppb.

The mean value for 57 determinations of 6 analytes spiked into sludge at the 125 ppb level was 126.4 ± 57.9 ppb.

The objective of Phase II of the interlaboratory study was to test the applicability of the Method to the analysis of samples which were much more difficult and complex than those used for Phase I. Significant revisions to the Method were made between completion of Phase I and initiation of Phase II.

These revisions were made to several critical areas, including:

- New multiple ion detection descriptors
- Addition of a carbon column cleanup procedure
- Requirements for sample size and final extract volume
- New analytes to be quantified
- DB-5 column requirements
- Deletion of DFTPP tune requirement
- Sample reanalysis requirements based on recovery criteria for the internal standards.

These revisions were based on the comments/suggestions provided by the participating laboratories at the conclusion of Phase I. The same five laboratories which took part in Phase I also collaborated in Phase II, and each was provided with identical packages of samples, analytical standards and documentation etc., similar to those provided for Phase I. Each laboratory was requested to analyze a total of 10 samples of 4 different sample types. As in Phase I, duplicate samples of each sample type were provided to check accuracy and precision. In addition, a third different sample from each of two sample types was also to be analyzed. The greatest difference between the requirements for Phase I and Phase II was the analytes which were to be quantitated. Whereas Phase I required the determination of certain selected CDD's and CDF's, the Method was tested under Phase II for the quantitation of total tetra- through octa-CDD's and -CDF's. This change as specified in the Method presented some difficulties in view of the use of different MID descriptors at different points along the GC elution profile. It is appreciated that not all of the isomers within a given series may be detected using this procedure. For instance, at least five early-eluting PeCDD isomers will probably overlap the late-eluting TCDD/TCDF isomers. Similar overlap may occur between the penta-, hexa-, and hepta-congener groups. However, the chromatographic windows prescribed were developed within the limitations of the PCDD/PCDF standards available to the referee laboratory during the course of this study. It is expected that, as additional reference standards become available, chromatographic conditions will be refined accordingly.

Data packages from the participating laboratories were audited with an emphasis on Method performance. In those instances where a large difference occurred among the values reported for a particular sample, the raw data were examined to try to determine if the difference was a Laboratory problem or a Method problem. One Laboratory evidenced analytical problems due to errors or not following instructions which affected their results for all of the samples. Only one-fifth the required amount of internal standard was added; this resulted in extremely low internal standard responses and biased quantitation. Because of these problems, the data from this laboratory be excluded from the statistical analysis as not being representative of Method performance. Problems with individual data points were also examined and were traced to a variety of causes. Calculation and data transposition errors were found; other discrepancies were traced to differences in instrument sensitivity, to differences in retention-time windows scanned, and to isomer peaks which met identification criteria in one laboratory and not in others.

As an indication of method performance, recovery data of the internal standards is presented in Tables 8 and 9.

In general, the Method performed well when the laboratories followed the protocol. A visual examination of the data showed that approximately 85 percent of the values reported by the 5 laboratories and used in the statistical analysis were consistent among the laboratories.

TABLE 8. INTERLABORATORY TEST OF METHOD 8280, PHASE II: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-2,3,7,8-TCDD

		Participating Laboratories					All Results		Excluding Lab II Results	
Sample	Referee Laboratory	I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
Fly-Ash*	89.8	103	98.1	59	64	101	85.1	23.5	82.1	25.2
	81.1	98	102	60	56	109				
Soil A	74.4	42.3	53.6	53.6	46	75	57.5	24.3	58.3	26.7
Soil B*	67.2	54.3	50.0	51	42	90	58.8	25.2	59.4	27.1
	62.2	54.3	62	45	46	82				
Sludge A	64.9	77.7	40.6	18	33	74	51.4	47.3	53.5	49.6
Sludge B*	53.8	78.7	40.9	69	72	72	63.4	26.1	67.1	23.1
	41.9	84.1	48.9	51	58	90				
Still-Bottom*	72.6	118	61.9	74	46	104	72.9	35.2	73.5	38.1
	84.8	23	78.3	69	53	90.5				

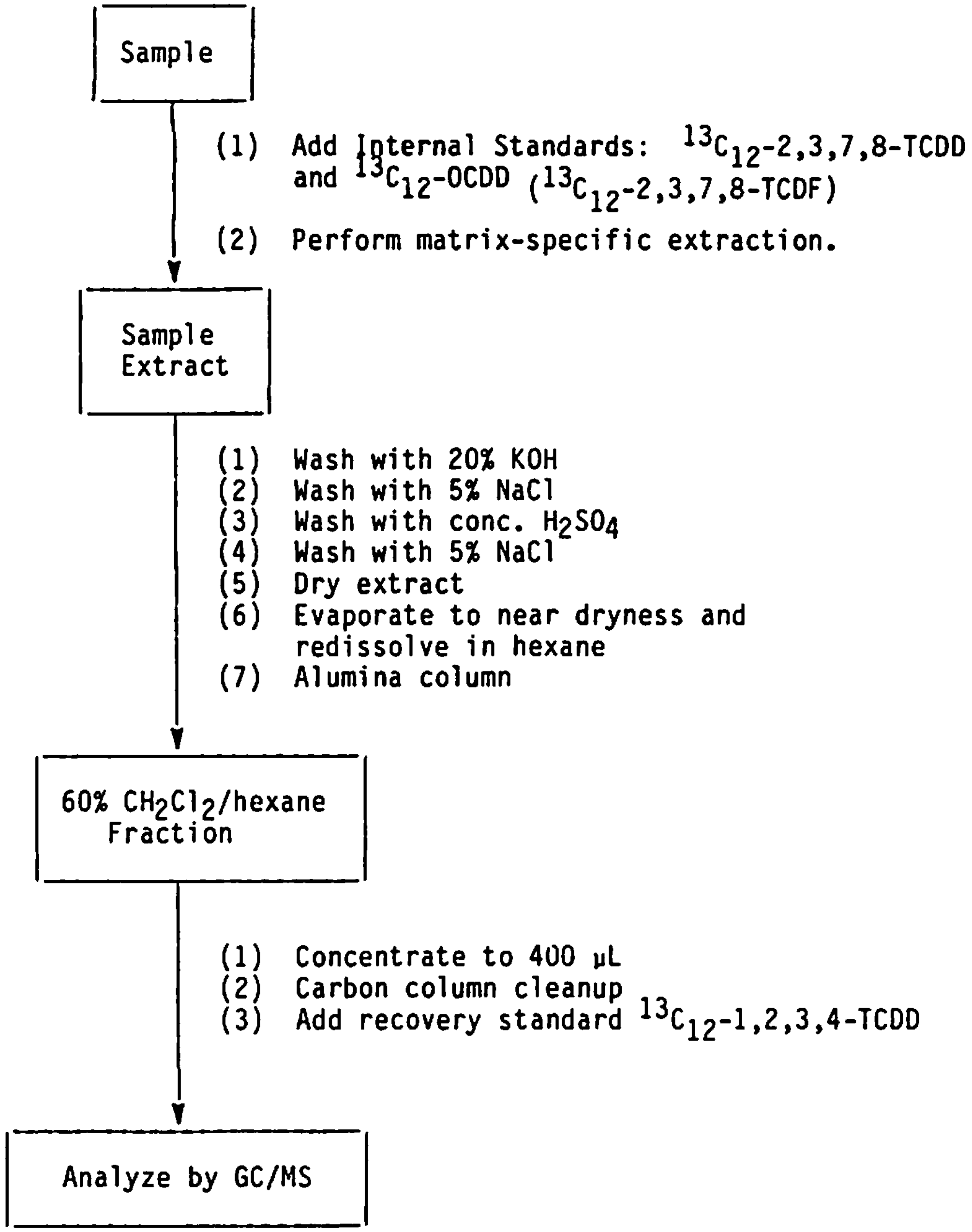
*Blind duplicates.

TABLE 9. INTERLABORATORY TEST OF METHOD 8280, PHASE II: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-OCDD

		Participating Laboratories					All Results		Excluding Lab II Results	
Sample	Referee Laboratory	I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
Fly-Ash*	75.5	98	90	34	64	102	74.0	33.5	74.8	36.7
	78.1	119	50	38	56	83				
Soil A	46.2	53	65	29	43	112	58.0	49.9	56.6	56.8
Soil B*	68.1	87	3.2	14	95	150	63.6	71.6	75.4	53.1
	67.3	67	5.8	29	58	119				
Sludge A	55.5	75	0[a]	37	40	46	50.7	30.2	50.7	30.2
Sludge B*	47.3	145	23	50	75	74	61.0	65.4	68.6	57.8
	39.2	132	24	28	48	47				
Still-Bottom*	96.4	180	0[a]	32	58	55	69.5	71.3	69.5	71.3
	125	30.8	0[a]	33	46	39				

[a] Not included in calculation of mean and standard deviation.

*Blind duplicates.



(1) Add Internal Standards: $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD ($^{13}C_{12}$-2,3,7,8-TCDF)
(2) Perform matrix-specific extraction.

(1) Wash with 20% KOH
(2) Wash with 5% NaCl
(3) Wash with conc. H_2SO_4
(4) Wash with 5% NaCl
(5) Dry extract
(6) Evaporate to near dryness and redissolve in hexane
(7) Alumina column

(1) Concentrate to 400 µL
(2) Carbon column cleanup
(3) Add recovery standard $^{13}C_{12}$-1,2,3,4-TCDD

Method 8280 flow chart for the analysis of PCDD's and PCDF's.

SINGLE-LABORATORY EVALUATION OF METHOD 8080 FOR ORGANOCHLORINE PESTICIDES AND PCB'S

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ABSTRACT

Method 8080 was developed for the determination of certain organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in liquids and solids. Liquid samples are extracted according to Method 3510 (separatory funnel) or Method 3520 (continuous liquid-liquid extractor) and solid samples according to Method 3540 (Soxhlet extraction) or Method 3550 (sonication), the extracts are concentrated, fractionated on Florisil and the fractions analyzed by gas chromatography (GC) on packed columns.

The Method 8080 protocol is being evaluated in a single laboratory on actual and simulated wastes. It was found that the Florisil cleanup method is problematic when both OCPs and PCBs are present; a cleanup and fractionation on deactivated silica gel is more advantageous. Sulfur in extracts can be removed with tetrabutylammonium sulfite. Toxaphene and chlordane pose special problems because of their multiple-peak responses.

The use of capillary columns instead of packed columns in the GC analysis is advantageous because better separations are obtained for complex samples containing combinations of OCPs, PCBs and other organics.

The final evaluation is in progress on liquid and solid waste samples containing OCPs and Aroclor 1016 and 1260 at three levels.

INNOVATIVE TECHNOLOGIES FOR HAZARDOUS WASTE ANALYSIS

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ABSTRACT

The analysis of complex waste matrices represents a challenge for the modern analytical chemist. The need for innovative technologies to address the growing needs of the environmental community, to provide greater sensitivity, specificity and to accomplish the desired goal of cost-effective analysis creates a dilemma. Many analytical chemical goals are mutually exclusive, sensitivity enhancement results in a loss of specificity, cost effectiveness will usually result in the loss of an important analytical parameter such as sensitivity and or selectivity. The use of combined (hyphenated) techniques provides additional analytical vectors which increase the combined techniques power. There are several hyphenated techniques which have been successfully applied to complex wastes analysis. The use of gas chromatography/infrared spectrometry/mass spectrometry (GC/IR/MS) represents one such technique. The ability to use the technique for the non-target analysis of complex wastes has been demonstrated. Data base retrieval of infrared spectra provides functional group information by which a mass spectral data base can be correlated. The use of another innovative technique, liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) also provides a robust organic analytical method. The ability to address the non-volatile, non-chromatographable fractoin of complex wastes represents an emerging Agency concern for which conventional methodologies can not be used to provide regulatory data or to write regulatory criteria. LC/MS/MS represents an on-the-fly technique capable of the ionization of non-volatile residues followed by the mass analysis of the resulting complex parent ions by collisional activation dissociation. The technique has been applied successfullly to dyes and dye effluents from industrial wastewater treatment. The use of reduced cleanup prior to analysis and on-the-fly mixture analysis provides a powerful analytical tool. Although not a hyphenated technique in the conventional sense, the introduction of immunoassay techniques, utilizing both polyclonal and monoclonal assay systems for rapid cost effective target compound analysis for organic compounds, provide a new tool for the chemist. The technique has been demonstrated and found to be equivalent to the more traditional analytical chemistries. These methods will offer rapid cost effective procedures for both screening and quantitation of many RCRA compounds which are highly polar and or non-volatile.

APPENDIX VIII ANALYSIS IN GROUNDWATER

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ABSTRACT

This presentation will focus on developments that have taken place concerning the Appendix VIII monitoring requirement since July 1985.

Appendix VIII to Part 261 of the RCRA regulations is a broad list of chemicals of concern under RCRA. In 1982, EPA promulgated ground-water monitoring regulations that required monitoring of all Appendix VIII constituents. This requirement is impossible to fulfill for reasons which I assume the audience is familiar with.

By the fall of 1985, controversy over this requirement had clearly become a major factor delaying the issurance of RCRA permits. In December 1985, a meeting of EPA and State experts was convened to address the problem. They prepared a list of specific chemicals, derived from Appendix VIII and the Superfund hazardous substances list, to generally replace Appendix VIII for ground-water monitoring.

That list was issued by EPA as guidance in February 1985, and as a regulatory proposal in July 1986. Future work will include the refinement of the present ground-water monitoring list, based on comments on the guidance and the proposal, and on ongoing work at EPA. A second phase effort will identify those chemicals that we really want to monitor, as opposed to those that we are able to monitor. It will produce a list of priority chemicals for a revised ground-water monitoring list, similar to the Clean Water Act priority pollutant list.

COMPARISON OF THE TOX (EPA) AND AOX (DIN) METHODS FOR THE DETERMINATION OF ORGANIC HALOGEN COMPOUNDS IN WATER AND SOLID WASTE

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ABSTRACT

EPA method 9020 and DIN method 38409-H14 are group parameter methods designed to quantify organic halogen compounds (OHC) in aqueous samples. The two methods, which were developed in the U.S. and in West Germany respectively, are based on the same analytical principles and involve the following major steps: adsorption of OHC on granular activated carbon (GAC), displacement of chloride ions on the GAC by nitrate ions, pyrolysis of the carbon and the OHC, and determination of the halide ions formed during combustion. Despite this general similarity, the two methods differ in several instrumental and procedural details, particularly with respect to the determination of purgeable OHC (POX), the handling of samples containing particulate matter, pre-analysis tests, use of a microcolumn or batch technique during the adsorption step, pyrolysis conditions, as well as calibration and quality control procedures. Differences between the methods are described and their implications on analyses of water, waste water and solid waste leachates are discussed.

EVALUATION OF GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) METHOD 8240 AND 8270 FOR APPLICATION TO APPENDIX VIII COMPOUNDS

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ABSTRACT

The Resource Conservation and Recovery Act (RCRA) Appendix VIII list of organic compounds represents a formidable challenge to method standardization. Since the last major Agency multi-analyte method development effort, priority pollutants, increased GC/MS availability and advances in capillary column technology have influenced the approach to method standardization. Notwithstanding the problems of dealing with the matrices involved with the RCRA regulations, the general approach to Appendix VIII method standardization can be contrasted with priority pollutants in the following manner:

(1) With the exception of highly toxic materials such as pesticides, mass spectrometry has clearly become the method of choice.

(2) Fused-silica capillary columns have led to standardized chromatography of semivolatiles, and wide-bore surface coated columns appear to be the solution for purge-and-trap.

(3) The Appendix VIII analyte list drives the development of HPLC/MS, heated purge/trap, and broad spectrum pesticide analyses.

The approach to Appendix VIII is contrasted with that for priorty pollutants. The results to date of efforts at the Enviromental Monitroing and Suport Laboratory - Cincinnati (EMSL-Cincinnati) to standardize generic methods for these analytes and those on the Michigan petition to amend Appendix VIII are presented.

THIRD SESSION

Wednesday, July 16, 1986
1:30 p.m. - 5:00 p.m.

Chairperson:
Gail A. Hansen
Chemist
Office of Solid Wastes
USEPA
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THE RATIONALE FOR FILTRATION OF GROUND WATER SAMPLES

Presented at the National Water Well Association
Ground Water Monitoring Meeting, Columbus, Ohio

Olin C. Braids, Ph.D.

Geraghty & Miller, Inc.
Syosset, New York

The issue of filtration of ground water samples is integral to discussions of proper protocol in ground water sampling. There are those who believe that filtration is essential to the preparation of a water sample in order to get a representative and accurate analysis. There are others who are equally convinced that filtration will deleteriously effect the water sample and lead to difficulties with the data acquired from it.

Each side of this issue has merit because the reasons for the ground-water analysis vary and the objectives in the analytical program also differ. There are legitimate situations in which a ground-water sample should not be filtered before it is analyzed for its chemical constituents in the laboratory and there are circumstances dictating that an accurate analysis is only obtained when filtration is accomplished. This discussion will address the situations in which filtration should be included in sample preparation.

Filtration in this context is filtration through a 0.45 um pore-size membrane. The same principles also apply if the filtration medium is glass fiber or paper. Frequently, practical limitations of time and sample characteristics dictate the use of glass fiber or paper as prefilters before the final membrane step.

In dealing with the subject of filtration, one must address the water-quality parameters that could be affected either by the act of filtration or by the failure to filter. The following characteristics of water are those that would be affected by filtration or the lack thereof.

The partial pressure of dissolved gases in water withdrawn from the aquifer could be affected by the process of filtration. The relationship of oxygen, carbon dioxide, and perhaps other trace gases influences the pH and the oxidation-reduction potential of the water. In cases where the partial pressure of a gas such as carbon dioxide is significantly affected by the added input from decomposition or some other process, the chemical characteristics of water can change when that relationship is disrupted.

The standard protocol of long standing for dissolved metals is to perform a filtration. Any suspended matter occurring in water is likely to have metal ions adsorbed on it. If the water is preserved with acid prior to analysis as the standard protocols call for, the metals are likely to be desorbed from the solids. This would result in dissolved concentrations of metals being higher than originally existed.

Iron is frequently found as a constituent of ground water in concentrations which result in its precipitation when the water is exposed to the oxygen of the atmosphere. Under these conditions the sample of ground water should be filtered as rapidly as possible to prevent contact with the air and to remove any suspended material prior to the addition of acidic preservatives. If the sample contains suspended matter and dissolved iron, addition of the acid prior to filtration may desorb metals from the suspended matter. If the sample is allowed to be in contact with air for even a matter of minutes prior to filtration, the iron may precipitate and co-precipitate or adsorb metals that were in solution. Acidification of the sample at this point may redissolve the iron but may also bring into solution more of the other metals than were in solution at the time the sample was collected.

The presence of suspended matter in water, where the water has been in contact with or is contaminated with very slightly soluble organic compounds poses a problem similar to that of the metals. Slightly soluble compounds such as PCBs, polynuclear aromatic hydrocarbons, phthalate, esters, and many pesticides are in this class. If an unfiltered sample is extracted with organic solvent and analyzed, the compounds will desorb and appear as if they were in solution.

Radioactive gases such as radon could be affected by filtration because of the pressure change across the filtration medium. There are methods as will be discussed later that can eliminate or minimize losses of gases or volatile compounds in water during the filtration procedure.

Many radioisotopes that may be included in ground-water analyses are isotopes of metals that would be associated with the suspended solids in a water sample. The fact that these elements are radioactive does not influence their chemical behavior. Thus acidic preservation of the water prior to filtration would result in their desorption from suspended solids.

Volatile organic compounds may be lost in the process of filtration if the water is exposed to the atmosphere or if the filtration occurs with a pressure change across the membrane caused by a vacuum. Most volatile organic compounds listed in the volatile category of the priority pollutants have low to moderate affinity for the solid substrate. Thus, water samples for the volatile analysis are frequently not filtered because the recovery by purging in the presence of suspended matter can be shown to be quantitative. Filtration of water in this context requires a filter placed in the water discharge line. Less desirably, water may be filtered as soon as possible after collection by another means of filtration. As noted, delaying filtration may complicate the acquisition of reliable data if the water has an appreciable iron concentration.

The issue of filtration of ground water is raised because many times water collected from monitoring wells carries suspended matter as a result of the nature of the sediments or construction of the well. Production wells used for drinking purposes or for other high-volume uses are usually constructed to tap a reasonably prolific aquifer and to produce water with good clarity. In contrast, monitoring wells are sometimes screened in silty or clayey zones and samples may have substantial amounts of fine sediment. The amount of suspended matter is an artifact of the method of water collection and well construction and is not reproducible through time. Any influence the sediment may have on the results of the chemical analysis must be looked on as biasing the sample.

This discussion is based on the premise that the ground water in question is produced from an unconsolidated aquifer or a crystalline rock aquifer. In some locations where solution cavitied aquifers are monitored, the aquifer water may be carrying sediment. In the former cases, the assumption is that sediment is not being carried in suspension.

HYDRIDE GENERATION METHODS FOR DETERMINATION OF ARSENIC AND SELENIUM

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ABSTRACT

Although hydride generation methods have long been used for the analysis of As and Se by AA, very little work has been done on simultaneous hydride generation for the ICP environment. This paper will present an outline of the sample prep and instrumental parameters for the determination of As, Sb and Se by ICP/Hydride. This will be followed by a brief discusssion of some quality assurance measurements which demonstrate the accuracy and precision of the method. It will be shown that the method can be used with CLP type digestates and has great potential for producing reliable data for As, Sb, and Se in waste samples.

INTRODUCTION

Hydride methods have been used with AA for many years for the analysis of As and Se, however, very little work has been done to date using the hydride approach with ICP Emission Spectroscopy. The work in this presentation has been generated using the method outlined in the April, 1982 Analytical Chemistry article by Nygaard and Lowry of the NEIC. This work was done using CLP type extracts to demonstrate the utility of the Hydride/ICP approach for EPA programs.

Sample prep is quite elementary. 5 ml of previously prepared digested sample extract is placed in a Teflon centrifuge tube. 5 ml of concentrated HCI is then added to the sample, the tube is capped and placed in a 95 degree hot water bath for 1/2 hour. This is to reduce Se to the +4 oxidation state. Appropriate standards, blanks, reference standards and QA samples (spikes, dups etc.) are also prepared in an identical fashion.

When cool, the samples are analyzed using the instrumentation described in the article by Nygaard and Lowry. The work in this paper was performed on 14 different days over a six month interval. This was done to demonstrate the day-to-day reliability of the method.

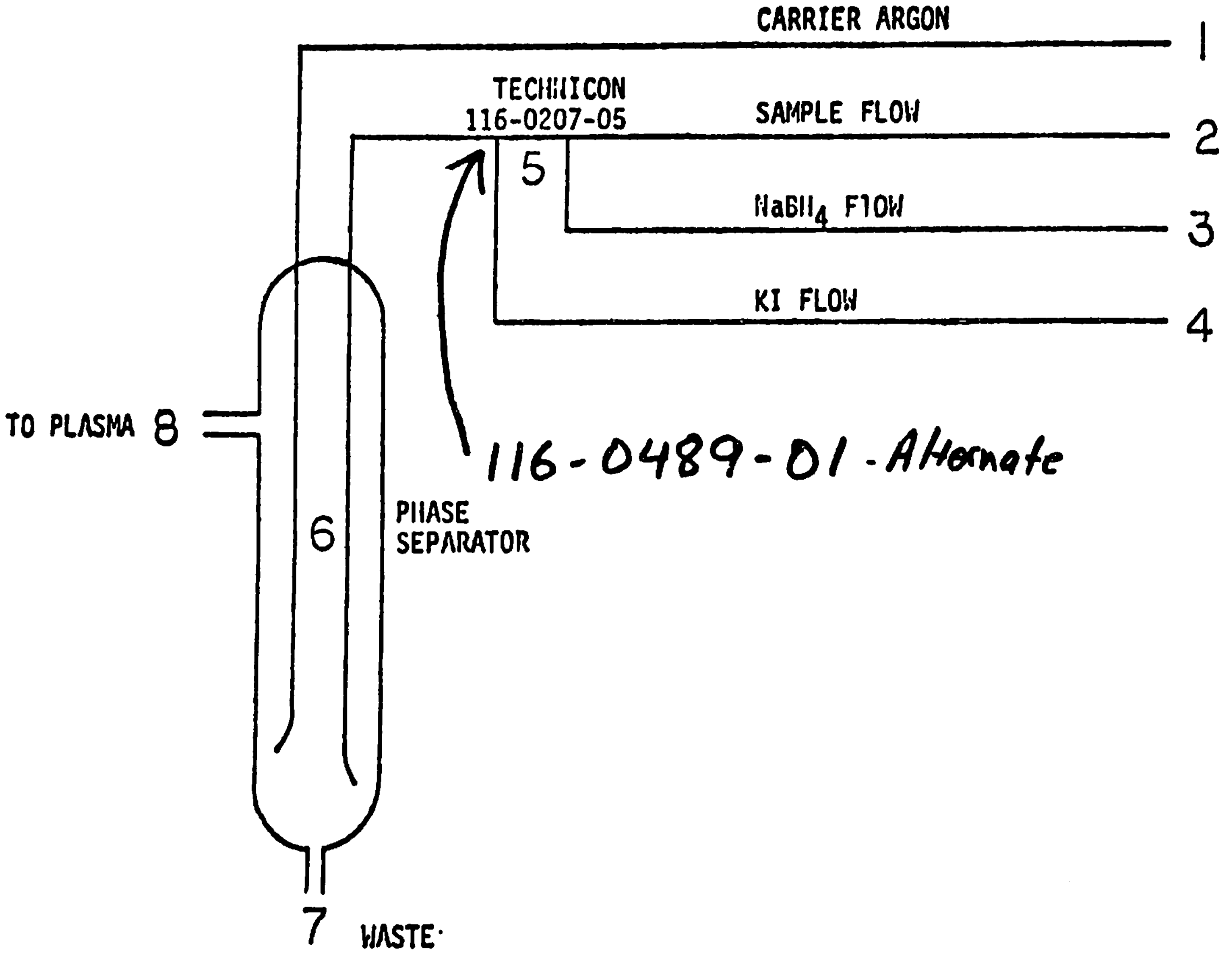
Analyses of EPA reference samples show in general about 5% RSD at the 100 µg/l level for all three parameters. In all cases shown the true value lies within 1SD of the returned average value. Lab-prepared, digested standards show similar behavior. Analysis of low-level standards indicate estimated detection limits of 4-5 ug/l for As and Se and about 7 µg/l for Sb. Estimation of detection limits from the analysis of blank samples show slightly lower values.

To demonstrate accuracy, analyses of spiked aqueous samples were also performed. For samples spiked at 100 µg/l the following recoveries have been determined. For As, a mean recovery of 100.3 µg/l with a standard deviation of 6.4 µg/l was determined on 25 individuals samples. For Se the numbers are 100.0 µg/l recovery, an SD of 4.9 µg/l and 20 individual data points. For Sb, the average recovery was 97.8 µg/l, with an SD of 5.2 µg/l and 19 data points.

Limited work has been done with solid samples to date. Not enough data points exist to show accuracy with solid samples. However, analysis of solid reference materials such as NBS River Sediment and EPA's Municipal Digested Sludge indicate good agreement with bench-mark values established by other labs.

In conclusion it is stated that the ICP/Hydride method outlined here shows good promise of being able to provide accurate and precise As, Sb and Se data for use in EPA programs.

The author would like to acknowledge the assistance in setting up this method which was provided by Ed Bour and Joe Lowry of EPA's NEIC facility in Denver.


CARRIER ARGON
1
TECHNICON
116-0207-05
SAMPLE FLOW
2
5
NaBH4 FLOW
3
KI FLOW
4
TO PLASMA 8
116-0489-01 - Alternate
6
PHASE
SEPARATOR
7
WASTE

All samples run the same way
5 ML SAMPLE + 5 ML CONC HCl
25ml Teflon centrifuge tube
1/2 hour in 95 degree water bath
cool, then run thru apparatus as described used extracts as prepared for solids and waters data collected on 14 different days
April - October

INSTRUMENT CONDITIONS

coolant gas 18 lpm
sample gas 0.8 lpm
RF Forward 1.75 kw
RF Reflected 10 watts
Observation Height 14.5 mm above coil
20 sec exposure, no background correction
As 193.8 nm linear to 5 mg/l
Sb 206.8 nm linear to 800 ug/l
Se 196.0 nm linear to 400 ug/l

REFERENCE VALUES FOR AS

	Ref 481-2	**Ref WS12-2**
True Value	235	48.1
N data pts	14	11
Mean Value	240.7	50.8
Std Dev	8.4	2.1

REFERENCE VALUES FOR SB

	WP8-4
True Value	83.2
N. data pts	12
Mean Value	82.0
Std Dev	4.2

REFERENCE VALUES FOR SE

	R481-2	WS12-2
True Value	50	76.3
N data pts	14	11
Mean Value	51.1	77.1
Std Dev	1.8	3.0

QUALITY ASSURANCE IN THE GROUND WATER MONITORING TASK FORCE FACILITY ASSESSMENT PROGRAM

MICHAEL J. KANGAS, JO ANN DUCHENE, AND TIMOTHY E. TYBURSKI, ICAIR LIFE SYSTEMS, INC., CLEVELAND, OHIO; AND PAUL H. FRIEDMAN, OFFICE OF SOLID WASTE, U.S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, DC

ABSTRACT

The U.S. Environmental Protection Agency (USEPA) Hazardous Waste Ground Water Task Force (HWGWTF) is conducting ground-water sampling at sites where 58 commercial land disposal facilities are located under its Facility Assessment Program to determine whether or not they are contaminating ground water with hazardous wastes. Laboratory analyses of ground-water samples from these sites are being performed for organic compounds, metals and inorganic and indicator parameters. This paper provides an overview of initial quality assurance (QA) activities applied to these analyses.

A Data Evaluation Committee (DEC) consisting of HWGWTF members from USEPA headquarters, regional offices and Office of Research and Development (ORD) laboratories provides QA overview for Facility Assessment Program activities. The DEC developed a Quality Assurance Project Plan (QAPP) specifically for the Facility Assessment Program. The QAPP establishes data quality objectives (DQO) which define the quality of the data desired from the ground-water sampling and analytical efforts. These DQO address data accuracy, precision, representativeness, completeness and comparability. The QAPP also defines roles and responsibilities of HGWWTF members and contractors and procedures to be followed in achieving the DQO.

This paper provides an overview of QA activities performed by the HWGWTF DEC and technical support contractors during evaluation of the first six facilities sampled under the program (Phase I) and provides examples of improvements planned for subsequent QA efforts based on experience gained during Phase I. Evaluation of analytical data and laboratory performance through integration of information from performance evalutation samples, analytical chemistry audits, statistical summaries and control charts of laboratory quality control data generated by Superfund Contract Laboratories is emphasized.

INTRODUCTION

In 1985, the U.S. Environmental Protection Agency (USEPA) Administrator established the Hazardous Waste Ground Water Force (HWGWTF) to evaluate the level of compliance with applicable hazardous waste regulations at 58 existing commercial hazardous waste land disposal facilities.

A Facility Assessment Group (Figure 1-1) was formed within the HWGWTF to evaluate potential ground-water contamination, assess compliance status and take actions necessary to resolve identified problems and areas of noncompliance at the 58 facilities (USEPA 1985a).

This paper focuses on one element of the Group's activities, providing quality assurance (QA) for laboratory analyses of ground-water samples collected under Phase I of the HWGWTF Program.

LABORATORY QUALITY CONTROL FOR PHASE I MONITORING

The Phase I HWGWTF Program involved evaluation of six of the 58 facilities. The remaining 52 facilities will be evaluated during subsequent phases of the Program. Phase I was a "shakedown" effort to identify and correct initial Program problems. Phase I involved analysis of ground-water samples for approximately 150-200 compounds (organic, metal, inorganic and indicator parameters and other tentatively identified compounds). The number of compounds will be expanded in subsequent phases to include more of the compounds listed in Appendix VIII of 40 CFR Part 261.

Phase I laboratory analyses were performed using Invitation For Bid (IFB) Regular Analytical Service protocols for metals, cyanide and organic parameters from USEPA's Contract Laboratory Program (CLP). Protocols specified in supplemental Special Analytical Service (SAS) contracts were used for inorganic and indicator parameter analyses. The list of analytes will be expanded during subsequent phases through use of SAS contracts.

The laboratory quality control (QC) requirments applied during Phase I are summarized in Table 2-1 for metal, inorganic and organic analyses.

PHASE I QUALITY ASSURANCE ACTIVITIES

The general and specific QA/QC requirements which CLP laboratories are required to follow are defined in the Scope of Work of their IFB (EPA 1985 b,c). This section describes the supplemental QA/QC procedures developed and applied by the HWGWTF Data Evaluation Committee (DEC) specifically for evaluation of laboratory performance and quality of data generated under the Facility Assessment Program.

QUALITY ASSURANCE PROJECT PLAN AND HWGWTF DATA EVALUATION COMMITTEE

Current USEPA policy requires that every monitoring and measurement project have a written and approved QA Project Plan (USEPA 1983). A QA Project Plan addresses 16 required elements (Table 3-1). The HWGWTF DEC is primarily respon-

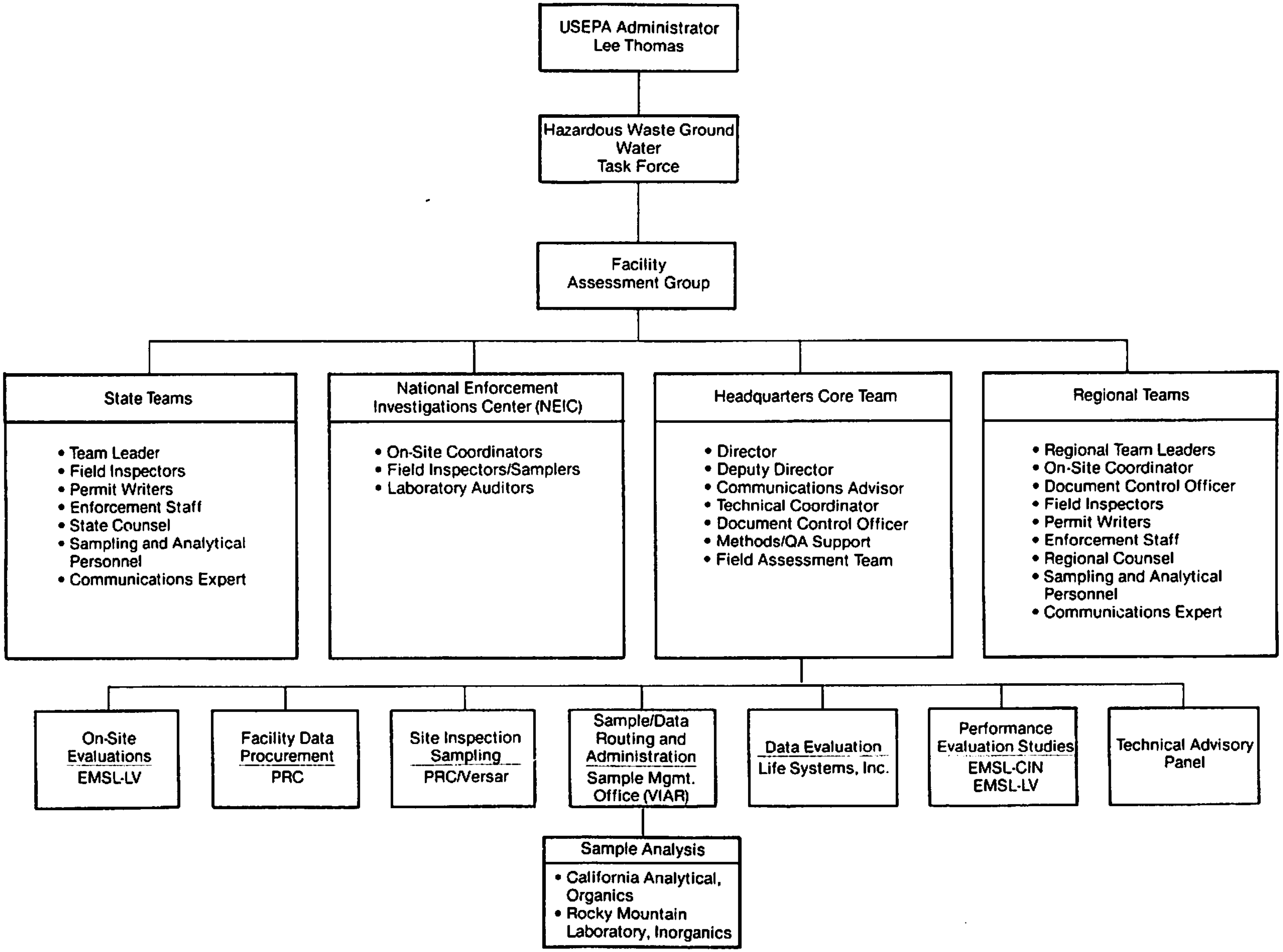


FIGURE 1-1 PHASE I HAZARDOUS WASTE GROUND WATER TASK FORCE FACILITY ASSESSMENT GROUP ORGANIZATIONAL AND FUNCTIONAL RELATIONSHIPS

TABLE 2-1 MAJOR CLP QUALITY CONTROL ELEMENTS FOR ANALYSIS OF METAL, INORGANIC AND ORGANIC PARAMETERS

Parameter Type	Quality Control Element
Metal and Inorganics	● Initial Calibration and Calibration Verification
	● Continuing Calibration Verification
	● Preparation Blank Analysis
	● Interference Check Sample Analysis
	● Matrix Spike Analysis
	● Duplicate Sample Analysis
	● Furnace Atomic Absorption (AA) Quality Control (QC) Analysis for Metals (Method of Standard Additions required under certain conditions)
	● Laboratory QC Sample Analysis
Organic	● Documentation of Gas Chromatography/Mass Spectrometry (GC/MS) Mass Calibration and Abundance Pattern
	● Documentation of GC/MS Response Factor Stability
	● Internal Standard Response and Retention Time Monitoring
	● Reagent Blank Analysis
	● Surrogate Spike Response Monitoring
	● Matrix Spike and Matrix Spike Duplicate Analysis
	● Specific Quality Assurance (QA)/QC for Pesticide Analysis

TABLE 3-1 REQUIRED ELEMENTS OF A QA PROJECT PLAN(a)

Title Page with provisions for approval signatures

Table of Contents

Project Description

Project Organization and Responsibility

QA Objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability

Sampling Procedures

Sampling Custody

Calibration Procedures and Frequency

Analytical Procedures

Data Reduction, Validation and Reporting

Internal Quality Control Checks and Frequency

Performance and System Audits and Frequency

Preventive Maintenance Procedures and Schedules

Specific Routine Procedures to be used to assess data precision, accuracy and completeness of specific measurement parameters involved

Corrective Action

Quality Assurance Reports to Management

(a) Source: USEPA 1983.

sible for developing and implementing the QA Project Plan for the HWGWTF Facility Assessment Program. Members of the DEC include representatives from USEPA Headquarters, the Office of Research and Development (ORD) Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV), the ORD Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-CIN) and a representative from each USEPA regional office. Several contractors provide support and participate in DEC activities. Major QA activities of the DEC are highlighted in the following sections.

ANALYSIS OF PERFORMANCE EVALUATION SAMPLES

Performance Evaluation (PE) samples produced and distributed by EMSL-CIN were analyzed along with field samples and blanks from each Phase I site. Results of PE sample analyses from the CLP laboratories supporting the Phase I effort were evaluated by EMSL-CIN against results from two referee laboratories and EMSL-LV. A report summarizing CLP laboratory performance was prepared and distributed to DEC members and support contractors.

LABORATORY QUALITY CONTROL EVALUATION

The DEC received three separate analyses of evaluating laboratory QC performance:

- A data audit performed by EMSL-LV.
- A Contract Compliance Screen performed by the USEPA CLP Sample Management Office (SMO)
- A contractor-prepared analysis of laboratory QC data on a case and program basis

The following sections summarize briefly each of these analyses.

THE EMSL-LV DATA AUDIT

The Phase I EMSL-LV data audit focused on evaluation of: (1) identification of organic compounds by GC/MS; (2) inductively coupled plasma, flame AA and furnace AA analyses of metal parameters; and (3) SAS protocols for inorganic and indicator parameters. Results were reported to the DEC verbally during regularly scheduled teleconferences.

THE SMO CONTRACT COMPLIANCE SCREEN

The SMO routinely assesses deliverable completeness and technical compliance with contract requirements to facilitate determination of payment recommendations and to identify problems in laboratory compliance. Copies of screening worksheets and summary forms are sent to each laboratory screened to resolve identified problems.

Copies of the worksheets, summary forms and additional laboratory submittals were also distributed to the EMSL-LV and the HWGWTF support contractor responsible for laboratory QC data analysis.

CASE AND PROGRAM LABORATORY QC DATA ANALYSIS

Following guidance provided in the QA Project Plan, the HWGWTF support contractor (ICAIR, Life Systems, Inc.) prepared an analysis of laboratory QC data generated for each facility/site (case) evaluted and a summary of accuracy and precision performance for all analyses performed under the Phase I Program. Performance was analyzed relative to Data Quality Objectives (DQO) for:

- Accuracy
- Precision
- Representativeness
- Completeness
- Comparability

The Program DQO were established and documented in the QA Project Plan before Phase I sampling was initiated. Program DQO are expressed as limits (average values) defining acceptable levels of performance on a case and program basis. Control limtis established from historical CLP data generally served as DQO for this program.

Tables 3-2 through 3-6 summarize Phase I DQO for accuracy and precision. Evaluation of case and Program accuracy, precision and completeness illustrate use of DQO.

ACCURACY PERFORMANCE

Accuracy of analytic methods is expressed as percent recovery of spiked compounds, both analytes (inorganic, indicator and organic parameters) and surrogates (organic analyses only) and known analyte concentrations in laboratory control samples (LCS) (inorganic and indicator parameters only). Percent recovery (%R) is determined as follows:

$$(\%R)\ \text{Recovery} = \frac{\text{Observed Concentration}}{\text{True Concentration}} \times 100 \quad (1)$$

Accuracy is evaluted in terms of program DQO (Tables 3-2 and 3-3) and actual performance. The actual accuracy achieved by laboratory analyses is summarized quantitatively as an average %R ± standard deviation and displayed in tabular form for each case (site) and graphically for the Program (Figure 3-1).

TABLE 3-2 ACCURACY GOALS FOR ORGANIC SURROGATES AND MATRIX SPIKE RECOVERY IN WATER SAMPLES(a)

Fraction	Compound	Average Recovery, %
VOA(b)	Toluene D8(c)	88-110
VOA	4-Bromofluorobenzene (BFB)(c)	86-115
VOA	1,2-Dichloroethane D4(c)	76-114
VOA	1,1-Dichloroethene	61-145
VOA	Trichloroethene	71-120
VOA	Chlorobenzene	75-130
VOA	Toluene	76-125
VOA	Benzene	76-127
BN(d)	Nitrobenzene D5(c)	35-114
BN	2-Fluorobiphenyl(c)	43-116
BN	Terphenyl D14(c)	33-141
BN	1,2,4-Trichlorobenzene	39-98
BN	Acenaphthene	46-118
BN	2,4-Dinitrotoluene	24-96
BN	Di-n-butylphthalate	11-117
BN	Pyrene	26-127
BN	N-Nitroso-di-n-propylamine	41-116
BN	1,4-Dichlorobenzene	36-97
Acid	Phenol D5(c)	10-94
Acid	2-Fluorophenol(c)	21-100
Acid	2,4,6-Tribromophenol(c)	10-123
Acid	Pentachlorophenol	9-103
Acid	Phenol	12-89
Acid	2-Chlorophenol	27-123
Acid	4-Chloro-3-methylphenol	23-97
Acid	4-Nitrophenol	10-80
Pest.(e)	Dibutylchlorendate(c)	24-154
Pest.	Lindane	56-123
Pest.	Heptachlor	40-131
Pest.	Aldrin	40-120
Pest.	Dieldrin	52-126
Pest.	Endrin	56-121
Pest.	4,4'-DDT	38-127

(a) Source: ICAIR, Life Systems 1985.
(b) Volatile organics.
(c) Surrogate compound.
(d) Base/neutrals.
(e) Pesticides.

TABLE 3-3 ACCURACY GOALS FOR INORGANIC AND INDICATOR ANALYSES[a]

Method or Parameter	Average Recovery, %
Atomic Absorption method	90-110
Inductively Coupled Plasma method	90-110
Mercury by Cold Vapor	90-110
Cyanide	90-110
Sulfate	80-120
Total Organic Halide (TOX)	80-120
Purgeable Organic Halide (POX)	80-120
Total Organic Carbon (TOC)	80-120
Purgeable Organic Carbon (POC)	80-120
Chloride	90-110
Nitrate	90-110
Ammonia Nitrogen	90-110
Total Phenol	80-120

(a) Source: ICAIR, Life Systems 1985.

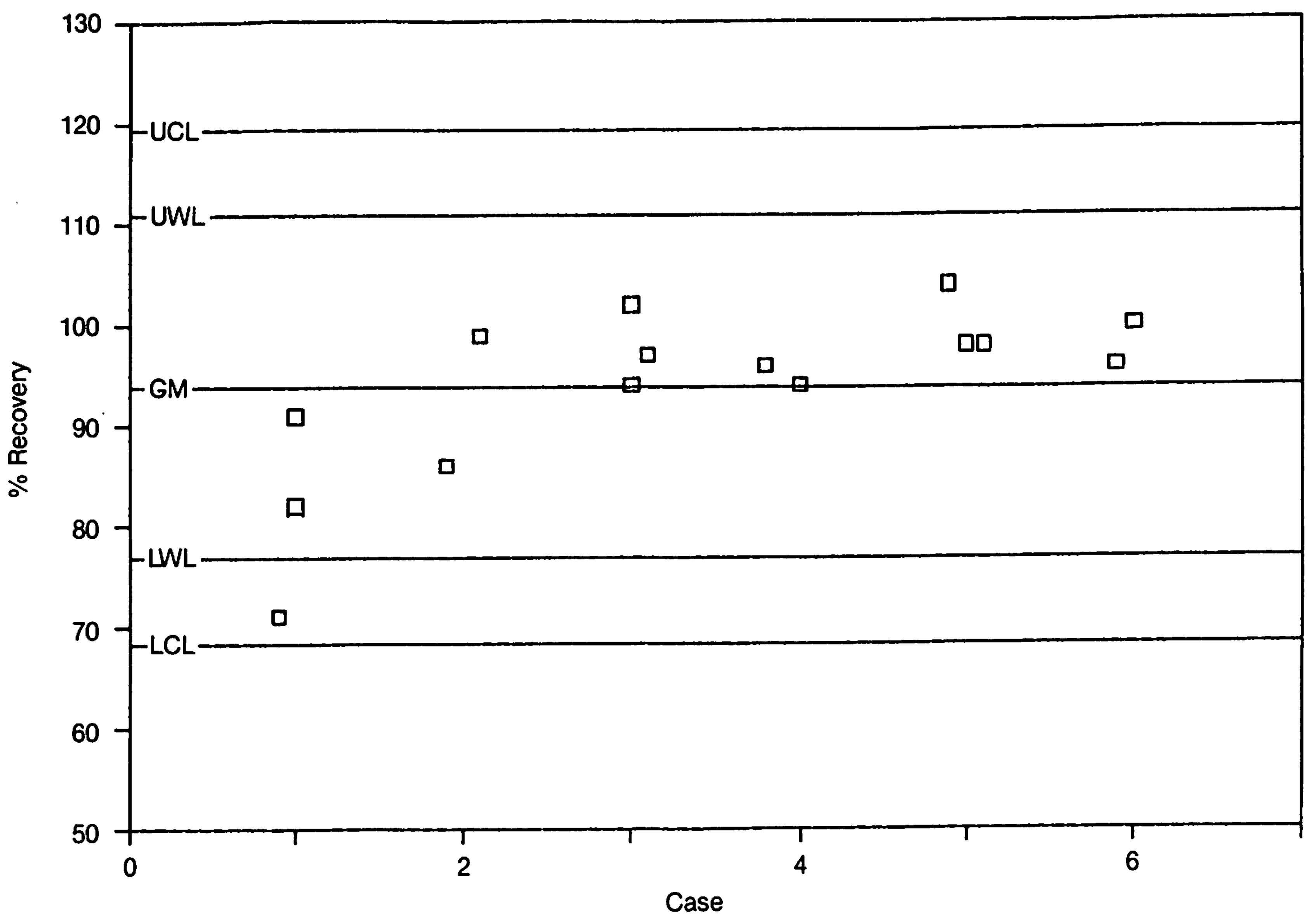


FIGURE 3-1 ACCURACY CONTROL CHART FOR TOTAL COBALT

PRECISION PERFORMANCE

Precision of analytic methods is evaluated using results of duplicate analyses to calculate the relative percent difference (RPD) for each duplicate pair:

$$\mathrm{RPD} = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \qquad (2)$$

where:

RPD = Relative Percent Difference

D_1 = First Duplicate Concentration

D_2 = Second Duplicate Concentration

Percent recovery is used in place of the duplicate concentration to calculate RPD for matrix spike and surrogate spike compounds. The RPD provides a quantitative estimate of precision which can be evaluated against CLP control limits, where applicable, and Task Force DQO (Tables 3-4, 3-5 and 3-6). Performance is summarized in tabular form for the case and graphically for the Program (Figure 3-2).

COMPLETENESS PERFORMANCE

Completeness is evaluated in terms of the total number of samples taken (from sample traffic reports) and the number of acceptable analyses performed (from laboratory QC reports). The number of acceptable analyses completed divided by the number of samples taken times 100 is an index of completeness. The DQO for data completeness based on percent analyses completed is 90% for this program.

For each facility sampled during Phase I, a laboratory QC Data Evaluation Report summarizing accuracy, precision and completeness performance was prepared and distributed to the DEC. Each report also provided:

- An analysis of laboratory control sample performance
- A summary of reported laboratory blank contamination
- An analysis of reported versus contract require detection limits
- A tabular summary of compounds and concentrations found in field, PE and blank samples
- Control charts summarizing program accuracy and precision performance to date for all parameters analyzed (Figures 3-1 and 3-2)

TABLE 3-4 PROGRAM PRECISION GOALS FOR MATRIX SPIKE/MATRIX SPIKE DUPLICATE ANALYSES(a)

Fraction	Compound	Average RPD(b) Limit, %
VOA(c)	1,1-Dichloroethene	14
VOA	Trichloroethene	14
VOA	Chlorobenzene	13
VOA	Toluene	13
VOA	Benzene	11
B/N(d)	1,2,4-Trichlorobenzene	28
B/N	Acenaphthene	31
B/N	2,4-Dinitrotoluene	38
B/N	Di-n-Butylphthalate	40
B/N	Pyrene	31
B/N	N-Nitroso-di-n-propylamine	38
B/N	1,4-Dichlorobenzene	28
Acid	Pentachlorophenol	50
Acid	Phenol	42
Acid	2-Chlorophenol	40
Acid	4-Chloro-3-methylphenol	42
Acid	4-Nitrophenol	50
Pest.(e)	Lindane	15
Pest.	Heptachlor	20
Pest.	Aldrin	22
Pest.	Dieldrin	18
Pest.	Endrin	21
Pest.	4-4'DDT	27

(a) Source: ICAIR, Life Systems 1985.
(b) Relative percent difference.
(c) Volatile organics.
(d) Base/neutrals.
(e) Pesticides.

TABLE 3-5 PROGRAM GOALS FOR PRECISION BY SURROGATE COMPOUND FRACTION(a)

Fraction	Average RPD(b) Limit, %
Volatile Organics	15
Base/Neutrals	50
Acids	40
Pesticides	30

(a) Source: ICAIR, Life Systems 1985.
(b) Relative percent difference.

TABLE 3-6 PROGRAM PRECISION GOALS FOR INORGANIC AND INDICATOR ANALYSES[a]

Method or Parameter	Average RPD[b] Limit, %
Atomic Adsorption method	30
Inductively Coupled Plasma method	30
Mercury by Cold Vapor	30
Cyanide	20
Sulfate	20
Total Organic Halide (TOX)	20
Purgeable Organic Halide (POX)	20
Total Organic Carbon (TOC)	10
Purgeable Organic Carbon (POC)	10
Chloride	10
Nitrate	40
Ammonia Nitrogen	10
Total Phenol	20

(a) Source: ICAIR, Life Systems 1985.
(b) Relative percent difference.

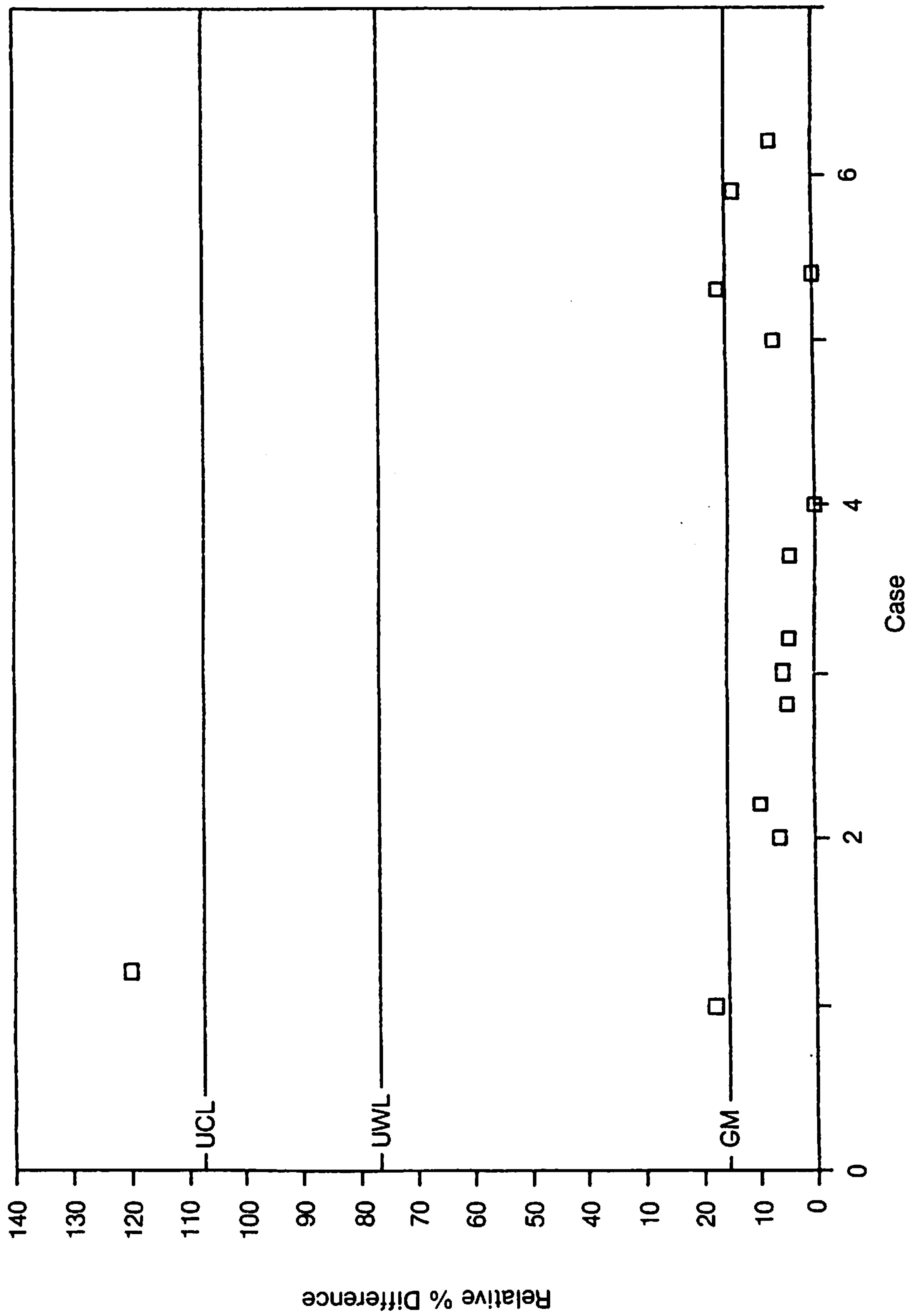


FIGURE 3-2 PRECISION CONTROL CHART FOR ENDRIN

Upon receipt of all reports for a case, the DEC conducted a teleconference to discuss their findings.

THE DEC TELECONFERENCE AND REPORT TO DATA USER

The DEC conducted a teleconference for each case to:

- Discuss laboratory performance and data quality
- Develop consensus regarding data useability for the case
- Develop recommendations for ways to improve laboratory performance and data quality in subsequent cases

Upon completion of the DEC teleconference, the DEC prepared and distributed a report to the appropriate data user (the USEPA National Enforcement Investigation Center or Regional Office) summarizing limitations of and appropriate use for laboratory data in required technical site evaluations.

FEEDBACK TO CLP LABORATORIES

Feedback to laboratories regarding problems and potential improvements resulting from Phase I activities included:

- Discussions between the SMO and the laboratory regarding reconciliation of problems identified through contract compliance screening

- Communications between the DEC and SMO, and subsequently between the SMO and the laboratory, regarding deficiencies identified during the DEC teleconference

- Direct communication between the EMSL-LV and the laboratory regarding technical problems and issues identified during the teleconference

Additional changes in IFB protocols and requirements resulting from Phase I QA activities are discussed in sections below.

EVALUATION OF THE PHASE I EFFORT

Following completion of Phase I sampling and analysis, the DEC met with all Phase I participants to discuss results of QA activities and to develop recommendations for implementation during subsequent phases of the program. This group concluded that the Phase I QA effort was generally a success, but reached specific conclusions regarding desired areas of improvement. Examples of the conclusions reached during the meeting included:

1. Analysis of PE sample results indicated consistent performance by laboratories among cases. Because of this consistency and the high cost of preparing, distributing, analyzing and evaluating PE samples, the Phase I PE analysis frequency (every case) was considered excessive.
2. Phase I PE samples were not prepared to match matrix constituents found at each site. Therefore, results of analysis of PE samples by participating laboratories were not considered representative of performance achieved in analysis of actual field samples.
3. Laboratory spike and duplication analyses were assigned by the laboratory during Phase I with no input from HWGWTF personnel familiar with the samples of greatest interest (those most likely contaminated) in each case.
4. Laboratory reported detection limits reported did not represent method detection limits.
5. Laboratory calculations for spike recoveries and duplicates were not routinely checked for arithmetic errors.
6. Retention factors used by the laboratories were not routinely monitored as part of laboratory performance evaluation.
7. The Laboratory QC Data Report format used during Phase I did not follow the order of discussion during the DEC teleconference.

IMPROVED QA FOR SUBSEQUENT PHASES

Recommendations for improvements developed during the DEC Phase I evaluation meeting generally paralleled specific conclusions regarding weaknesses in initial QA procedures. Examples of improvements include:

1. Reduction in the frequency of PE sample analysis and evaluation. Laboratories will be required to analyze PE samples at the beginning of their contract only, instead of one with each set of samples from a site.
2. Spike and duplicate analyses will be performed on samples from wells suspected of being contaminated. Laboratories will perform spike and duplicate analyses of samples selected by the HWGWTF personnel reviewing site background information instead of selecting these analyses according to in-house procedures.

3. At least one DEC representative will be included in routine on-site evaluations conducted at laboratories supporting the HWGWTF Facility Assessment Program.

4. Expand the QA evaluation process to include field measurements of pH and conductivity.

REFERENCES

ICAIR, Life Systems, Inc. 1985. Hazardous Waste Ground Water Task Force Facility Assessment Program Quality Assurance Project Plan. ICAIR, Life Systems, Inc. Project No. 211393 (PRC Engineering Project No. 277). Life Systems, Inc. September, 1985, Cleveland, OH.

ICAIR, Life Systems, Inc. 1986. Laboratory Quality Control Data Evaluation Report for GSX Services of South Carolina, Inc. Facility, Pinewood, South Carolina. ICAIR, Life Systems, Inc., Project No. 211393 (PRC Engineering Project No. 277). Life Systems, Inc. January, 1986, Cleveland, OH.

USEPA. 1983. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. U.S. Environmental Protection Agency. USEPA Office of Exploratory Research. February, 1983. Washington, DC.

USEPA. 1985a. Hazardous Waste Ground Water Task Force Facility Assessment Program Plan. U.S. Environmental Protection Agency. USEPA Hazardous Waste Ground Water Task Force. April, 1985. Washington, DC.

USEPA. 1985b. Contract Laboratory Program Statement of Work for Inorganics Analysis, Multi-Media Mutli-Concentration (SOW No. 785). U.S. Environmental Protection Agency. USEPA Contract Laboratory Program. July, 1985. Washington, DC.

USEPA. 1985c. Contract Laboratory Program Statement of Work for Organics Analysis, Muliti-Media-Concentration (Attachment A). U.S. Environmental Protection Agency. USEPA Contract Laboratory Program. July, 1985. Washington, DC.

FIFTH SESSION

Thursday, July 17, 1986
1:30 p.m. - 5:00 p.m.

Chairperson:
Denise Zabinski
Chemist
Offices of Solid Wastes
USEPA
401 "M" Street, S.W.
Washington, D.C. 20460

DEVELOPMENT OF PERFORMANCE EVALUATION SAMPLE SERIES FOR THE GROUNDWATER MONITORING SURVEY AT DUMP SITES

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ABSTRACT

Development of performance evaluation (PE) sample series for the Groundwater Monitoring Survey of Dump Sites - PE samples are developed and provided to U.S. Environmental Protection Agency (USEPA) contract laboratories analyzing ground water monitoring samples collected from hazardous waste sites, using SW-846 methods. The PE sample series for the first six sites consisted of three groups: (1) full-volume organic samples, volatiles and base/neutrals analyzed by the gas chromatograph/mass spectrometer (GC/MS) capillary column technique and direct injection, (2) full-volume trace metal samples analyzed by inductively-coupled plazma (ICP) and atomic absorption (AA) methods and (3) general chemical analyses for minerals, total organic carbon (TOC), total organic halides (TOX), purgeable organic hildes (POX), purgeable organic carbon (POC), phenols, cyanide, etc. Beginning in FY86, dioxins and herbicide PE samples were added to the above three groups. The PE samples are sent to the USEPA contractor field sampling team who incorporates the organic and trace metal full-volume samples into the stream of samples collected at each site, thereby providing double blind PE samples. The general chemical analytes are provided in ampuls and the contract laboratories are instructed to remove an aliquot and dilue to one liter. The results of the PE Program for the first 15 sites will be discussed.

OSWER LABORATORY EVALUATION PROGRAM - A PROGRESS REPORT

FLORENCE M. RICHARDSON, OFFICE OF SOLID WASTE, U.S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, D.C.

ABSTRACT

The Office of Solid Waste and Emergency Response has an ongoing laboratory evaluation program for EPA Regional, State and Contractor Laboratories. The program is voluntary and entails the periodic analysis of performance samples using specified methods to allow laboratories to evaluate their capability to analyze RCRA/CERCLA samples using SW-846 methods.

The program is structured so that it is a self-auditing operation. Samples are periodically sent to the designated laboratory contact along with specific instructions and analytical standards necessary for the analyses. The samples range from very simple aqueous solutions to more complex matrices characteristic of wastes. Participating laboratories receive four sets of samples per year. Results are submitted to EPA for evaluation against referee values.

IMPACTS AND INTERFACE OF CERCLA MONITORING REQUIREMENTS WITH OTHER STAFF AND FEDERAL PROGRAMS

KATHE L. STAUBER, DENNIS M. STAIKEN, PH.D., ROBERT L. FISCHER, PH.D., AND ROBERT R. HIRST, OFFICE OF QUALITY ASSURANCE, NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION TRENTON, NEW JERSEY

ABSTRACT

The New Jersey Department of Environmental Protection is responsible for implementing environmental policy and administering a regulatory structure in accordance with Federal and State statutes. The Department's quality assurance program provides a mechanism which enables the Department to administer programs based on reliable monitoring and anlaytical data. The QA program uses several elements to control QA activities in adminstering the Federal/State NPDES, Safe Drinking Water Act (SDWA), and RCRA programs. These elements include the use of a State Laboratory Certification Program, specialized QA permit requirements, use of QA project plans, and use of laboratory and field audits and perforamnce evaluation (PE) samples.

Implementation of the CERCLA program has required an integration of its unique QA requirements with the other State programs. A conrerstone of the U.S. EPA CERCLA program is use of the Contractor Laboratory Program (CLP). The CLP program requires participating laboratories to use specified CLP procedures which are periodically revised. In addition, CLP labs analyze CLP performance evaluation samples and undergo EPA audits. The analytical and QA deliverables from CLP labs are also unique and require extensive analytical/QA documentation. In addition, CERCLA monitoring requirements require specified procedures/methods for groundwater monitoring, sampling, and analysis, and for soil and air analysis.

The comprehensive nature of the CERCLA program spans multimedia environmental matrices (i.e. groundwater, soil, air, etc.). Consequently, administration of the program often impacts or directly transgresses other programs. As an example, a site may overly an aquifer which requires CERCLA groundwater monitoring. The water table may also supply or impact potable water under the SDWA program. The site may also be or impact a RCRA or ECRA (NJ Environmental Cleanup Responsibility Act) site, and if continuous surface discharge wells are installed, they may need a NPDES permit. These situations commonly occur. Unfortunately, the monitoringf and analytical requirements of each program are different.

The Department QA program had to integrate aspects of the CERCLA program within the context of a NJDEP QA program to avoid undue program fractionation. To accommodate the needs of the CERCLA program, a State analytical services contract was established. This State Contract Laboratory Program interfaces with much of the EPA CLP program with rigid QA requirements (known as Tier I deliverables) when the labs are analyzing CERCLA samples. To avoid statutory contradictions within programs, labs which analyze drinking water samples in connection with a CERCLA case must be a NJDEP-certified drinking water laboratory. Other portions of the State CLP span non-CERCLA analytical tasks for aqueous and nonaqueous matrices, and require a modified QA deliverables package (knows as Tier II). This Tier II data deliverables package was adopted as a NJDEP QA policy which is upgrading the QA procedures in other programs. The information required with Tier II packages includes results of blanks, duplicates, tune performance checks (GC/MS), surrogates, etc. State groundwater discharge permits now require that self-compliance monitoring data be submitted to the Department in the Tier II format. On occasion, laboratories outside the State CLP program may be used by site contractors. In these cases, laboratories are audited and must adhere to the same QA requirements as CLP labs.

Several key issues remain unresolved. There are differences in groundwater sampling requirements between CERCLA and NPDES/NJPDES groundwater monitoring. There are also differences in analytical approaches and methods in evaluating groundwater contamination as it affects CERCLA, RCRA, ECRA, NJPDES, and SDWA programs. The Department QA program will continue to integrate these issues as they affect State programs.

When Congress enacted legislation in 1981 which created the Superfund program for cleanup of hazardous contaminated sites, a new realm of monitoring requirements and analytical methods was also created. The U.S. Environmental Protection Agency was delegated the responsibility for administering the funds for the cleanups, and consequently established the Contract Laboratory Program (CLP) to manage the analytical and quality assurance aspects of the program and to maintain sufficient qualified laboratories on a term contract to handle the analytical workload. The samples to be collected at Superfund sites were determined to contain innumerable contaminants at unknown concentration levels in matrices that were complex and variable in nature. Although methodologies for analysis of inorganic and organic contaminants existed at the time, the methods were either in a proposed form or were not validated completely. The USEPA chose to establish a set of methodologies which were modifications of existing methodologies. The methods were published in the

CLP's Information for Bid (IFB) document as required methods to be used by contract laboratories when providing analytical services to the Agency under the Superfund program. The advent of these methodologies and the ensuing confusion over their application in some states has led to a number of conflicts with other Federal and State regulatory programs. These conflicts often manifest themselves at sites where program jurisdictions overlap. The following discussion includes general comments on conflicts which have arisen in New Jersey.

FUNDAMENTAL DIFFERENCES IN MONITORING REQUIREMENTS

In New Jersey, as in many other states, the state has been delegated primacy for administering regulations governing drinking water, surface and subsurface disposal of municipal and industrial wastes, and maintenance of quality of air and water resources. The Department of Environmental Protection is the agency which regulates these areas in New Jersey. These programs are generally fee-based permitting programs which incorporate routine compliance monitoring requirements designed to eliminate sources of contamination of the State's resources. The monitoring segments of these programs also provide a substantial database for evaluating long-term trends in environmental quality.

Monitoring requirements at Superfund sites differ substantially from the situations described above. The requirements are site-specific, intensive, and necessarily cumbersome to achieve the goals of the program. Analytical data generated at the sites must be beyond reproach in a court of law in order to recover the cost of the cleanup from responsible parties. Since the objective of the program is to clean up sites expeditiously, there is no long-term trend analysis of the site, nor is there any form of compliance monitoring. The data available at the site is generally short-term at best. Therefore, it is crucial that the regulatory agency gather as much data and supporting documentation as possible.

DIFFERENCES IN ANALYTICAL REQUIREMENTS

Most environmental management programs are mandated by Federal regulations and legislative acts, including the Safe Drinking Water Act (40 CFR Part 141), the Clean Water Act (40 CFR Part 136), and the Resource Conservation and Recovery Act (40 CFR Parts 260-265). Consequently, the Federal regulations also mandate specific analytical methodologies and monitoring requirements. Analytical methodologies used to report data to the NJDEP are regulated by the Laboratory Certification Program, which monitors the use of the required analytical procedures. Enforcement of environmental management regulations is often dependent on reliable data derived from sample analysis using the required methods.

The methods employed by CLP laboratories for the Superfund program are integral parts of a contract between the U.S. Environmental Protection Agency and its contractors. Defensibility of the analytical methods is dependent upon compliance with the terms and conditions of the CLP's IFB documents rather than with a Federal or State regulation. Although the actual differences in analytical procedures are often minor, the IFB methods are intended to be used for samples with moderate or high levels of contaminants. An example of this can be found in the level of contamination allowable in IFB method blanks. The IFB methods allow for up to 50 ppb of certain contaminants in the method blanks, while the methods required by 40 CFR Parts 141 and 136 require that NO contamination be present above the method detection limit (MDL). MDL's themselves differ substantially as the IFB's "Contract Required Detection Levels" are suited to moderate or high levels of contamination. The MDL's for drinking water or water/wastewater analysis must be capable of detecting trace quantities of contaminants. In the case of drinking water, the IFB criteria for method blanks and MDL's are significantly above the existing or proposed maximum contaminant levels (MCL's) or health-based criteria. Spiking levels for determining analytical accuracy and precision are set at a level which is too high to be representative of trace contaminant levels (MCL's) or health-based criteria. Spiking levels for determining analytical accuracy and precision are set at a level which is too high to be representative of trace contaminant analysis.

Sample holding times are another notable difference between the IFB methods and regulatory methods. For example, the maximum allowable holding time for purgeable organics as required by NJDEP's Division of Hazardous Site Mitigation is 7 days. This contradicts the holding time for the same samples covered by 40 CFR Parts 136, 141, and 260-265, which is established at 14 days. Analytical results from samples held for more than 7 days are rejected for use under Superfund, but are acceptable for other regulatory programs.

The IFB document specifies the required surrogate and internal standard compounds to be used for each analysis, when applicable. These compounds, in most cases, are different than those required and/or recommended in 40 CFR Parts 136, 141, and 260-265 for similar methodologies. This difference separates the QA/QC measures for the analyses.

Nowhere are the differences in analytical, data handling, and deliverables requirements more evident than in a laboratory that is certified by an agency, such as NJDEP, to report compliance data under the regulations and also provides analytical support for Superfund projects. In a commercial laboratory where economics play a major role in determining the laboratory's analytical specializations, the Superfund program is a source of motivation. The laboratory concentrates its efforts on becoming a "CLP Laboratory," thus dedicating its instruments to analyses of waste samples collected from Superfund sites. Although the effort pays off in several ways, economically as well as technically, the change in methodologies, regardless of how subtle, jeopardizes their legal status as a "certified" laboratory. In situations such as this, clients requesting analytical services for projects not related to Superfund or the CLP often have no choice but to accept and pay for deliverables not required for the data's intended use. In other laboratories, where both sets of requirements are adhered to, the cost of doing so can be prohibitive. This often includes dedication of separate instrumentation, personnel, and other costly resources.

There are conflicts between CERCLA monitoring and other monitoring programs when dealing with the data usage. If a facility applies for a RCRA permit and is regulated as such for several years, a data bank is collected on that site. The level of data deliverables and validation for the site is not intensive due to the historical data collected on the site. If the RCRA site is later regulated as a Superfund site, then the previous data is invalidated for use in site characterization.

ADMINISTRATION AND ENFORCEMENT

Some similarities exist between the CLP and the New Jersey Laboratory Certification Program in the area of administration. Both programs require formal application and submission of a fee (the fee is collected annually by the certification program). The laboratories must then perform acceptably on a set of proficiency evaluation samples. Assuming satisfactory performance on the PE samples, the laboratories then undergo a thorough on-site audit and evaluation of instrumentation, personnel qualifications, quality control, etc.

After contract award (CLP) or issuance of certification, enforcement of the provisions of either program differ. Because of the regulatory nature of the laboratory certification program, laboratories which do not comply with the applicable regulations are subject to fines and suspension or revocation of their certification. Suspension or revocation of certification disqualifies a laboratory from reporting data in connection with SDWA, NPDES/NJPDES, or RCRA until such time as corrective action measures have been implemented. In addition, the Department may audit any of the laboratories' records at any time if it determines that such action is warranted. Any data which is determined to be unacceptable to the Department may be rejected. In contrast, the recourses available to the CLP contract user are generally limited to non-payment for deliverables for a given sample or set of samples. If the USEPA cites a CLP Laboratory for consistent violations of the terms of the IFB, the laboratory may be placed in a "cure program" until performance improves or other terms are achieved.

INTERFACES OR CERCLA WITH OTHER PROGRAMS

Over the past two years, the New Jersey Department of Environmental Protection has attempted to reconcile some of the differences in monitoring and analytical requirements between CERCLA and the major Federally-mandated regulations. The Department initially embarked on the development of a "Uniform Laboratory Standards" document in 1984. The document's intent was to standardize as much of the analytical and quality control processes as possible without leading laboratories out of compliance with the applicable methodologies. The document also standardized sampling equipment cleaning procedures for the Department. By mid-1985, the CLP program had incorporated substantial revisions in the IFB document, making the Uniform Laboratory Standards document somewhat outdated. At the same time, the Department initiated development of a new analytical services contract to replace the contract which was about to expire. The Department seized the opportunity for a second attempt at reconciling some of the differences.

The scope of work in the new analytical services contract (known as X-085) reflected much of this effort while still maintaining differentiation in analytical methods. The contract is divided into four "tasks:"

Task I	Air Analysis
Task II	Aqueous Sample Analysis (SDWA, NJPDES)
Task III	Nonagueous Sample Analysis (RCRA, NJPDES)
Task IV	USEPA CLP Analysis (CERCLA)

The contract scope of work concentrated on applying quality control and data handling requirements from the IFB methods which were beyond those addressed in the regulatory methods and did not conflict with those methods. Examples of this are use of system performance check compounds (SPCC's) and calibration check compounds (CCC's), handling of surrogate and matrix spike data outside of control limits, and definition of deliverables.

The deliverables requirements are probably the most significant extract from the CLP. All laboratories are required to supply deliverables in two formats, called Tier I and Tier II. Tier I deliverables are an adaptation of the CLP deliverables specifications, including methodology summaries, laboratory chronicles, chain of custody documentation, chromatograms, raw data, and tabulation of all results and quality control data. Tier II is an abbreviated version of the CLP deliverables package, which includes only enough information and data to perform a cursory evaluation of the results. This format was developed in order to decrease turnaround times and to accommodate the lesser documentation needs of the SDWA, NJPDES, and RCRA programs.

CONCLUSION

The IFB methodologies and Federally-mandated methodologies for SDWA, NPDES, and RCRA all have merits for their intended uses. The IFB document provides for full documentation of sample results and more stringent quality control for all analyses connected with CERCLA short-term site-specific projects. Their application to moderately and highly contaminated multi-media samples has been executed and reasonably well validated to the USEPA's credit. However, their use for analysis of trace contaminants and for compliance analysis for SDWA, NPDES, and RCRA awaits final resolution.

The Federally-mandated methodologies from 40 CFR Parts 136, 141, and 260-265 have undergone extensive validation studies and are continually supported by additional long-term data generation. The Department's interpretation of the regulations has resulted in promulgation of these methodologies and a certification program to monitor and enforce their use. The Department will continue to seek and implement common procedures, but will do so in cooperation with the U.S. Environmental Protection Agency. The Department supports further method research in hopes of eventually eliminating some of the existing fractionations between the various program analytical requirements.

ANALYSIS OF NON-HOMOGENEOUS MIXTURES

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ABSTRACT

The Office of Quality Assurance (OQA) within the New Jersey Department of Environmental Protection administers a laboratory certification program for the Safe Drinking Water Act and the Clean Water Act (New Jersey Pollutant Discharge Elimination System). All laboratories which report environmental measurement data to the Department in compliance with the Acts must be certified by OQA. In the NJPDES Program, permits are issued to each facility which discharges industrial or municipal waste to sewage collection systems, surface waters, or groundwater. The NJDEP Division of Water Resources writes specific monitoring requirments into each permit and reviews periodic discharge monitoring report submitted by the dischargers. In recent years, many facilities in New Jersey, some of which are also NJPDES facilities, were designated as RCRA facilities. Many additional monitoring requirements were included into the facilities' monitoring requirements, including analyses for contaminants in complex, nonaqueous matrices (i.e. soils, sludges, nonaqueous liquids). The NJPDES program also began to place much emphasis on disposal problems associated with sludge, which also added to the need for validated analytical methods.

Many analytical procedures exist for analysis of contaminants in complex matrices. Some of these methods, such as those published in the USEPA's Test Methods for Evaluation of Solid Waste (SW-846), have been promulgated by the Agency and are required methods for programs like RCRA. Many analytes remain without validated methods while others require methods specific to the matrix under examination (such as sludge). The Department of Environmental Protection seeks to regulate as many nonaqueous analytical procedures as can be validated. It therefore became crucial that a protocol for validating new or modified methods for nonaqueous sample analysis be established to assure reliable monitoring of RCRA and NJPDES facilities.

To accomplish this task, the Office of Quality Assurance, in conjunction with the Division of Water Resources and the Division of Waste Management, has developed a procedure to validate new or modified methods. The process includes research of existing literature, single laboratory assessment of the methods, and interlaboratory studies of method

performance. The goal of these protocols is to provide a mechanism for NJDEP to "approve" methods for use with nonaqueous samples and to enforce the methods to assure the maximum possible comparability of results between laboratories.

INTRODUCTION

The New Jersey Department of Environmental Protection, Office of Quality Assurance has administered a laboratory certification program for the Safe Drinking Water Act and the Clean Water Act (New Jersey Pollutant Discharge Elimination System) for many years. All monitoring data reported to the State for compliance with the various programs administered by the Department must be produced by laboratories certified by the Office of Quality Assurance. As the number of programs in the Department has increased, many additional monitoring requirements and the analysis of more complex samples has been required of these certified laboratories. To accomplish this task the Office of Quality Assurance has increased the number of programs for which laboratories can be certified and the analytical procedures that are required in the analysis of the samples by promulgating such methods as those in the USEPA's "Test Methods for Evaluation of Solid Waste" (SW 846) and the certification of laboratories for RCRA analysis. However, since many programs require the analysis of substances that do not have validated methods or require methods specific to a certain matrix, the Department has developed a procedure to review and validate new or modified methods.

One program manages the disposal of sludge under the New Jersey Sludge Quality Assurance Regulations (SQAR). These regulations require sewage treatment plants to analyze sludge for selected chemical parameters and certain physical properties. After the regulations were promulgated, the Department found that there were no standardized methods for sludge analyses and that the quality of the data submitted could not be interpreted for the ultimate disposal of the sludge. The Department therefore established a Sludge Methods Task Force to evaluate and establish the standard validated methods needed for the analysis of sludge as required by SQAR. This Task Force is composed of individuals chosen from industry, sewage treatment plants, academia, EPA and volunteers from several state agencies. This Task Force developed a general procedure for the adoption of the standardized methodologies. This procedure consists of a review of the literature and a survey of laboratories to find candidate methodologies. The methods are then reviewed by the other members of the Task Force and rewritten into a standard format. After the method is given temporary approval by the committee, the method is circulated to a panel of laboratories for their review and comments. Each comment that is returned to the Task Force is then evaluated; the method is again reviewed and given a final approval for inter and intra-laboratory validation.

The analysis of metals in sludge was the first procedure that was subjected to the validation procedure. Intralaboratory testing evaluated four methods for sample preparation; dry ashing, matrix acid digestion, high pressure decomposition (PARR Bomb) and matrix acid/hydrogen peroxide digestion. Atomic absorption spectroscopy was used for quantitative analysis.

Five replicates of each of two sludge samples were digested using each of the digestion methods. The digestate was then analyzed using a model 360 Perkin-Elmer atomic absorption spectrometer. Matrix acid/hydrogen peroxide digestion and the high pressure decomposition methods yielded higher recoveries and were consistent with each other. Economic and availability considerations made the matrix acid/hydrogen peroxide digestion procedure the method of choice.

The revised method was then subjected to an inter-laboratory study in which fourteen laboratories were given a dried municipal sludge obtained from the EPA. Each laboratory was asked to analyze five replicates and report the results to the Task Force. The results of this study indicated that the data generated was within the EPA established ranges. Therefore, it was concluded that the matrix acid/hydrogen peroxide digestion would be used for the determination of metals in sewage sludge and was recommended for final approval by the Task Force for inclusion into the Regulations Governing Laboratory Certification.

Presently, there are five more methods ready for validation. These are methods for the analysis of pH, total residue, volatile and ash of total residue, oil and grease, and phenols. The Sludge Methods Task Force has designed an interlaboratory study for the validation of these methods. The study will consist of the collection of liquid and solid sludges at two concentrations, (i.e. high and low contamination) homogenizing each batch and delivering to participating laboratories for replicate analysis. A local laboratory will be employed for the homogenization process and for referee analyses. Prior to initiation of the study the laboratories will participate in a symposium where the method and validated procedure will be discussed to assure that all the methods are clearly understood and uniformly applied.

The Sludge Methods Task Force is in the process of preparing a report presenting the progress of the development of these methods. The report discusses the background of the task force and the necessity of uniform methods for sludge analysis. The analytical parameters needed by the NJDEP for sludge regulation are addressed as well as the procedure to develop methods for accurate assessment of these parameters. The methods outlined in the report are "proposed and recommended." The proposed methods are those methods designed by the task force which have not been through interlaboratory validation. The "recommended" methods are those methods which have been fully validated and are recommended to the NJDEP as the preferred methods for these analyses. The Sludge Methods Task Force report will be issued yearly to reflect the progress of the task force and to update proposed methodologies.

The NJDEP requires that all analytical data submitted to DEP within NPDES and SDWA programs be from certified labs. The State Lab Certification Regulations were recently revised to upgrade and extend the coverage of the Lab Certification Program to include RCRA and various State Programs. Provision was made within the new Certification Program to initiate implementation of the recommended sludge methods and to further validate the procedures. Laboratories performing sludge analyses will have to be certified within the Certification Program. The Program certifies by category of analysis:

Category 1 - Drinking Water (SDWA)
Category 2 - Water/Wastewater/Sludge (NJPDES)
Category 3 - Waste Analysis (RCRA, NJPDES, ECRA)

Within each category, a lab is certified by methods (appropriate for subcategories of inorganics, organics, limited chemistry, etc.)

Laboratories conducting sludge analyses will be required to use recommended procedures and submit results to the State with specific data deliverables requirements. This specific QA/QC data will be incorporated into a Quality Assurance data base to establish yearly statistical acceptance parameters for the methods. During this process, we will also initiate establishment of sludge analytical performance evaluation samples to survey the performance of participating laboratories and enforce Department standards. It is envisioned that the scope of analyses will expand as the Sludge Methods Task Force and the Office of Quality Assurance recommend additional methods for incorporation into the regulations.

HAZARDOUS WASTE ANALYSIS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) AND LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS)

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ABSTRACT

The Hazardous Waste Program has evolved over the past 10 years. During this time several additions and changes were made to the regulations which require testing water, leachates, and groundwater for organic toxic constituents. Mass spectrometric methods provided in SW-846 are generally adequate for the determination of gas chromatographable Appendix VIII compounds, however, newer MS techniques can be used to extend the number of analytes and eliminate chromatographic interferences.

Newer MS techniques, such as LC/MS, can be used for determining polar toxic organics in wastes and waste leachates. Specifically, Thermospray/LC/MS offers the ability to determine polar organics with high analysis speed and good sensitivity. Thermospray/LC/MS is best suited for the determination of water soluble, non-volatile compounds which cannot be determined by conventional extraction and gas chromatographic methods. This technique can be used to rapidly screen samples since it produces molecular ions (or adducts) and several fragment ions useful for identification of organic compounds. Sample introduction can be achieved through a sample loop (for rapid screening) or normal reverse-phase liquid chromatography.

Both GC/MS and LC/MS are evaluated for the analysis of real and simulated complex lecahates and waste extracts. A comparison of these methods is presented with respect to the types of compounds determined, sample preparation, estimated detection limits, analysis costs, and applicability of these techniques for routine waste leachate analysis.

INTRODUCTION

The Hazardous Waste Program has evolved over the past 10 years. During this time several additions and changes were made to the regulations which require testing wastes, leachates, and groundwater for organic toxic constituents. Mass spectrometric methods provided in SW-846 are generally adequate for the determination of gas chromatographable Appendix VIII compounds, however, newer MS techniques can be used to extend the number of analytes and eliminate chromatographic interferences.

Recently EPA solicited comment on reducing the number of analytes for groundwater analysis to those amenable to GC/MS.

While several polar Appendix VIII compounds would rarely be encountered in the environment (i.e., aflotoxins, mytomycin, etc.) many environmentally significant compounds are quite polar and not readily accessable via GC/MS. Phenols are one example of large class or compounds which fall into this category.

Newer MS techniques, such as LC/MS, can be used for determining polar toxic organics in wastes and waste leachates. Specifically, Thermospray/LC/MS offers the ability to determine polar organics with high analysis speed and good sensitivity. This technique can be used to rapidly screen samples since it produces molecular ions (or adducts) useful for identification of organic compounds. Sample introduction is achieved through a sample loop (for rapid screening) or normal reverse-phase liquid chromatogrpahy.

EXPERIMENTAL

Chemicals and samples

Authentic standards of phenols used in this study were obtained from Supelco Inc., and used without additional purification. The toxicity leachate extract was provided by ENSECO Laboratory, Cambridge, MA. Information provided by ENSECO with the sample indicated that the sample contained phenols and other low molecular weight organic acids.

Instrumentation

The instrument used for GC/MS was a Finnigan MAT 5100 EF equipped with a 30 m, 0.25 mm id, 0.25um film capillary column. The column liquid phase was DB-1. Samples were injected, using the splitless technique, at 50 deg C. The column was programed to 270 deg at 10 deg/min.

The instrument used for LC/MS was a Finnigan MAT 4600 equipped with a Finnigan Thermospray inlet. All data were obtained in the negative ion mode using a conversion dynode multiplier operated at 5Kv on the conversion dynode. The solvent system used was 30% Methanol in 0.1 N ammonium acetate. The LC column used was an RP 18.

RESULTS AND DISCUSSION

The reconstructed ion chromatogram for the GC/MS results is presented in Figure 1. The major peaks in the chromatogram correspond to cresols and low molecular weight organic acids. Identification was made by comparison of spectra to the 42,000 compound EPA/NIH library. The sample was the acid extract from a TCLP leachate from a hazardous waste sample. The leachate (pH 5 acetate buffer) was extracted with methylene chloride after pH adjustment to 2. The resulting extract

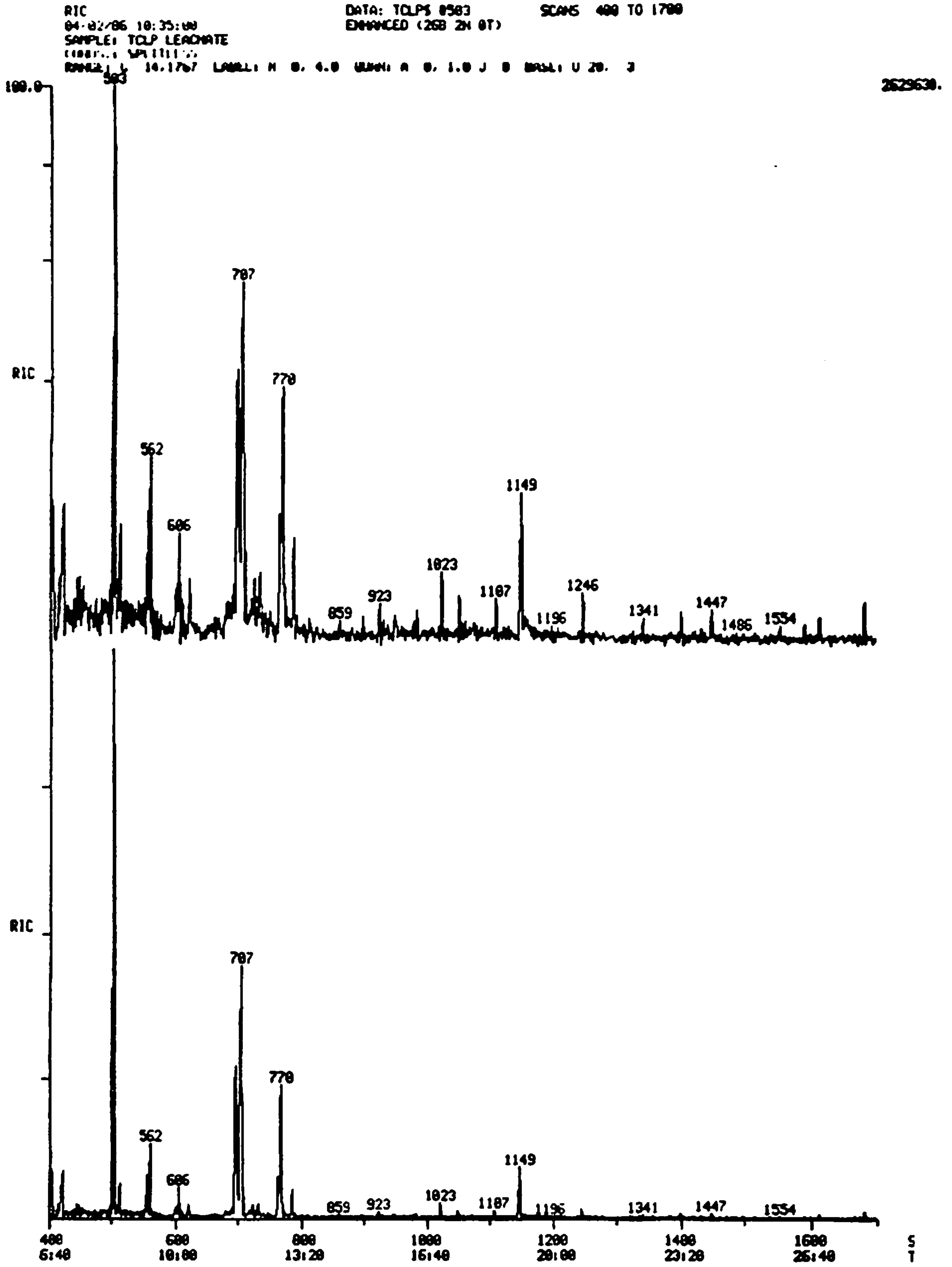


Figure 1: Reconstructed ion chromatogram log and linear scale.

contains a high level of acetic acid. The extract was reduced to 1 ml using a Kuderna Danish concentrator.

The sample contained high levels of phenols (mostly cresols) and low molecular weight organic acids. The high acid concentration did not appreciably effect the gas chromatography on the system used. No other compounds besides cresols and organic acids were identified in this extract. The estimated detection limit for this analysis was 20 ppb based on the injection of 10 ng of DFTPP.

Phenol was not observed in this chromatogram since the solvent and acetic acid interfered with the mass spectra of early eluting peaks (up to about 6 min.) The analysis time was about 35 minutes including data processing time.

The sample was also analyzed via LC/MS (Figure 2). Initially the sample was introduced through the sample loop to determine whether phenols were present. The spectrum obtained indicated that phenols could be present. The spectrum shows that Nitrophenol, Dinitrophenol, and Methyldinitrophenol may be present since ions at the proper molecular weights are present. The sample was then injected onto the LC column and chromatographed. The resulting chromatogram is presented in Figure 3. This figure shows that molecular ions consistent with the three phenols mentioned above elute in chromatographic peaks within about 15 minutes.

The sample was then spiked with a phenol mix which contained 5 ng each of 4-Nitrophenol, 2,4-Dinitrophenol, and 2-methyl-4, 6-Dinitrophenol. The intensity of the single ion chromatograms increased by 163,416, and 466 height units/ng injected respectively for the three compounds (Figure 4). The unspiked sample was therefore estimated to contain 16, 3, and 3 ng of the phenols respectively. (This type of calculation is for estimation purposes only since it amounts to a one point standard addition.) To relate these concentrations to the original sample (500 ml leachate) the actual leachate sample would contain about 6 ppb of 4-Nitrophenol, 1 ppb of 2,4-Dinitrophenol, and 1 ppb of the 2-Methyl-4, 6-Dinitrophenol.

The system was also checked to determine whether there was any carry-over in the sample loop from one sample injection to the next by injecting a blank. The blank (Figure 5) shows some small peaks corresponding to the molecular ions at the correct retention times. The intensity of these ions are quite low. The signal-to-noise ratio for each of these can be estimated from the figure at 4:1, 2:1, and 4:1 respectively with peak heights corresponding to 232, 602, and 201. The estimated amount of material carried over therefore is about 10%.

The results of this preliminary study demonstrate the utility and versatility of Thermospray/LC/MS. While no attempt was

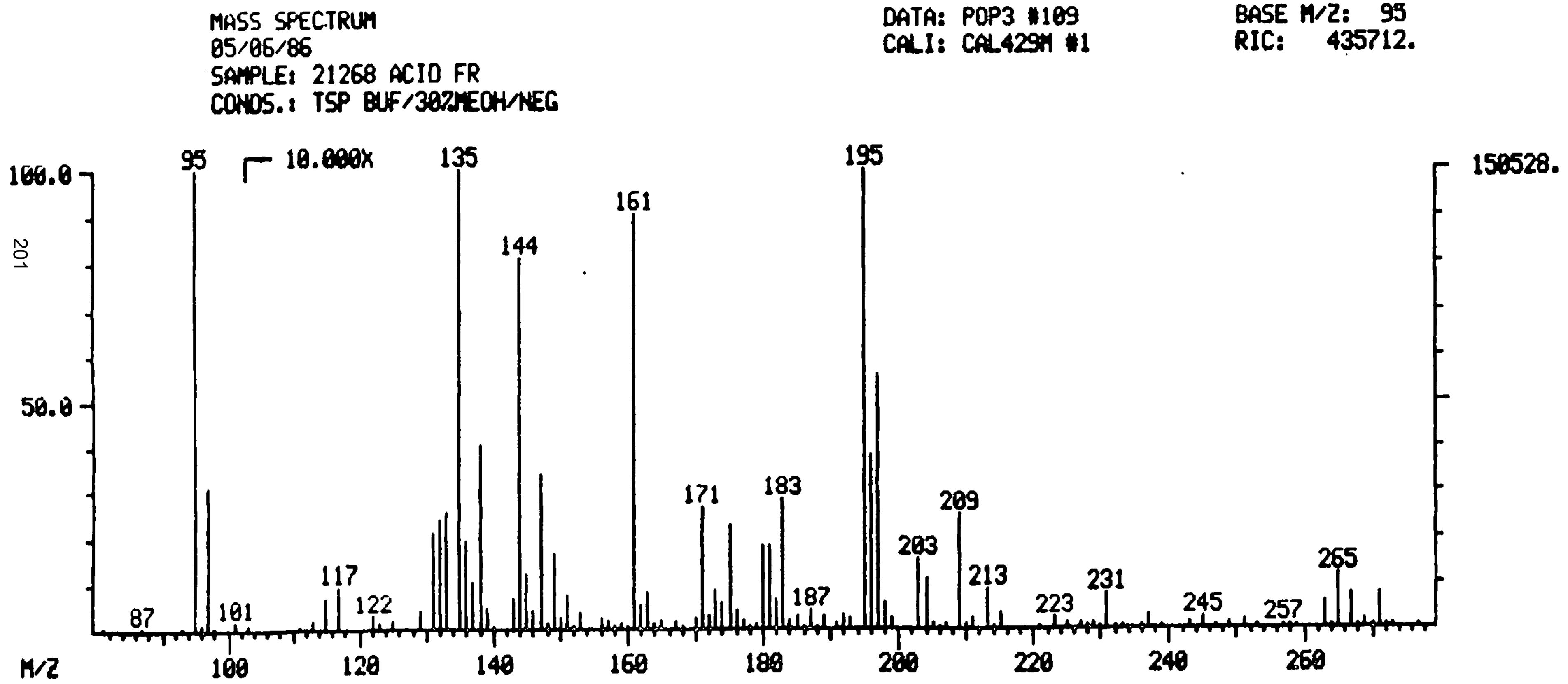
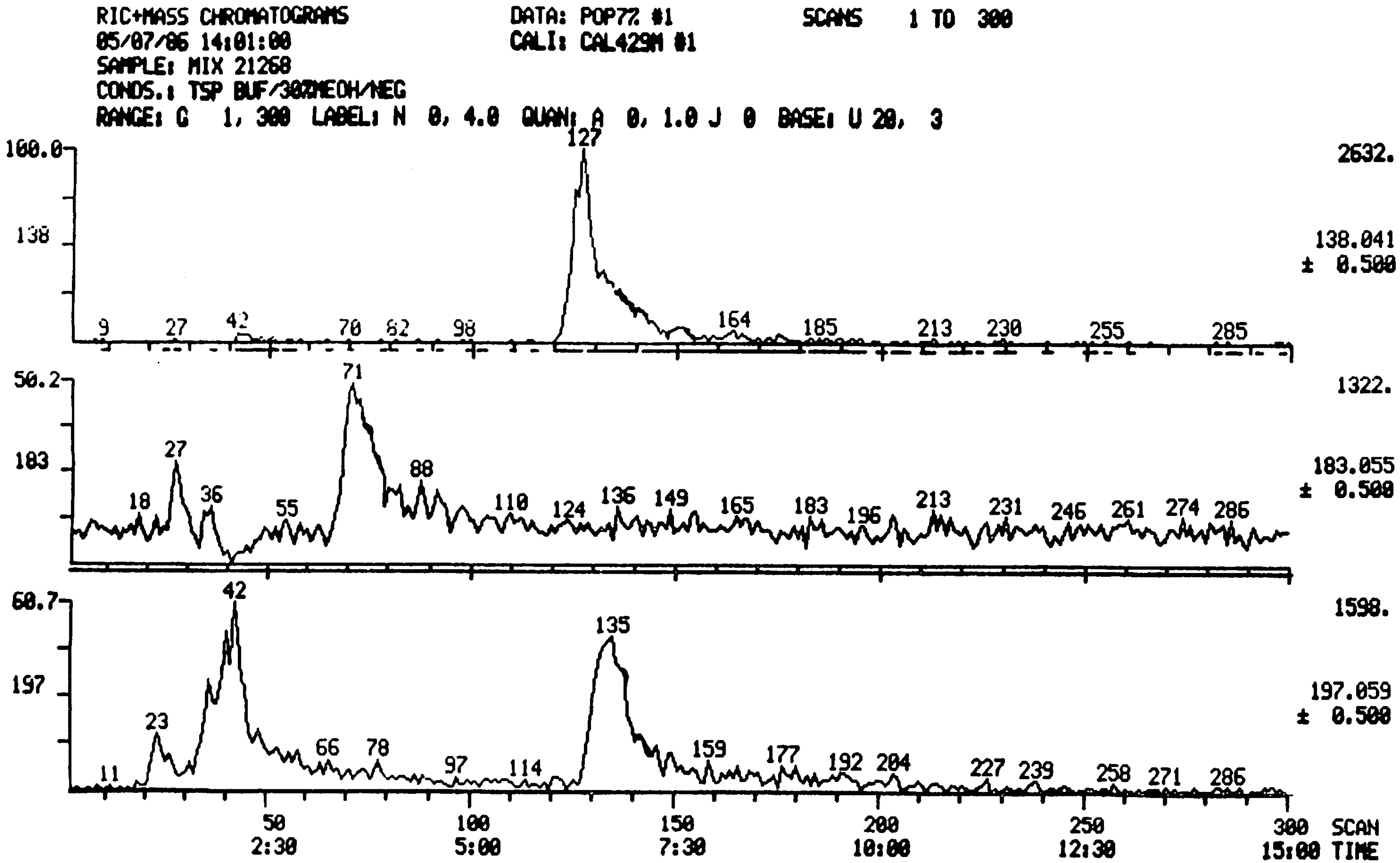
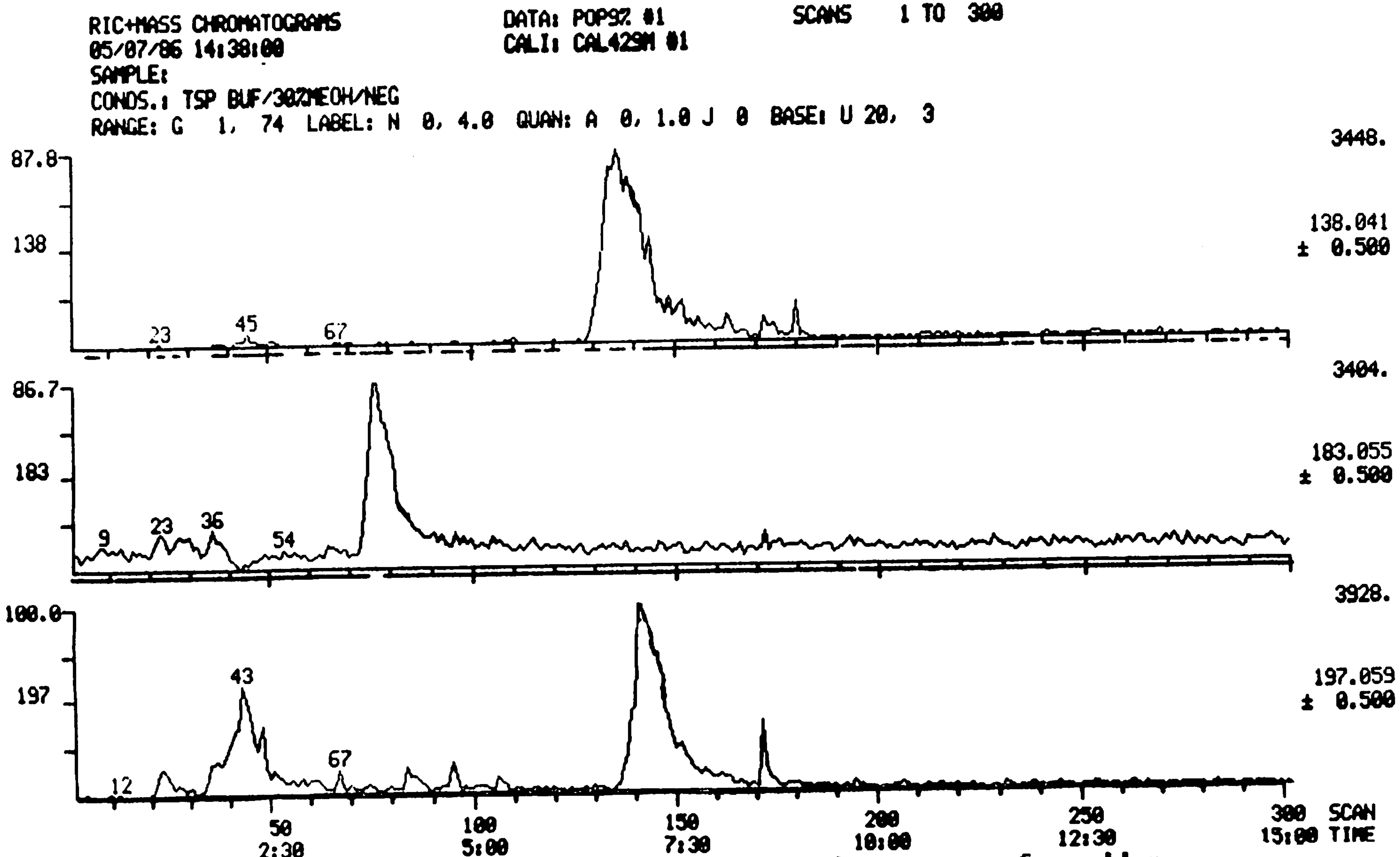


Figure 2: Mass spectrum of leachate obtained by Thermospray LC/MS.



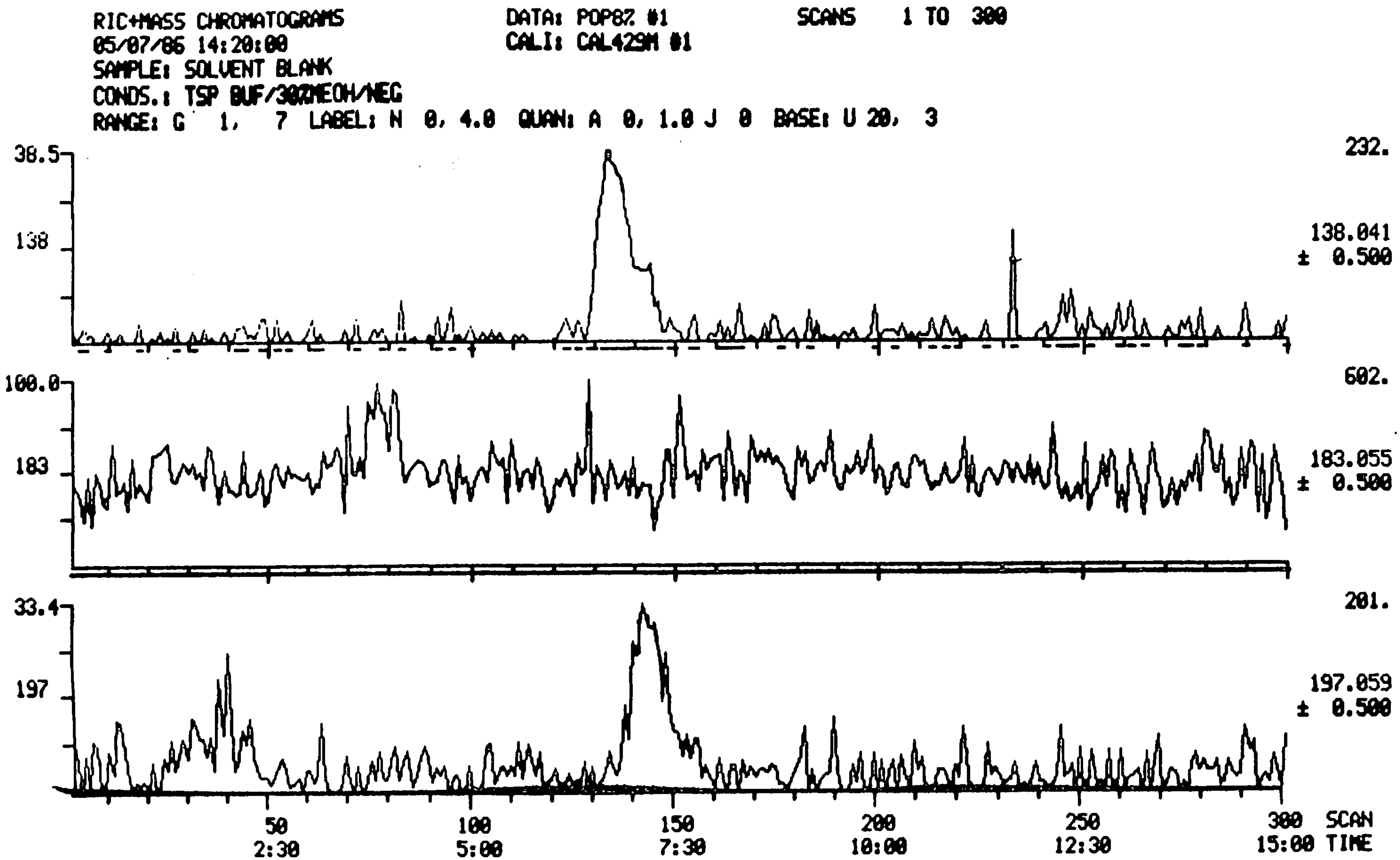
```
RIC+MASS CHROMATOGRAMS                DATA: POP77 #1          SCANS   1 TO  300
05/07/86 14:01:00                     CALI: CAL429M #1
SAMPLE: MIX 21268
CONDS.: TSP BUF/30%MEOH/NEG
RANGE: G   1, 300  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 3: Single ion chromatograms for the phenols in the leachate sample.



```
RIC+MASS CHROMATOGRAMS              DATA: POP97 #1          SCANS    1 TO  300
05/07/86 14:38:00                   CALI: CAL429M #1
SAMPLE:
CONDS.: TSP BUF/30%MEOH/NEG
RANGE: G   1,  74  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 4: Single ion chromatograms for the phenols after addition of 5 ng of each.



RIC+MASS CHROMATOGRAMS
05/07/86 14:20:00
SAMPLE: SOLVENT BLANK
CONDS.: TSP BUF/30%MEOH/NEG
RANGE: G 1, 7 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: POP87 #1
CALI: CAL429M #1

SCANS 1 TO 300

Figure 5: Blank injection. Some carry-over is observed.

made to optimize either chromatographic conditions or the solvent system it was possible to analyze a complex leachate sample for phenols in about 15 minutes. GC/MS of this sample revealed high concentrations of organic acids and cresols, however, the other phenols were not detected and the analysis time was about twice as long as the LC/MS run.

The data indicate that the two techniques are generally complimentary and that LC/MS is superior for determining phenolic compounds, especially those that produce a strong negative ion (i.e., nitrophenols, etc.) Furthermore, the LC/MS system is capabale of delivering the entire sample to the ion source through the sample loop thus allowing rapid screening of samples for the possible presence of phenols before proceeding with the factual analysis.

The sensitivity of the Thermospray LC/MS system is very high for the compounds determined. The phenols containing heteroatoms, other than oxygen, produce very strong molecular ions. This has also been observed for halogenated phenols. Petachlorophenol, for example, produces very strong molecular ions at 263 and 265. This behavior is exactly as predicted using a classical Hammet approach. The phenolic negative ion is stabilized by groups which have electron withdrawing characteristics. Moreover, nitro groups are able to resonance stabilize the resulting negative ion as shown in Figure 6. Similarly, chloro, bromo, cyano, etc. substituted phenols would also be expected to exhibit electron withdrawing characteristics and therefore stabilize the negative phenol ion.

In the negative ion mode organic acids are not normally observed. This is most likely due to low ionization efficiency (i.e., R-COO- is not formed unless the resulting charge can be stabilized) or, if the ion is formed it rapidly fragments and no ions indicative of actual molecular species are observed. The first case is probably the most likely.

The per analysis cost is determined from the sample preparation and analysis procedures used. Analysis time therefore affects one part of the overall cost. Generally, the less time an analysis takes the lower the cost, up to a point. In the case of GC/MS of acid fractions the analysis portion of the cost is based on an analysis time of about 35 minutes. (This is about average for most labs we have spoken with.) LC/MS can be done in about half that time and thus one would expect the overall cost using LC/MS to be lower. The cost reduction will not, however, be half that of GC/MS since the sample preparation procedure for each method is the same. As analysis time is reduced the overall cost of the test will approach the cost of sample preparation. In any case LC/MS should offer a less expensive alternative to GC/MS for many phenolic compounds. Furthermore, if a screening procedure is

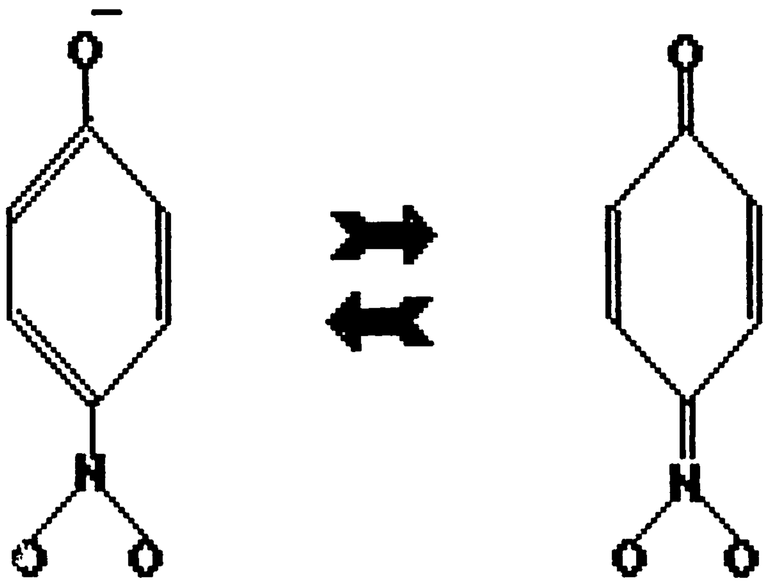


Figure 6: Through resonance of nitro group

used the analysis time will be reduced by an order of magnitude and hence the analysis cost will be even lower.

SUMMARY

The data presented here generally indicate that GC/MS and LC/MS are complimentary techniques for hazardous waste and leachate analsyis. While the data are limited, LC/MS was demonstrated to be a viable technique for analysis of several phenolic compounds that were not detected using GC/MS.

UPDATE ON A COOPERATIVE INVESTIGATION OF TEST METHODS FOR SOLIDIFIED WASTE CHARACTERIZATION

J. STEGEMANN, ENVIRONMENT CANADA WASTEWATER TECHNOLOGY CENTRE; N. CATHCART, ENVIRONMENT CANADA INDUSTRIAL PROGRAMS BRANCH; D. FRIEDMAN, OFFICE OF SOLID WASTE, U.S. ENVIRONMENTAL PROTECTION AGENCY, AND A. LIEM, ALBERTA ENVIRONMENTAL CENTRE

ABSTRACT

A cooperative program is being conducted to investigate the suitability of a number of laboratory test methods for determining the chemical and physical properties of a large variety of solidified wastes. The participants in this study are Environment Canada, the U.S. Environmental Protection Agency, Alberta Environment, and fifteen companies involved in developing or marketing solidification technology. The details of the study and its present status will be reviewed.

The objectives of this study are: (1) to develop a uniform testing protocol for solidified waste to be used to determine the degree of hazard reduction achieved by the treatment, and (2) to create a data base of the properties of solidified hazardous waste achieveable with present technology which will assist in setting standards and provide a basis for futher developmental work.

Each of the participating companies has applied the solidification system of its choice to as many as five wastes. Three laboratories have applied a protocol of twelve tests to the products of these solidification treatments to determine their intrinsic physical and chemical properties. In addition, Louisiana State University has performed microstructural characterization of selected solidified products. A report of the final results is expected to be available in the spring of 1987.

INTRODUCTION

Landfilling is the chosen disposal method for many hazardous wastes which are nonrecyclable, or nondestructable, or for which the disposal options of recycling or destruction are too costly. Solidification processes* are designed to improve wastes for landfilling by ameliorating their physical properties, or immobilizing the contaminants to prevent groundwater contamination, or both.

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* In the context of this paper, the term "solidification" refers also to processing sometimes termed "stabilization" and "fixation".

The numerous vendors of solidification processes make various claims as to the different degrees to which their processes affect the properties of concern. At present, no set of standard tests exists for measuring the efficacy of solidification processes.

A study has been initiated by Environment Canada, in cooperation with the U.S. Environmental Protection Agency, Alberta Environment, and fifteen Canadian, American and European companies involved in developing or marketing solidification technology, to develop a uniform assessment protocol for evaluating the properties of a variety of solidified wastes (1)

OBJECTIVES

The objectives of the cooperative program are:

1) To assess the suitability of a protocol of 12 short-term test methods for characterizing physical and leaching properties of a wide variety of solidified wastes,

2) To develop a data base of properties of solidified wastes which will assist in setting standards and allow comparative evaluation of solidified wastes and raw wastes,

3) To provide a basis for further work towards the development of accelerated test methods and mathematical models to estimate long-term stability, and

4) To promote the use of the test methods as standards which would allow uniform evaluation of solidified wastes.

BACKGROUND

A solidified waste matrix is typically formed by pozzolanic reactions such as those which occur between lime and fly ash and in portland cement. Other materials such as clays, polymers and proprietary specialty sorbents may also be used to effect contaminant containment. Immobilization of contaminants in solidified wastes may be a result of chemical reaction, physical entrapment, or adsorption to the solidified matrix.

A common approach to evaluating the performance of a solidified waste is the attempted simulation of disposal site conditions (related to climate, geology, etc.) with laboratory testing. This type of approach has a number of disadvantages:

1) It is difficult to simulate field conditions with lab-scale tests.

2) One test (or a small number of tests) cannot be applicable to many disposal site conditions,

3) It is impossible to simulate the effects of long periods of time, and

4) Specific reasons for the qualitative performance of the waste form are not determined.

Another approach is to attempt to characterize the intrinsic properties of the solidified waste in terms of the chemical and physical factors which affect the leachability of the waste form:

1) The degree of chemical immobilization of the contaminants, i.e., the contaminants may be chemically bound in a variety of compounds of varying solubilities and reactivities, or they may be physically adsorbed or trapped in the solidified waste matrix. The mechanism of immobilization affects the response of the waste to different groundwater characteristics, particularly with regard to pH.

2) The potential for contact of the groundwater with the waste, i.e., the hydraulic conductivity of a waste, as well as that of its surroundings, determines whther mobile contaminants are transported through the solidified waste matrix by advection or diffusion. Resistance to weathering, and compressive strength may also affect the surface area of waste in contact with the leaching groundwater.

The approach of intrinsic property detemination has advantages corresponding to the disadvantages of the first approach:

1) Wastes with particular intrinsic characteristics can be matched to the disposal scenarios to which they are most suited,

2) Intrinsic characteristics may be used as source terms in mathematical models for estimating the effects of long periods of time, and

3) The specific nature of a waste form's qualitative characteristics will be known, and subject to improvement.

The protocol of twelve short-term laboratory tests proposed in this study is designed to characterize the intrinsic physical and chemical properties of solidified wastes.

The results from the assessment protocol are not intended to be interpreted directly in terms of site-specific environmental impact. This would require additional information regarding disposal site conditions and long-term stability of the waste (from accelerated testing and mathematical modelling).

TESTING

The twelve tests in the assessment protocol may be classified as physical or leaching tests as listed in Table 1.

Table 1
THE TEST METHODS(2)

Physical Tests	Leaching Tests
Bulk Density	Sequential Chemical Extraction
Water Content	Equilibrium Leach
Solids Specific Gravity	US EPA Toxicity Characteristic Leaching Procedure (TCLP)
Permeability	Acid Neutralization Capacity
Unconfined Compressive Strength	Dynamic Leach
Freeze/Thaw Weathering	
Wet/Dry Weathering	

The physical tests and the TCLP are discussed elsewhere (3). A short description of the remaining leach tests follows:

SEQUENTIAL CHEMICAL EXTRACTION

This procedure is used to examine the speciation of heavy metal contaminants in a waste. Knowledge of the bonding characteristics of the metals leads to an improved understanding of the environmental leachant characteristics that could affect their mobility.

The test is conducted by extracting a sample of ground waste with media of increasing aggressiveness which separate the contaminants into five fractions:

A) ion-exchangeable metal ions
B) hydroxides, surface oxides and carbonate bound metal ions
C) metal ions bound to hydroxides and iron and manganese oxides
D) metal ions bound to organic matter and sulphides
E) residual metal ions

EQUILIBRIUM LEACH TEST

This test is designed to measure the effective aqueous solubility of the contaminants.

A sample of waste is ground to -100 mesh and continuously mixed with distilled water at a liquid to solid ratio of 4:1. To ensure that equilibrium is attained, the test is run for seven days, after which the extraction liquid is separated from the solids and analyzed for the contaminants of interest.

ACID NEUTRALIZATION CAPACITY

The ability of a waste to neutralize acid is important because metals tend to become more soluble in low pH environments.

To measure a waste's capacity for acid neutralization, a sample of solidified waste is ground to -100 mesh and divided into subsamples which are placed in extraction bottles containing increasing amounts of acid. The bottles are tumbled until equilibrium is attained and the pH of each of the solutions is measured.

DYNAMIC LEACH TEST

A small cylindrical specimen of solidified waste is immersed in distilled water. The leachant is replaced at intervals calculated according to a simple diffusion model, such that the mass of contaminant leached in each interval is the same. The results are used to calculate an apparent diffusion coefficient and a leachability index which are indicators of the contaminant mobility through the matrix under diffusion control.

OTHER TESTS

In addition to the above tests, micromorphological and microchemical characterization of the solidified products for selected wastes will be carried out at Louisiana State University (LSU), using chemical extractions, X-ray powder diffraction, energy dispersive X-ray analysis (EDX), and scanning electron microscope analysis (SEM).

STUDY OUTLINE

The study involves numerous participants with responsibilities as listed in Table 2.

Five raw wastes were chosen for use in the study based on suggestions from all participants.

An attempt was made to select wastes which would:

1) Provide a comparison to results from previous work undertaken at Environment Canada's Wastewater Technology Centre (WTC) (4) and U.S. Army Corps of Engineers' Waterways Experiment Station (WES) (5),

2) Include a range of wastes routinely solidified by a number of vendors of solidification technology,

3) Include wastes containing problem contaminants, and

4) Maintain the international nature of the cooperative program.

Table 2
PARTICIPANTS AND THEIR RESPONSIBILITIES

Environment Canada, Conservation and Protection, Industrial Programs Branch	- Project management
USEPA Office of Solid Waste	- Engage Dynamac Corporation - Engage Radian Corporation - Peer review of report
USEPA Water Engineering Research Laboratory	- Sponsor this and complimentary project at Waterways Experiment Station
Dynamac Corporation	- "third party" acting as intermediary between testing labs and industrial participants to protect proprietary information
Radian Corporation	- Assist with raw waste collection and characterization
Ontario Ministry of the Environment Laboratory Services Branch	- Assist with raw waste collection

Table 2

PARTICIPANTS AND THEIR RESPONSIBILITIES (Cont'd)

Environment Canada, Conservation and Protection, Wastewater Technology Centre (WTC)	- Assist in project management - Provide background data - Participate in preliminary study of interlaboratory reproducibility - Assist with raw waste collection and characterization - Perform testing on raw and solidified wastes - Major contribution to final report preparation
Alberta Environmental Centre (AEC)	- Provide background data - Organize and participate in preliminary study of interlaboratory reproducibility - Assist with raw waste characterization - Perform testing on raw and solidified wastes - Major contribution to final report preparation
U.S. Army Corps of Engineers Waterways Experiment Station (WES)	- Participate in preliminary study of interlaboratory reproducibility - Peer review of report
Louisiana State University (LSU) Dept. of Mechanical Engineering	- Carry our microstructural and microchemical characterization
Industrial Participants	- Perform solidification of wastes

The fully characterized wastes were provided by the WTC, Radian Corporation and WES. The five wastes and the contaminants of interest for the leaching tests are described in Table 3.

Table 3
WASTES AND CONTAMINANTS OF INTEREST

Waste	Contaminants of Interest	Approximate Concentration (ppm, wet weight basis)
WTC Synthetic Solution	Arsenic	2600
	Cadmium	4400
	Chromium	1600
	Lead	8300
	Phenol	3600
WES Synthetic Sludge	Cadmium	4700
	Chromium	22000
	Mercury	400
	Nickel	22000
Aluminum Coil Plating Waste	Aluminum	24000
	Arsenic	90
	Chromium	1000
	Lead	100
	Thallium	50
	Cyanide	2000
Dredge Spoil	Chromium	100
	Copper	70
	Lead	140
	Mercury	0.3
	Zinc	700
	Polychlorinated Biphenyls (PCB)	1
Wood Preservation Soil	Pentachlorophenol	5500
	Polyaromatic Hydrocarbons (PAH)	300
	Arsenic	100
	Lead	40

A five gallon (U.S.) pail of each waste and information regarding its chemical and physical characteristics were sent by the waste collector to each of the fifteen industrial participants, at a rate of one waste per month. The industrial participant was given one month to experiment with the waste, and was then sent a solidification kit (containing molds and directions for specimen preparation) from the third party, Dynamac Corporation.

It is the task of Dynamac to protect proprietary information. The companies are participating under the agreement that their identities will remain unconnected with any particular solidified products unless they choose otherwise.

After solidifying the waste by their desired process, according to instructions provided in the solidification kit, the industrial participant allowed the solidified material to cure for 28 days on site before shipping it to Dynamac.

Upon receipt of the solidified products, Dynamac relabelled the product of each industrial participant with a unique secret code, and distributed the samples to either WTC, AEC, WES, or LSU for testing. In general, testing was initiated after 56 days of curing, but some departures from the intended schedule occurred. Figure 1 shows the schedule of activities for the study.

WTC, AEC, and WES are applying the protocol of 12 test methods to the solidified products, such that each test is run in duplicate for each solidified product by two laboratories. Quality control samples consisting of blanks, duplicate standards and split samples for each waste are also being analysed in each laboraboty.

LSU is carrying out microstructural and microchemical characterization for the solidified products from the Wood Preservation Soil and the WES Synthetic Sludge.

After testing, the experimental results will be collected and analysed by WTC. Dynamac will send each industrial participant the results for their particular solidified products to give them the opportunity to choose to have their products identified with their corporate name in the final report.

CURRENT STATUS

Testing of the solidified products is expected to be completed by the end of August, 1986, with chemical analysis of leachates to be finished by the end of October (Figure 1). The final report for the study will be made available in May, 1987 at the Fourth International Hazardous Waste Symposium on Environmental Aspects of Stabilization/

Figure 1: PROGRAM SCHEDULE - INVESTIGATION OF TEST METHODS FOR SOLIDIFIED WASTE CHARACTERIZATION

DATE	1985					1986												1987				
ACTIVITY	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M
Shipment of raw waste and raw waste characteristics to industrial participants	1 2		3	4	5																	
Shipment of solidification kits to industrial participants		1 2		3 4		5																
Solidification		-1- -2-		3	4	5																
Shipment of solidified samples to testing facilities				2		3 4		5	1 (2) (3)													
Testing begins				2		3	4	5	1 (2) (3)													
Testing ends												1 3 2	4 5									
Results sent to industrial participants for acknowledgement														5	4 2	3 1	* Response					
FINAL REPORT																						***

Where numbers 1 to 5 refer to the following wastes:
1. WTC Synthetic Solution
2. Dredge Spoils
3. Aluminum Coil Plating Waste
4. Wood Preservation Soil
5. WES Synthetic Sludge

( ) Brackets refer to samples received late

Solidification of Hazardous and Radioactive Wastes to be held in Atlanta, Georgia.

In the course of the study, the assessment protocol will have been applied to almost 300 samples, representing 69 different solidified products. This will provide a thorough validation of the test methods under investigation and a solid data base of solidified waste properties.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Trevor Bridle and Dr. Pierre Cote from Environment Canada's Wastewater Technology Centre, Mr. Peter Hannak from Alberta Environmental Centre, the Environmental Engineering Group from US Army Corps of Engineers' Waterways Experiment Station, Dr. Harvill Eaton from Louisiana State University, and Dr. Carleton Wiles fom US EPA for their contributions to the program. Our thanks also to the industrial participants for the solidified waste products.

REFERENCES

(1) Cathcart, N., "Investigation of Test Methods for Solidified Waste Characterization: A Cooperative Program", Presented at the 6th National Conference on Waste Management in Canada, Vancouver, B.C., November 5-7, 1984.

(2) EPS Wastewater Technology Centre/Alberta Environmental Centre, "Test Methods for Solidified Waste Characterization", Draft Report, January, 1986.

(3) Hannak, P., Liem, A.J. and Cote, P., "Methods for Evaluating Solidified Waste", Presented at the USEPA Second Annual Symposium on Solid Waste Testing and Quality Assurance, Washington, D.C., July 15-18, 1986.

(4) Cote, P.L. and Hamilton, D.P., "Leachability Comparison of Four Hazardous Waste Solidification Processes", Proceedings of the 38th Annual Purdue Industrial Waste Conference, May 10-12, 1983, pp. 221-231.

(5) Jones, J.N., Bricka, R.M., Myers, T.E. and Thompson, D.W., "Factors Affecting Stabilization/Solidification of Hazardous Waste", Proceedings: International Conference on New Frontiers for Hazardous Waste Management, Pittsburgh, PA, September 15-18, 1985, USEPA 600/9-85/025.

SIXTH SESSION

Thursday, July 17, 1986
7:30 p.m. - 9:30 p.m.

Chairperson:
Kenneth Jennings
Environmental Scientist
Office of Waste Program Enforcement
USEPA
401 "M" Street, S.W.
Washington, D.C. 20460

CORRECTIVE ACTION UNDER RCRA, INTERIM MEASURES

JACQUELINE MOYA AND KENNETH JENNINGS, OFFICE OF WASTE PROGRAMS ENFORCEMENT, U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C.

ABSTRACT

Section 3008(h) of RCRA gives EPA authority to issue Administrative Orders or seek judicial relief requiring corrective action or send other response measures deemed necessary to protect human health or the environment. This authority is based on information that a release has or is occurring into the environment from a facility, and provides for the broad applicability of corrective actions and response measures.

Extensive and time consuming investigations may be required to develop a comprehensive corrective measures study (CERCLA Remedial Investigation equivalent) for a facility. During this period, the release could continue unabated which could allow the spread of contamination or the continuance of conditions that may endanger human health or the environment. Interim measures are actions that should be taken in advance of longterm remedial measures to prevent releases or additional contamination, and to reduce, abate or remove the exposure threat presented by releases.

INTRODUCTION

One of the administrative authorities granted the United States Environmental Protection Agency by the Hazardous and Solid Waste Amendments of 1984 is the 3008(h) corrective action authority. This authority is extremely important in that it empowers EPA and eventually the States to order the owner-operator of a facility which has released contamination to the environment to undertake action(s) to arrest and reverse the effects of that release in any environmental medium. The nature of releases is often extremely complex and potentially far reaching, especially where several media are involved. It is, therefore, prudent often times to take immediate action to remove the source of contamination or to take immediate action to remove the source of contamination or impede its progress until a final, comprehensive solution is designed. Immediate actons of this kind are called interim measures. The guidance developed by OWPE draws heavily from the experience of the Office of Emergency and Remedial Response in implementing the immediate/planned removal portions of the National Contingency Plan. What follows is a summary of that guidance.

TYPES OF INTERIM MEASURES

Corrective action orders should incorporate actions (interim measures) necessary to protect human health or the environment. Interim measures are actions that should be taken in advance of long term corrective measures to prevent releases or additional contamination, prevent or reduce the further spread of contamination, and reduce, abate or remove the exposure threat presented by releases. During the selection of an interim measure, the Agency should consider the magnitude of the potential threat to human health or the environment. The Agency's authority to seek relief by requiring an owner/operator to perform specified activities is directly correlated to the protection of human health or the environment. Therefore, if the threat is minimal or the risk has yet to be determined, simple monitoring of ground water, surface water, soil or air may be the types of action required. For example, if a release to ground water is minimal and the aquifer is not used by the nearby population, a program to pump and treat may not be appropriate. If the threat is greater or as more information becomes available through initial or additional sampling and analysis, more serious actions should be contemplated either by incorporating actions into a single "phased" order or by issuing separate orders.

Attached is a list of some possible interim measures. It was compiled from several actions and past CERCLA remedial guidance.

INTERIM MEASURES

Containers

a) Overpack/re-drum
b) Construct storage area/move to storage area
c) Segregation
d) Sample/analyze and dispose
e) Excavation/disposal
f) Temporary cap

Surface Impoundments

a) Reduce head
b) Remove free liquids and/or highly mobile wastes
c) Stabilize/repair side walls/increase freeboard/install geotextile
d) In-Situ solidification
e) Cover (control air release or overflow due to rain)
f) Interim ground water measures
g) Run-off/run-on control (diversion or collection devices)

h) Document the concentration of constituents left in place when a surface impoundment handling characteristic wastes is clean closed*

* When this type of surface impoundment is clean closed, there may be constituents left in place. Some of these health or the environment (e.g., corrosive waste may contain heavy metals).

Landfill

1) Run-off/run-on control (diversion or collection devices)
b) Reduce head on liner and/or in leachate collection system
c) Repair leachate collection/removal system or french drain
d) Install new leachate collection/removal system or french drain
e) Temporary cap/cover (asphalt, synthetic or clay)
f) Interim ground water measures
g) Excavation/disposal

Waste Pile

a) Run-off/run-on control (diversion or collection devices)
b) Cover (polymeric membrane, geotextile or clay)
c) Solidification
d) Interim ground water measures
e) Removal of the waste pile for more secure storage
f) Excavation/disposal

Ground Water

a) Sampling and analysis
b) Delineation of plume
c) Interceptor trench/sump/french drain
d) Pump and treat/in-situ treatment
e) Cut-off walls (slurry or bentonite)

Surface Water Release (point vs non-point)

a) Overflow/underflow dams
b) Filter fences
c) Run-off/run-on control (diversion or collection devices)
d) Regrading/revegetation
e) Cover with geotextile
f) Sample and analyze surface waters and sediments or point source discharges

Tanks

a) Leak or cracks detection/repair
b) Relining
c) Partial or complete removal
d) Pipeline removal or replacement
e) Secondary containment

Soils

a) Sampling and analysis
b) Run-off/run-on control (diversion or collection devices)
c) Temporary cap/cover
d) Excavation/disposal

Gas Migration Control

a) Pipe vents
b) Trench vents
c) Gas barriers
d) Gas collection system
e) Gas treatment system
f) Gas recovery
g) Air monitoring sytem

Particulate Emissions

a) Truck wash (decontamination unit)
b) Re-vegetation
c) Application of dust supressant

Other Types of Action

a) Fencing to prevent direct contact
b) Alternate water supply to replace contaminated drinking water
c) Temporary relocation of exposed population
d) Extend contamination studies to off-site areas
e) Other actions necessary to protect human health or the environment
f) Temporary or permanent injunction
g) Suspend or revoke authorization to operate under interim status

SEVENTH SESSION

Friday, July 18, 1985
8:00 a.m. - 12:00 p.m.

Chairperson:
J. Howard Beard
Chief
Physical Science Section
Office of Waste Program Enforcement
USEPA
401 "M" Street, S.W.
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ISSUES AND PROBLEMS RELATED TO CERTIFICATION AND PERFORMANCE EVALUATION OF HAZARDOUS WASTE TESTING LABORATORIES

FRED SETO, PH.D., KUSUM PERERA, PH.D., CINDY DINGMAN, BARTON SIMMONS, AND ROBERT STEPHENS, PH.D., CALIFORNIA PUBLIC HEALTH FOUNDATION, BERKELEY, CALIFORNIA

ABSTRACT

In the course of performing its duties as a lead agency to administer the California Hazardous Waste Control Program, the California Department of Health Services has received several hazardous wastes analysis reports which showed dubious analytical results. Consequently, a program for certification of harzardous waste testing laboratories was mandated in 1982 with the primary objective to improve the quality of laboratory data. The program was implemented in April, 1985. The response from the hazardous waste testing laboratories has been enthusiastic. As of June, 1986, the Department has received 115 certification applications including 8 laboratories from outside California. Some issues and problems are as follows:

(1) Number of Parameters and difference matricies -The large number of analytical parameters and various matricies require specific analytical methods or modified methods in terms of sample preparation and instrumentation conditions.

(2) Test Categories - The available categories for certification do not include all tests required of laboratories for waste classification and monitoring. Many of the required methodologies have not been validated.

(3) Proficiency Test Samples - Analyses of proficiency test (PT) samples by an applicant laboratory provide some indication of the laboratory's performance capability. However, the task of preparation and validation of a PT sample library is enormous considering the large number of parameters, matrices, and concentrations.

(4) On-Site Visit - On site inspection of an applicant laboratory's operation and activities is a useful measure of its capability.

Generally, the program has been feasible and successful in terms of improving the quality of data generated by hazardous waste testing laboratories. Experience in the establishment and conduct of this program will be presented.

OVERVIEW OF RCRA ENFORCMENT

KENNETH JENNINGS, OFFICE OF SOLID WASTE, U.S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, D.C.

ABSTRACT

The Office of Waste Programs Enforcement (OWPE) is part of the Office of Solid Waste and Emergency Response (OSWER). The charge of OWPE is the enforcement of RCRA and CERCLA which is accomplished through its two divisions. This discussion is focused on RCRA enforcement. The various administrative orders and procedures are discussed in some detail.

INTRODUCTION

The Office of Waste Programs Enforcement (OWPE) is one part of the larger Office of Solid Waste and Emergency Response within the United States Environmental Protection Agency. It is the charge of OWPE to enforce the regulations pertinent to the Resource Conservation and Recover Act of 1976 (RCRA), including the Hazardous and Solid Waste Amendments of 1984, and the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA). On a more practical level, OWPE provides leadership in policy and technical matters of enforcement to the EPA Regions and States and strives to promote the coordination of enforcement activities with those of the other offices within OSWER. Of particular relevance to this symposium is the effort of OWPE and the Office of Solid Waste (OSW) to coordinate the needs and objectives of enforcement with the promulgation of regulations and the issuance and maintenance of permits under RCRA.

OWPE is divided into two divisions for RCRA and CERCLA. The RCRA division is comprised of two branches, Compliance and Implementation, and Guidance and Evaluation. The Compliance and Implementation Branch provides technical support to the Regions and States on specific enforcement cases and facilitates the implementation of enforcement guidance in the field. This Branch also manages the coordination of Regional enforcement activities with the objectives of the RCRA Implementation Plan. The Guidance and Evaluation Branch (GEB) has two major duties. It is largely responsible for working with OSW to ensure that regulations promulgated are enforceable. Secondly, this Branch is responsible for the development of technical and policy guidance for use by EPA Regions and States. Two notable examples are the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (draft) and Compliance Order

Guide (final). The former provides technical guidance to compliance/enforcement personnel and permit writers on what constitutes a compliant ground-water monitoring system. The RCRA Ground-Water Monitoring Compliance Order Guide is a description of how regulatory compliance should be sought for facilities with inadequate ground-water monitoring systems.

OWPE has several administrative order authorities at its disposal with which to compel owner or operators to comply with the regulations. The selection of which authority or combination of authorities to use should be based on case specific considerations (see the RCRA Ground-water Monitoring Compliance Order Guide for more details). The 3008a, 3008h, and 3013 authorities are summarized below.

§3008(A) ORDERS

A 3008(a) order may be issued only for violation of one or more Subtitle C requirements. Therefore, when enforcement personnel and the permit writer determine a facility's ground-water monitoring program to be technically inadequate, enforcement personnel should determine whether any of the technical inadequacies constitute violations of Part 265 Subpart F, Part 270, or Part 264.

In some cases the regulations are specific as to what findings of fact would indicate violations. For example, if an owner/operator has installed only two downgradient wells, the facility is clearly out of compliance with 265.91(a)(2) of the regulations, the section that requires installation of at least three downgradient wells. Likewise, if a facility does not have some of the records specified in the regulations (e.g., an assessment outline), or has not performed some of the required analyses, then the owner is clearly in violation. The decision concerning the existence of a violation becomes more involved when it is based upon evaluating the adequacy of a facility's ground-water monitoring system beyond the minimum requirements.

In great part, the heightened level of analysis required to evaluate the overall adequacy of a system evolves from the regulations' reliance on broad performance standards. Given the great variability between sites in terms of wastes handled, hydrogeology, and climate, it is impossible to design a regulatory system that defines for all cases exactly what constitues an adequate ground-water monitoring program. As a result, the Agency relies on performance standards to define "adequate."

The performance-oriented provisions of Subpart F set high standards for interim status ground-water monitoring systems, and enforcement personnel should not underestimate the power and applicability of this language. For example, even though the regulations establish a minimum of one background monitoring well, a single well is seldom sufficient because owner/operators must design their systems to meet the background-well performance standard listed in 265.91(a)(1). Section 265.91(a)(1) requires appropriate locations and depths to yield samples representative of background water quality not affected by the facility. If a facility's well array does not meet this standard, the owner/operator is out of compliance with the regulations.

§3013 ORDERS

Section 3013 orders may be issued to a facility only when the Administrator determines that the presence or release of hazardous waste at the facility may present a substantial hazaard to human health or the environment. The facility need not be violating RCRA regulations to qualify for action under 3013.

Prior sampling of contamination is not necessary to support a 3013 order. In the case of a facility that has not conducted any ground-water monitoring activities, the potential for release of hazardous waste, the nature of the site's underlying hydrogeology and the proximity of an aquifer or populated area will usually be sufficient, with expert opinion, to support a 3013 order. In some cases, the Region may wish to use 3007 authority to sample one or more wells at a facility in order to provide direct evidence of a release. Given that direct evidence is often unnecessary to establish the applicability of 3013, the Region should probably avoid direct sampling unless it is confident that existing wells will intersect the suspected plume. Guidance issued Septembr 26, 1984 provides further discussion of the grounds for issuance of 3013 orders. (See memo from Courtney Price and Lee Thomas entitled, "Issuance of Administrative Orders Under Section 3013 of the Resource Conservation and Recovery Act").

§3008(H) ORDERS

Section 3008(h) of RCRA provides that the Administrator may issue an order or file a civil suit requiring corrective action or other appropriate response measures whenever (s)he determines that there is or has been a release of hazardous waste into the environment.

As described in the September 1985 draft guidance on the scope and use of 3008(h), the Agency is interpreting the term "release" to include any spilling, leaking, pumping, pouring, emitting, erupting, discharging, injecting, escaping, leaching, dumping, or disposing into the environment. To show that a release has occurred, the Administrator does not necessarily need sampling data. Such evidence as a broken dike at a surface impoundment should also support a determination that a release has occurred. In some cases, information on the contents of a land disposal unit, along with information on the contents of a land disposal unit, along with information on the site hydrogeology and the design and operating characteristics of the facility may be enough for an expert to conclude that a release has occurred.

Section 3008(h) orders (and civil suits) may be used to address releases not only to the ground water, but to other media as well. The draft 3008(h) guidance states that the authority covers releases of hazardous wastes into surface water, air, the land surface, and the sub-surface strata. The term "hazardous waste" is not limited to those wastes listed for identified in 40 CFR Park 261. For 3008(h) purposes, the term hazardous waste also includes the hazardous constituents identified in Appendix VIII of Part 261. Section 7003 orders may be used in the event of an imminent and substantial hazard. CERCLA section 106 and 104 orders may also be used on a limited basis at RCRA-managed facilities to take long term or immediate corrective actions respectively.

The RCRA Division of OWPE is dedicated to the strict, timely and constructive enforcement of the RCRA regulations. OWPE has been and will continue to be a resource to the Regions and States in both technical and policy areas. Through a close working relationship with OSW, OWPE envisions continued progress in safe guarding human health and the environment from RCRA-managed hazardous waste.

SW-846 UPDATE

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ABSTRACT

This will be an overview of SW-846, the Office of Solid Waste's sampling and analysis manual, giving special consideration to format and content. It will also include a discussion of the relationship between the guidance and regulations from various OSW programs and the methods. This will present OSW's concept for the further development of the manual and discuss issues concerning the methods.

TESTING ISSUES ATTENDANT TO IMPLEMENTATION OF THE RCRA REGULATORY PROGRAM

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ABSTRACT

As part of its efforts to implement the 1984 amendments to the Resource Conservation and Recovery Act (RCRA) and to improve the implementability of the RCRA regulatory program, EPA is developing increasingly more quantitative property based regulatory definitions. Such regulations include the expanded Toxicity Characteristic which was recently proposed and OWS's efforts to develop concentration based listings. Implementation of such regulations brings with it a number of technical issues and questions. This paper will address several of the testing issues including:

1. when and how often should a facility test its residuals to insure compliance with the regulations;
2. how should the Agency establish regulatory thresholds when the sensitivity of the analytical methods are the controlling factor;
3. what type of quality assurance/quality control program should be incorporated into the RCRA regulatory program.

INTRODUCTION

Measurement plays a key role in all aspects of the hazardous waste management program. As the program becomes increasingly more quantitative with performance criteria for facility operation and for identifying hazardous and banned wastes the critical role of the procedures employed to determine a given property will only increase. Questions such as whether or not a waste is a hazardous waste; is the waste banned from land management; is the permeability of the facility liner sufficiently low to prevent leakage; is the facility leaking; is the remedial engineering activity accomplishing the job of cleanup as it was designed to do. These are all questions which require that accurate measurements be taken in order for the proper decisions to be made.

WASTE ANALYSIS

The first question facing generators and operators of waste management facilities is whether the waste they are dealing with is a hazardous waste within the meaning of RCRA. Answering this question raises several issues. These include:

- When is testing required and under what circumstances can other knowledge of the waste be used to classify the waste,
- What methods to use in sampling and testing the waste,
- How much testing is enough (i.e., how many samples need be taken to insure that the data is representative of the waste and, how often does the testing have to be repeated due to process variability),

When is Testing Required When Characterizing a Waste?

EPA does not require testing, instead it requires that a good faith evaluation of the waste's properties be made before the waste is stored, treated, or disposed of. However, what constitutes a good faith effort, or when should one test is a constantly occurring question.

The RCRA regulations (40 CFR 262.11) require that persons, other than households, who generate wastes must evaluate their wastes to determine if they meet the definition of a hazardous waste. In addition to testing to determine if a waste is a hazardous waste, testing is also required of persons treating, storing, or disposing of hazardous waste to insure that the operations are not resulting in harm to the environment.

EPA's RCRA regulations have generally not required test data. Rather, threshold levels of each property have been established and it has been left up to the regulated community to determine whether testing is needed to insure compliance with the applicable standard.

This approach, offers the regulated community a great deal of flexibility. However, with the flexibility comes the responsibility to perform an adequate evaluation. Whether or not to test then depends on how much information one has on the waste or waste generation process. Specifically, what raw materials are used, what contaminants might reasonably find their way into the waste during product purification (e.g., distillation). If one can, through chemistry principles and process engineering considerations, be certain that none of the toxic constituents could reasonably be expected to be present in the waste at a level which would exceed the regulatory thresholds, then one has demonstrated that the waste is not hazardous or banned from land disposal. If, on the other hand, one does not have sufficient data on the material to defend one's judgment, then testing should be done. The amount of testing then becomes a function of one's knowledge of the process and any preliminary testing results.

Under the framework proposed for the Toxicity Characteristic, the determination of whether a waste is a hazardous waste continues to depend on whether the concentrations of constituents in the TCLP extract exceed the applicable regulatory levels. Given the importance that hazardous waste identification plays in the regulatory program, EPA is re-evaluating the above mentioned policy and deciding whether or not to require periodic waste testing.

EPA is considering three general approaches to such a testing requirement. First, EPA could continue just to require generators to evaluate whether or not their wastes exceed applicable regulatory levels, but not specifically require testing to make this determination. Second, EPA could require testing of wastes at a frequency specified by regulation. Third, EPA could require the generator to test, while documenting the determination of the appropriate testing frequency based on guidance provided by the Agency.

Although not requiring testing places the least burden on the regulated community, EPA is concerned that this approach may not promote voluntary compliance and that it could hamper enforcement efforts against those members of the regulated community who do not comply voluntarily with the regulations.

Another possible approach is to require periodic testing, specifying in the regulations both the method and the frequency of testing. Thus, testing might be required on a seminannual or annual basis. This approach would make enforcement of the regulations easier and would likely induce a higher level of voluntary compliance since the regulations would be highly specific with regard to what constitutes an acceptable testing program and what actions and inactions would constitute violations.

There are, however, several problems with such an approach. First, there are problems inherent in specifying an appropriate testing frequency. Based on data from our own industry studies efforts and data from the Office of Water's Effluent Guidelines Program, it is clear that many waste streams are extremely variable in concentrations of chemical constituents from one plant to another, even when the same general process is employed. Variability exists not only from one generator to another, but also spatially and temporally within a single plant.

A third possible approach is to require generators to perform testing on their wastes, but not to specify a testing frequency in the regulations. Rather, generators would be required to determine an appropriate testing frequency based on guidance developed by EPA and to document, in their records, this frequency determination. The advantage of this approach is that process-specific factors could be taken into account in determining the appropriate testing interval. Thus, although there would be some additional burden on generators to determine, based on the guidance, the appropriate frequency for testing tailored to specific factors relating to his process, there would be less of a chance of requiring unnecessarily frequent testing. This approach does, however, present greater enforcement difficulties than does the approach of specifying generic periodic testing intervals.

How Much Testing is Needed?

Irrespective of which approach is eventually adopted, the problem of developing a testing program appropriate to the waste at hand needs to be addressed. The problem remains as to how to assure that the waste sample subjected to testing is representative of both the batch and the process from which they are derived. This problem arises not only in regard to hazardous waste identification, but also in connection with other waste sampling requirements.

In this paper, I will attempt to address one aspect of this question; how does one determine how many tests to perform to ensure compliance with the regulation? I will limit my discussion today to testing for purposes of complying with the Toxicity Characteristic and the Land Disposal Ban. I will not attempt to delve into the detailed statistics of testing. Instead, I will discuss the philosophy of testing as it applies to the RCRA program. For additional information on RCRA testing requirements, I refer you to the EPA manual "Test Methods for Evaluating Solid Waste," SW-846. This manual contains a more thorough discussion of the RCRA testing regulations.

Hazardous waste evaluation (e.g., is a waste hazardous, is the waste banned from land disposal) is a problem not of determining what the actual value of a property is but rather whether it is above some defined regulatory threshold. From the standpoint of testing, this is a critical distinction since it is much less expensive to answer this question than to detemine actual values. Although this discussion will not emphasize statistics, the amount of testing that should be conducted is greatly influenced by the fact that the absolute value of the property is not critical. Examining the question from the point of view of the generator evaluating a waste, the question becomes one of determining: How certain do I have to be that the property does not exceed the threshold value? The question for the analyst then becomes: How precisely does one have to determine the value to answer the question with a high enough degree of confidence?

The correct amount of testing is the minimum amount which will avoid the legal and environmental consequences of an incorrect determination; taking into account the expense of testing. As SW-846 describes, the Agency has taken the position that evaluation to the 98% confidence level is sufficient when determining whether or not a waste is a hazardous waste. What this means is that persons who conduct enough testing to demonstrate that they have attained this level of confidence will be considered to have made a good faith effort to comply with the regulations.

The next aspect of the how often to test question revolves around the problem of process changes. Wastes should be reevaluated whenever a significant change is made in the process generating the waste. However, when does a process change become sufficient to be considered to be significant and thus necessitate re-testing? This is another area where no clear answers can be given. Whether or not the change is significant hinges on whether the change could affect the properties of the waste that is being evaluated. For example, toxic elements are generally more leachable from acidic wastes than from alkaline wastes. Thus, if one changed from using an alkaline boiler cleaner to an acidic one, then it would be prudent to re-evaluate, or even re-test, the boiler cleaning sludges that are generated. Assuming the question is one of whether or not the waste exhibits th Toxicity Characteristic.

For the owner/operator of a facility that handles wastes from many generators the problem is much more difficult. Here the facility is not in control of the generation process and has much less knowledge of the waste's properties. Before an owner/operator treats, stores or disposes of any hazardous waste he must obtain a detailed chemical and physical analysis of the waste. This does not mean that the facility has to personally test each waste. An owner/operator may elect to rely on data supplied by the customer for the initial waste characterization. However, the waste management facility remains liable for any incorrect characterizations.

In addition, off-site facilities must inspect, and if necessary, analyze each hazardous waste movement received at the facility to determine whether it matches the identity of the waste specified on the manifest. This inspection can be anything from visual inspection coupled with physical analysis to a fingerprint type analysis to in-depth analysis testing.

Given the cost and delays attendant to waste testing and the liability improper decisions can present to the facility, the Agency has presented a method for facilities to use in determining recharacterization frequency. It is intended primarily for facilities to use in determining recharacterization frequency. It is intended primarily for facilities that receive wastes from off-site generators, however, it may also be modified for use by on-site facilities. The method allows the following criteria to be evaluated when determining how often to recharacterize the waste:

- The potential for restricted wastes to be combined in a waste shipment that is normally permitted.
- The design limitations of the hazardous waste management process.
- The likelihood of the waste undergoing changes that will affect its manageability.
- The prior history of the waste generator performance and reliability.

Weighing factors, ranging from one to five, are assigned to each of these criteria to assess its relative importance. After assigning weights, probabilities ranging from zero to four should be chosen for each criterion indicating the likelihood of a given generator and waste meeting that criterion. For example, what is the likelihood of a contracted waste having a restricted waste mixed in its shipment. The criterion weight and probability are then used to calculate the percent of a generator's shipments that should be recharacterized each year. Further details on conducting these calculations can be found in "Waste Analysis Plans - A Guidance Manual" EPA Publication No. EPA/530-SW-84-012, October 1984 (GPO No. 055-000-00244-4, Telephone: 202-783-3238).

In addition to the material in SW-846 and the Waste Analysis Plan Guidance Manual, OSW will be developing a guidance manual on representative sampling that will address these concerns and anticipates publication in mid 1987.

Detection Limits vs. Quantitation Limits for use as Regulatory Thresholds

The leachate test levels that the Agency has developed for use in the Land Disposal Ban and the Toxicity Characteristic based on toxicological considerations range from the ppm to the sub-ppb level. This presents a problem for the Agency since some of these concentrations are below the measurement range of the currently available analytical methods.

EPA believes that the appropriate way to deal with this problem is to establish analytical method based regulatory levels. Such levels could be set at the analytical detection limit or, as an alternative, they could be set at the limits of accurate quantitation.

Use of either detection limits or quantitation limits would allow for regulatory levels that fall below the analytically measurable level to be periodically updated as advances are made in analytical methodology. In evaluating how to resolve this issue, the Agency has to weigh the fact that the limit of detection for a given analyte and method would tend to vary more from laboratory to laboratory than would the quantitation limit which is significantly higher and thus freer from interferences and less analyst/instrument sensitive.

FACILITY OPERATION MONITORING

One of the major issues facing the hazardous waste management industry is how to monitor a facility's operation to insure that it both meets the terms of its permit and is not causing environmental damage. Our ability to monitor many of the factors affecting facility operation is in its infancy. Techniques are expensive and, in some cases, are of unproven accuracy. Issues facing us here include:

- For each type of opreation, what parameters need to be monitored in order to insure adequate performance of the process,

- What methods are available for such monitoring and can less expensive methods be developed to accomplish the same task.

When an applicant designs or applies for a permit for a hazardous waste management facility, questions relating to waste properties, facility applicability, process effectiveness and operational quality control need to be addressed. All these require measurement of one or more properties. Attendent to these measurements are a number of additional issues. These include:

- How do facilities insure that client wastes arriving at the plant for treatment or disposal have the same properties as those initially evaluated,

- What testing should be performed to prevent wastes banned from land disposal from being disposed of in such facilities,

- What testing should be required of storage facilities, especially short-term shortage units or transit accumulation units,

- What testing should be required of a treatment facility (e.g., incinerator, stabilization unit, chemical destructor) prior to issuance of a permit to determine the boundary conditions of the process (e.g., how to test to determine the range of constituents and concentrations that can be fed to the incinerator without causing the destruction/ removal efficiency to drop below that which is acceptable),

- How to determine the background environmental levels (e.g., ground water quality) prior to construction of the facility (e.g., thoroughness of testing) and what to do when the quality (e.g., sensitivity) of the monitoring methods improves after the facility is in operation (e.g., should one have to reevaluate the site or should a facility be allowed to continue to use the old methods).

ENFORCEMENT

How to insure that the data being gathered by the regulated community is accurate enough for correct decision making. The RCRA program is a self implementing program where the EPA or authorized State establishes action levels and the regulated community takes action based on the properties of the waste or facility.

Given the precision of the various aspects of the testing that is performed and the problem of obtaining truly representative samples with limited sampling, how high an excursion above the regulatory threshold should be permitted before enforcement action is initiated.

Given the large number of facilities and factors that need to be evaluated when making compliance inspections, what types of tests should be used for screening facilities in order to reduce the cost of the inspections.

Finally, given the complexity of waste testing, what type of quality assurance/quality control program should be incorporated into the RCRA program to insure that persons and companies conducting such testing both know how to do the tests, and properly perform such testing.

POSTER SESSION

LIQUID RELEASE TEST (LRT) FOR LIQUID LOADED SORBENTS

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ABSTRACT

The Liquid Release Test (LRT) for liquid-loaded sorbents is needed to detect the potential release of held liquids when sorbents are subjected to pressures from landfill overburdens.

This presentation describes the relation of the test to the different mechanisms by which liquids may be released from sorbents, and the development of a commercially available compressed-air driven consolidometer test unit. Two commercially available Zero Headspace Extractors were shown to be suitable for the test: the model 3740-ZHB ZHE made by the Associated Design and Manufacturing Company, and the model SD 1P58 1C5 ZHE made by the Millipore Corporation.

Initial liquid release ranges were defined for five sorbents and five organic liquids. Sorbents tested were Floor Dry, Florco, S-N-D, Fuller's Earth and bituminous fly ash. Liquids tested were aqueous calcium sulfate solution, aqueous acetone solution, diesel fuel, trichloroethylene, and xylene.

The test protocol was subjected to a single laboratory evaluation, including a ruggedness test. The ruggedness test showed that changes in sorbent-sorbate equilibration time prior to testing; test pressure, pressure application mode, testor drive direction, and sample size did not affect the test results significantly, when the changes were kept reasonably small within the range of laboratory differences to be anticipated. Small changes in the liquid loading within the range of initial liquid detection did not affect the results significantly either. A 5-minute change in test duration produced a difference in results (increase in proportion of liquid releases observed) that was very nearly statistically significant at the 0.05 probability level.

Based on the ruggedness test, the standard deviation of a Liquid Release Test (set of 3 tests) is estimated at 0.29 proportion releases.

INTRODUCTION

To carry out its responsibilities under RCRA, the Environmental Protection Agency needs a test method to indicate whether liquids can be released from sorbent materials under landfill pressures. Although the Paint Filter Test is a quick and easy field test that gives reproducible results, it does not address the release of liquids when sorbents are compressed.[1] Since amendments to RCRA require regulations that prohibit the landfilling of liquids absorbed in materials that biodegrade or release the liquids when compressed, an adequate Liquid Release Test (LRT) must be developed.[2]

Many sorbent materials of organic and mineral origin are in commerical use for the containment and removal of liquids from spill sites and for shipment of hazardous liquids. Although the sorbtive capacity of these materials is well-known, their ability to retain liquids under landfill conditions has not yet been fully evaluated. For this reason, the LRT test development required consideration of the mechanisms of liquid release from sorbents in landfills and of the characteristics of the relationship between liquid concentration and its potential for release.

MECHANISMS OF LIQUID RELEASE

Soil mechanics theory points out four mechanisms by which liquids may be released from sorbents:[3]

1. The liquids may be squeezed out by consolidation of the sorbents under over-burden pressures;

2. The liquids may drain from the sorbents under gravitational suction;

3. The liquids may be leached or washed from the sorbents by water percolation; and

4. The sorbents may biodegrade, thereby losing their ability to retain liquids.

Test methodologies with principles of application related to the first two mechanisms were considered for evaluation. A consolidation test using simulated over-burden pressures was investigated because it relates to the squeezing out of liquids by consolidation. A centrifuge test using weights on top of the samples was investigated because it relates to the squeezing out and the gravitational suction mechanisms. A methodology related to the leaching mechanisms was not studied since leaching is covered by another test, the Toxicity Characteristic Procedure (TCLP). Sorbent biodegradation was not used to define a test methodology because sorbents that biodegrade are specifically banned from landfill use.

TEST DEVELOPMENT

Because of the large number of variables involved in calculating pressures to be expected in a given landfill, the test was designed such that it could be applied over a range of pressure. Studies by Peirce and Shah indicate that the pressures to 45 lb/in^2, (310 kPa) are to be expected, depending upon the density and depth.[4,5]

CONSOLIDATION TEST

Two types of test units were utilized in the development of the consolidation test: the conventional consolidometer and the Zero Headspace Extractors employed for the Toxicity Characteristic Leaching Procedure (Figures 1, 2, and 3).

Consolidometers designed and used at Duke University to measure hydraulic conductivity were modified for use in the consolidation test (Figure 1). The top and bottom of the unit were made of polyvinyl chloride, while the cylinder and piston were made of transparent cast acrylic. Teflon disks 0.8 mm thick were placed above and below the sample. Approximately 30 holes spaced from 0.5 to 1 cm apart were drilled into the disks using a 1 mm diameter drill bit. A filter paper was positioned next to each Teflon disk to collect any liquid which moved from the test sample under the vertical loading. The perforated disks were used to facilitate movement of this liquid to the paper while preventing the filter paper from collecting liquid from the sample by capillary suction.

A 100-gram sample of the liquid loaded sorbent was placed in the test unit between the perforated Teflon disks, with absorptive filter papers placed against the opposite sides of the disks. A compressive force was applied through the piston stem for a specified time. Release of liquid was indicated when a visible wet spot was observed on either filter paper, or distinct droplets of liquid were present on the inner surface of either Teflon disk.

Initial tests focused on two typical sorbent materials: Fuller's Earth and Floor Dry, and two liquids: 0.01 N aqueous calcium sulfate and 5-volume percent acetone in water. These sorbent materials were selected to provide a range of sorbent characteristics used commercially.[6] The calcium sulfate solution was selected because it is widely relied on by researchers and practitioners as a standard water for investigation of landfill liner permeability. The acetone solution was selected as a representative solvent found at hazardous waste landfills.[7]

Over-burden pressures cause the bulk densities of sorbents to increase under compaction, reducing the effective pore

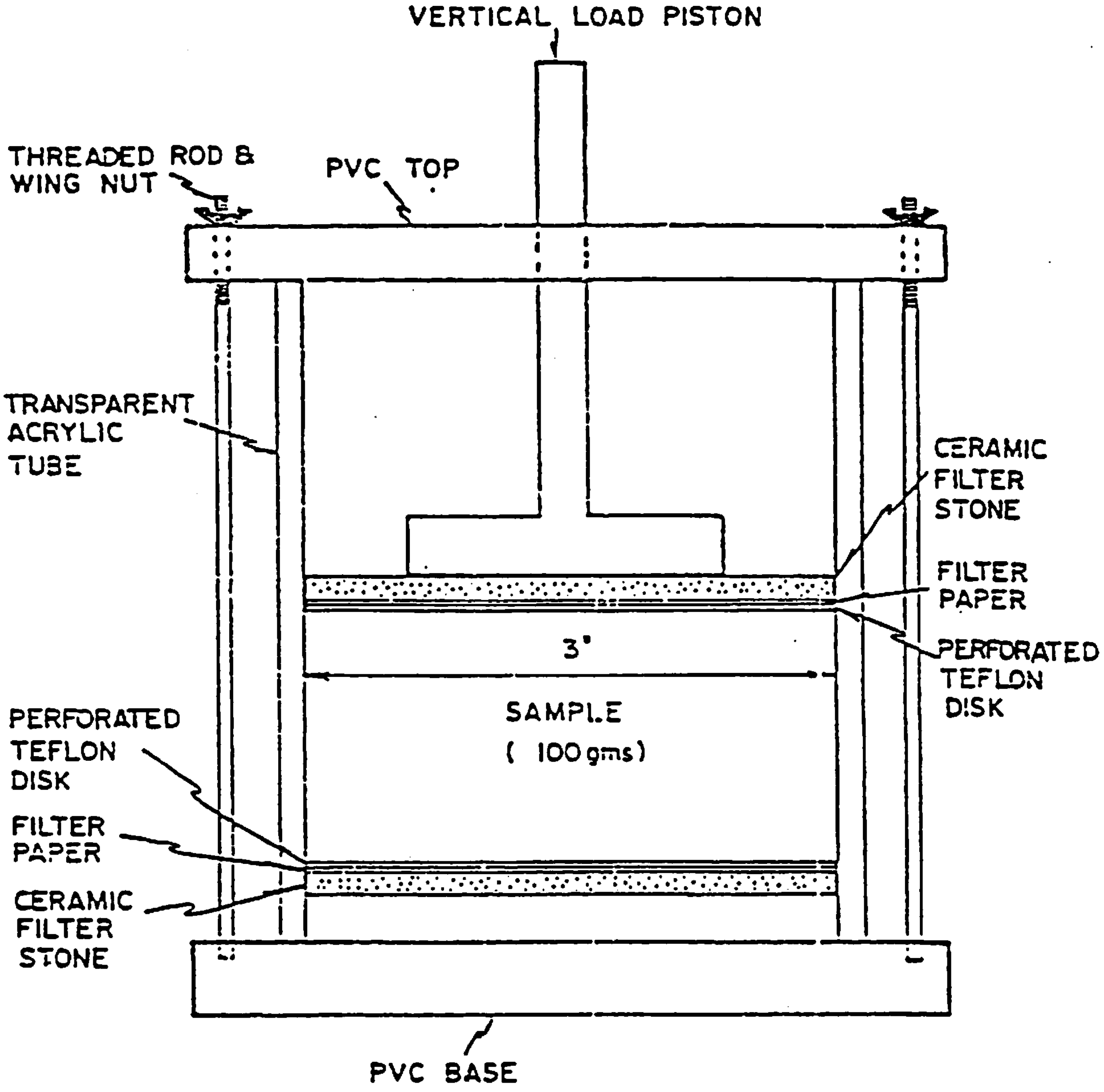

Figure 1. Pressure test consolidometer.

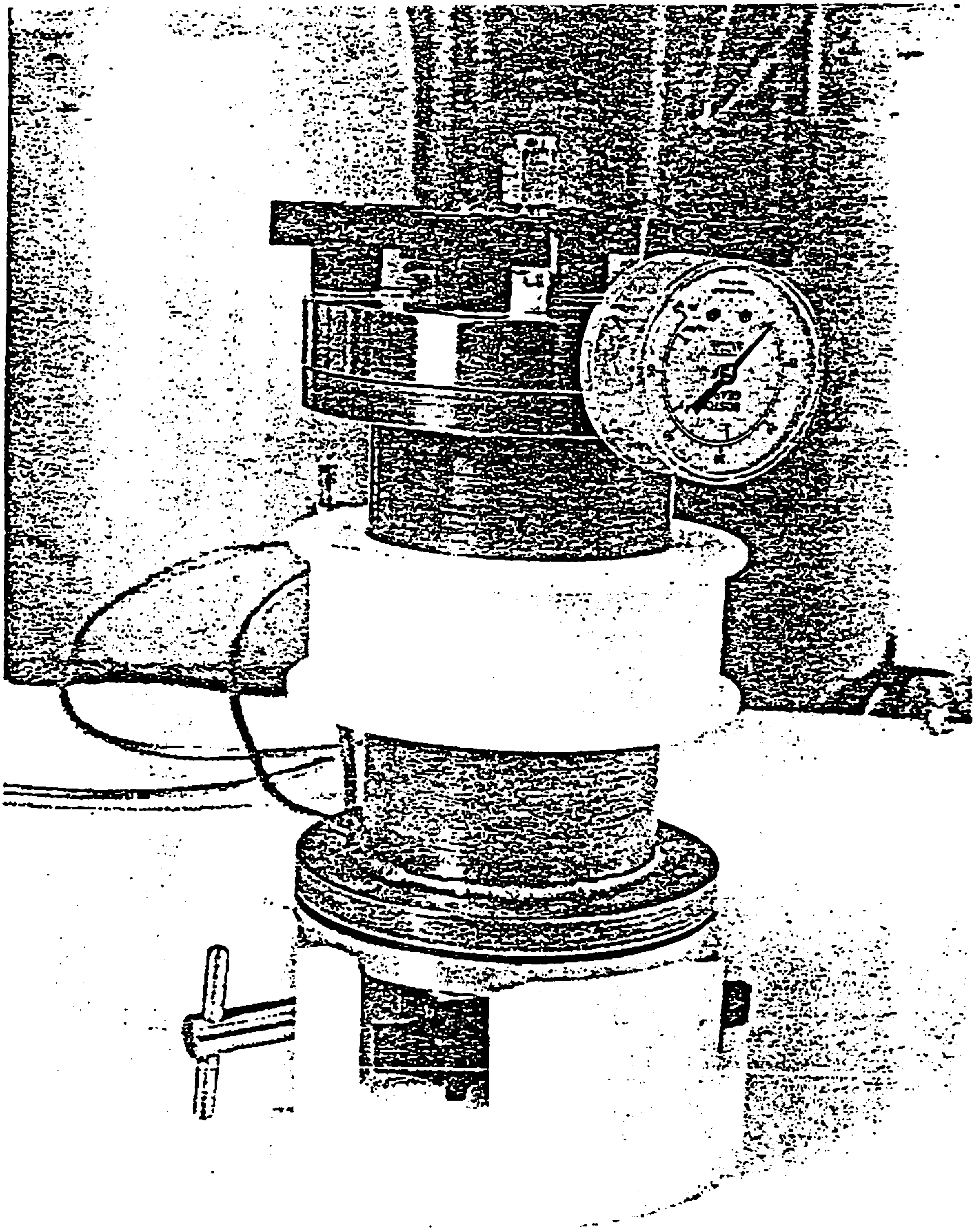

Figure 2. ZHEV, Associated Design and Manufacturing Co. Model.

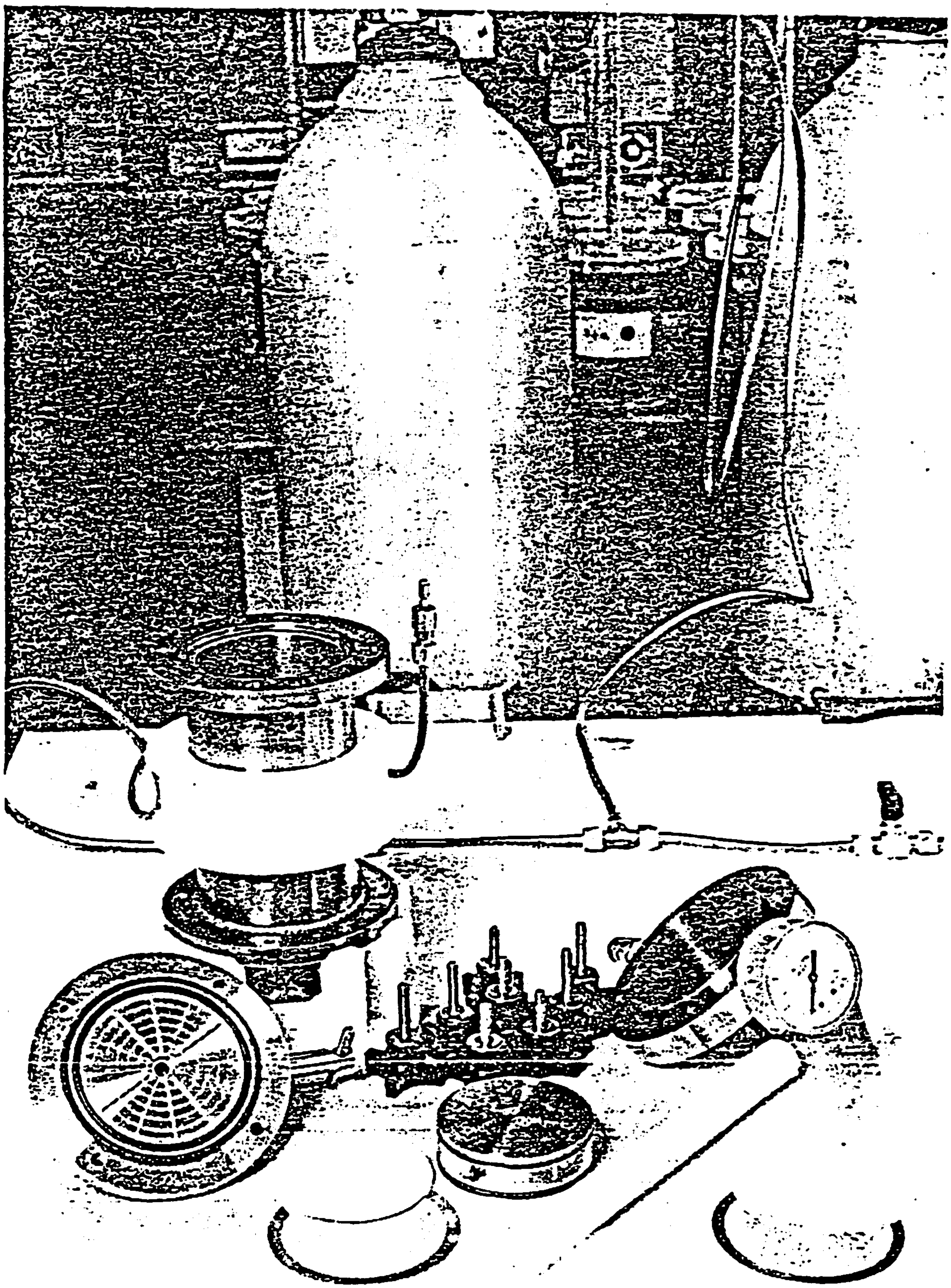

Figure 3. ZHEV, Associated Design and Manufacturing Co. Model, disassembled.

volume of the material and allowing the liquid to be released. The compaction was measured as the fall in height of the protruding stem of the piston. The compaction of the sorbents was measured at 15-second intervals for the first minute of the test. After that, measurements were taken at one minute intervals. The tests were continued until equilibrium consolidation conditions were achieved. For these sorbents, a consolidation rate of less that 0.001 cm per minute was selected as the definition of a state of equilibrium. This equilibrium was generally achieved 10 minutes after the load was applied. Accordingly, initial test data were collected using a 10-minute testing time. The testing time was later extended to 30-minutes to allow more time for drainage of any released liquid.

Two commercially-available compressed-air driven Zero Headspace Extraction units were used for tests of additional sorbents and liquids. These units were the Model 3740-ZHB Vessel made by the Associated Design and Manufacturing (ADM) Company (Figures 2 and 3) and the model SD1P581C5 Vessel made by the Millapore Corporation. With the test time extended to 30 minutes, these units gave results equivalent to those obtained with the consolidometer. The ADM unit was easier to use, and most of the results reported herein were obtained with it. Except for the longer testing time, the test procedure was the same for these units as for the consolidometer. These units have no stem on the pistons, so that compaction rates cannot be measured with the accuracy available with the consolidometer. On the other hand, the units can be used for two tests of sorbents: the Liquid Release Test and the TCLP.

A range of liquid loadings was investigated to establish the liquid release characteristics of the sorbents under pressure. Initially pressures of 103 and 310 kPa (15 and 45 lb/in^2) were both used. Later tests used only the higher pressure.

Three tests cells were used to provide three replicate tests for each liquid load. Each test result is a pass/fail rating indicating whether the liquid was not released (test passed) or was released (test failed). Replication of the test is necessary in order to provide an estimate of the percent of the tests that show release of liquid. As shown in Figure 4, this percent is zero for low liquid loadings, and 100 for excessive liquid loadings. Between these extremes, there is a transition zone within which the percent of tests showing release varies from 33 to 66 (for greater numbers of replicates, the percentages would show greater numbers of intermediate values). This transition zone has been defined as the initial released liquid detection range of the test. These ranges are shown in Table 1. Because the sorbent materials are natural materials, they may be expected to vary somewhat in composition and physical

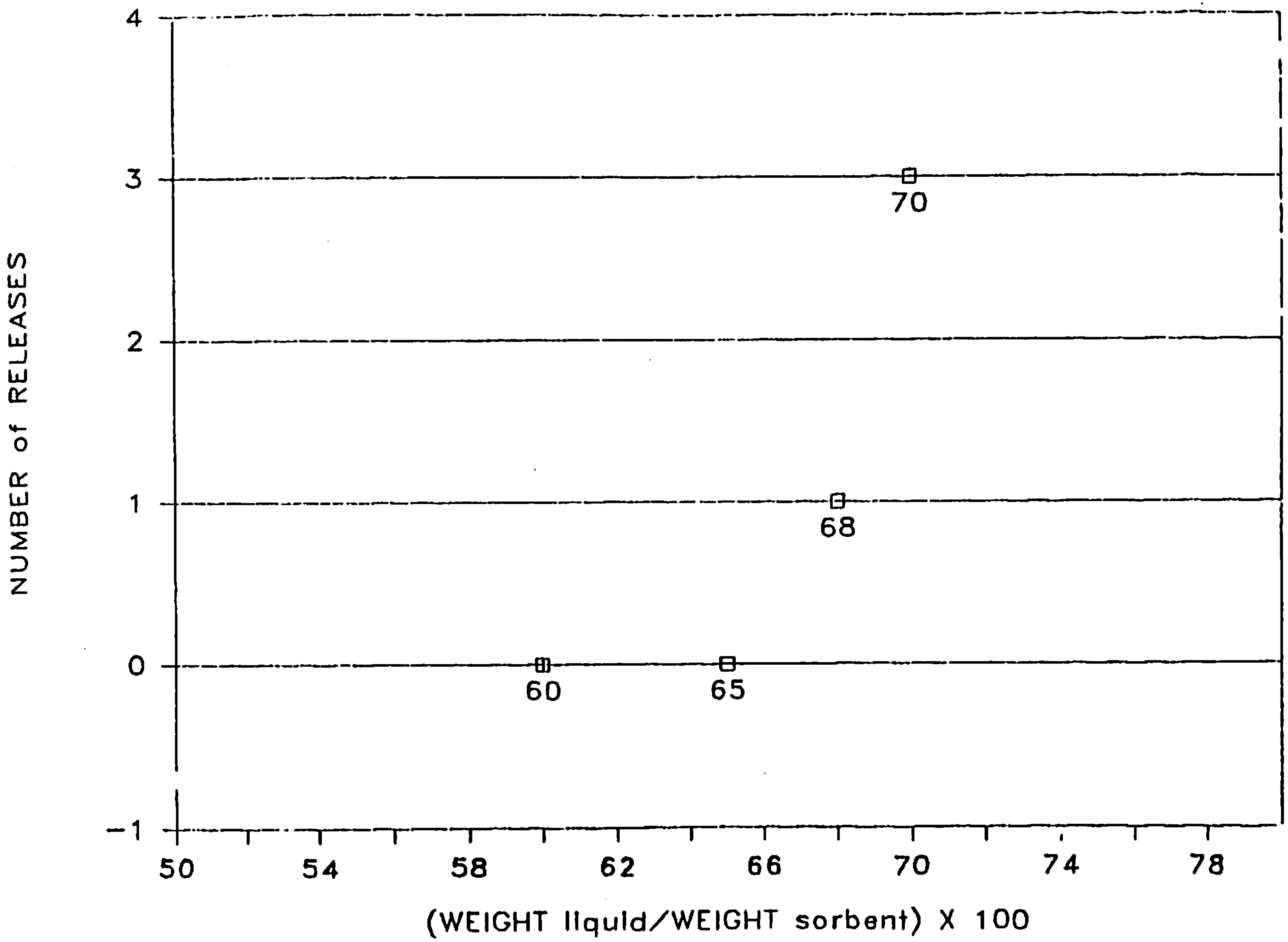

Figure 4. Diesel Fuel/Florco Liquid Release Characteristics, Sorbent Pressure Test

TABLE 1. CONSOLIDATION TESTS OF SORBENTS AND SORBATES
INITIAL RELEASED LIQUID DETECTION RANGES, W/W PERCENT[a]

	Liquid, w/w%				
	Diesel Fuel	Trichloroethylene	Xylene	Acetone Solution[b]	Calcium Sulfate Solution[c]
Fly Ash, Bituminous	<10	42[d]	<10	--	--
S-N-D	40-45	78-83	45-50	--	--
Florco	65-68	115[e]	65-68	--	--
Floor Dry	80[e]	140-155	80-85	90-120	140-190
Fuller's Earth	--	--	--	60-75	55-65

[a] W/W PERCENT = (wt liquid/wt sorbent) x 100

[b] 5 vol % acetone in water

[c] 0.01 N $CaSO_4$ in water

[d] one liquid release in three tests

[e] two liquid releases in three tests

structure from lot to lot, and these ranges should be expected to vary from lot to lot also.

CENTRIFUGE TEST

In evaluation the centrifuge methodology for sorbent testing, the effects of a range of centripetal force from 95 to 968 g's were explored. Since the higher portion of this range was obtained using lead weights placed on top of the sample, the range represents primarily the difference depths of overburden that might be placed upon a loaded sorbent. It also provides a range of hydraulic gradients (ratios of head loss to length of flow path) both including and exceeding the gradients expected over a depth of landfilled material. The consolidation test does not provide this gradient.

The tests were conducted using relatively small samples in filtration tubes fabricated for use in a table model laboratory centrifuge. The tubes were fabricated using standard 24 mm i. d. Pyrex glass tubing, a coarse grade fritted glass plate (40 to 60 micron pore size), and a standard taper ground glass joint. The plate was sealed into the tubing to provide a filtration base and support the sample. Figure 5 shows the construction details. A glass cup was fitted onto the tapered joint beneath the plate to collect released liquid. Lead disks, 24.0 g each were used to provide weight loadings on top of the sample and were sized to provide 0.5 mm tolerance and thus fit easily into the sampler, on top of the sample. A lid, or plastic seal, was used to prevent evaporation of liquid from the sample during the test. This filtration tube fitted into a standard 50-ml centrifuge shield.

A piece of coarse-grade Fisher filter paper was placed in the filtration tube to cover the fritted glass plate. The sample, sorbent with known liquid content, was weighed into the tube, and lead disks were placed on top. Pairs of samples were placed opposite each other in the centrifuge. The pairs were adjusted to essentially equal gross weight by varying the sample size slightly. During the tests, the samples were subjected to the lowest chosen g force by setting the equivalent rpm. After maintaining this force for 15 minutes, the sample container was reweighed to determine the weight loss. The reweighed sample was then subjected to the next higher selected g force for 15 minutes, and the weight loss again determined. This repeated application of successively higher g forces was continued over the desired range, with weight losses determined at each step. In selected tests, a final centrifugation was carried out for an additional hour in order to obtain data for analysis as to ultimate weight loss. Centrifuge tests were conducted both with the glass cup in place beneath the filtration tube, and without the cup. In either case, the glass pieces

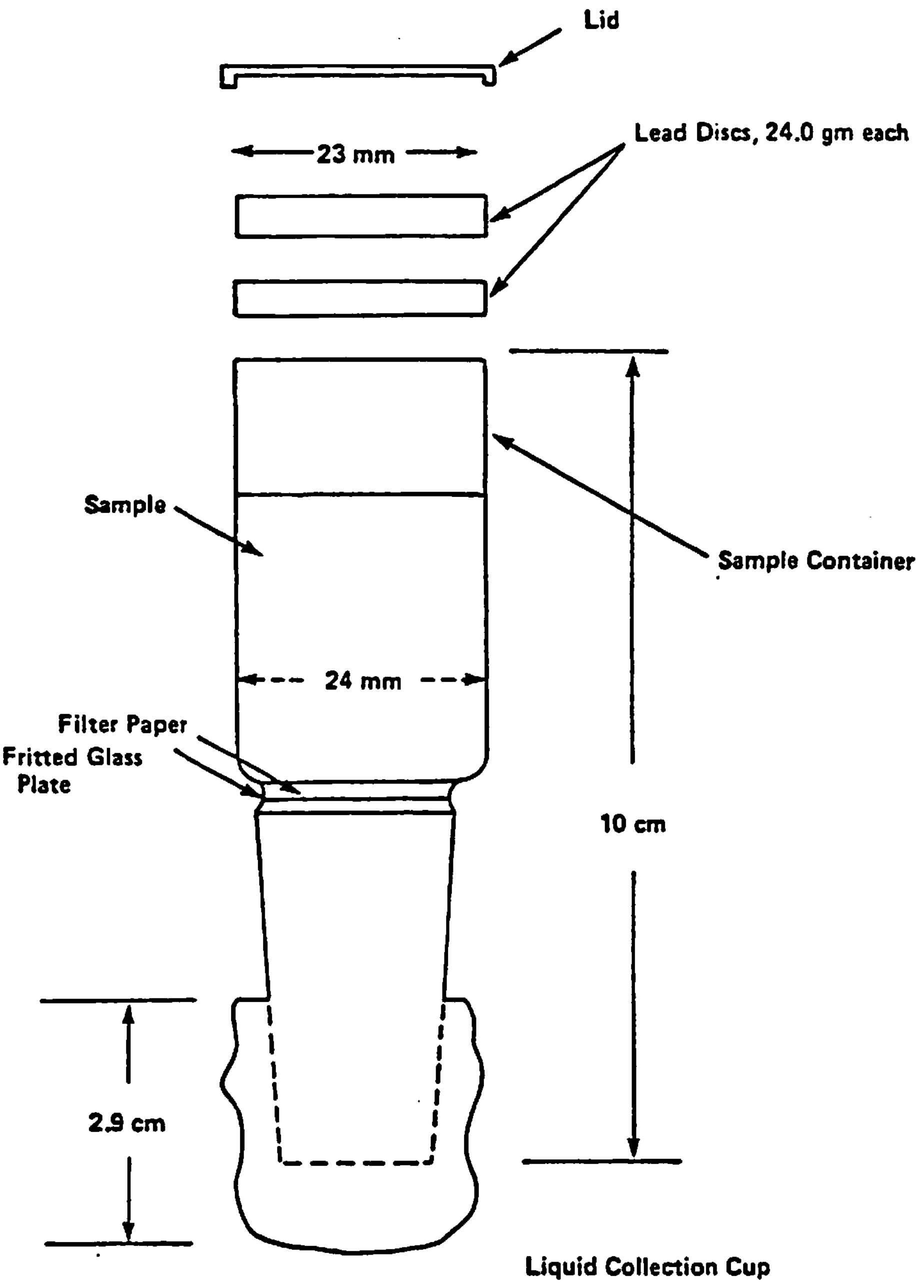

Figure 5. Sample cell for centrifuge test.

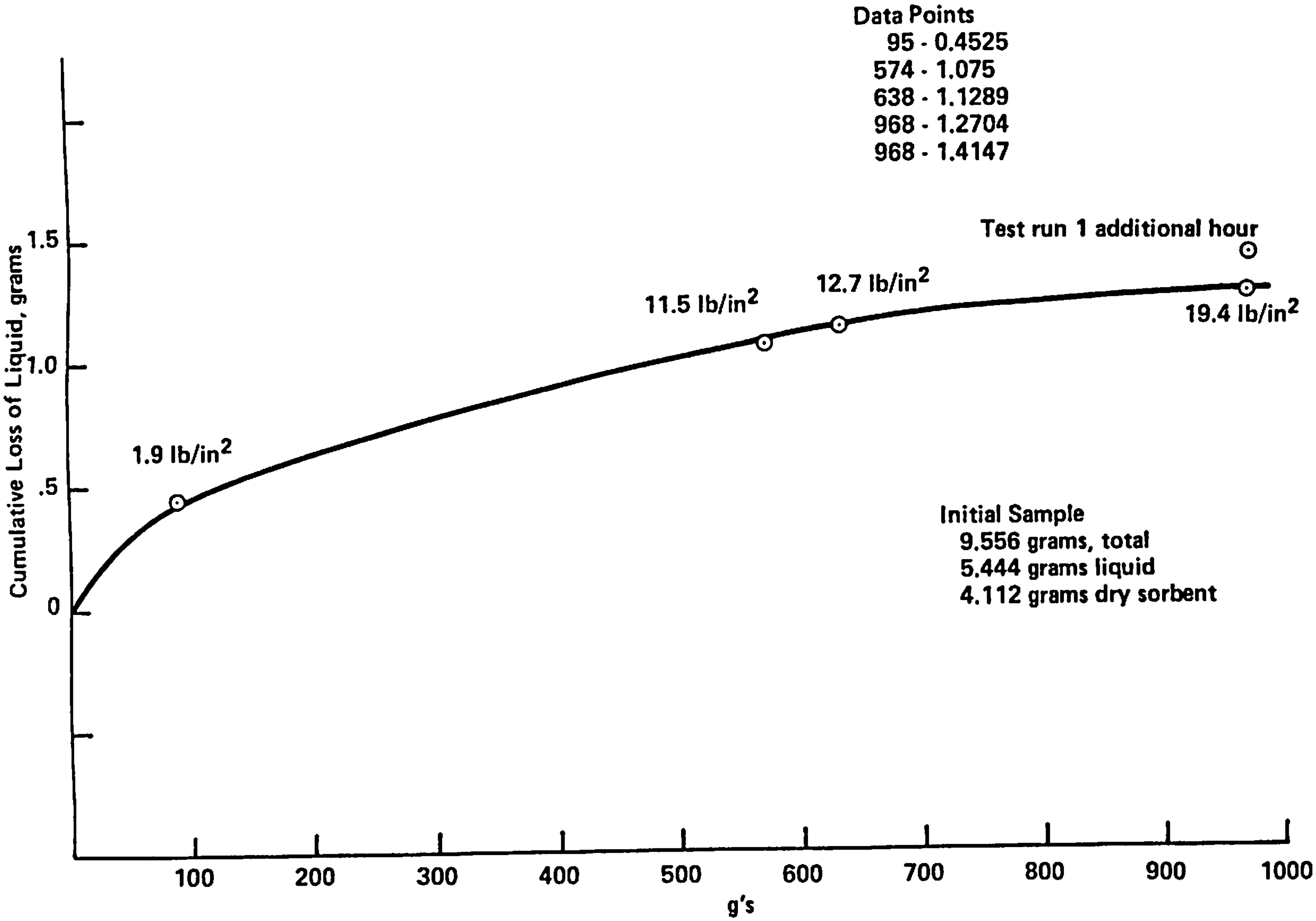

Figure 6. Release of 132.4 w/w % calcium sulfate solution from floor dry under applied centrifugal forces.

were supported within the centrifuge shield by a rubber cushion.

Tests were carried out using Floor Dry samples loaded with calcium sulfate solution or with acetone solution. Tests were also run using the Fuller's Earth sorbent, but only the acetone solution was investigated. Liquid loadings tested included those within the release range for the consolidation test (Table 1) and those below this range.[8] Figure 6 shows the results for Floor Dry loaded with 132.4 w/w% Calcium Sulfate solution. This sample was tested without the use of the lead weights. During the first 15 minutes, 0.4525 gram of liquid was released at a g force equivalent to 1.9 lbs/in_2. Successive tests, at 11.5, 12.7 and 19.4 lb/in2 resulted in incremental additional liquid losses of 0.6225, 0.539, and 0.1415 grams respectively over a total testing time of one hour. The sample was then tested for another hour, giving an additional liquid release of 0.1443 grams. Floor Dry was also tested within the range of acetone solution loadings for which consolidation test showed liquid release. These tests confirmed the release.

Tests using Fuller's Earth were carried out using only the acetone solution. Loadings within the range of liquid release shown by the consolidation test were confirmed. A 51.2 w/w% loading of liquid showed a slight release (0.0069 grams out of 2.3372 total contained in the sample) at 12.1 lb/in^2 in 15 minutes. This liquid loading is below the range of 60-75 found with the consolidometer. Tests of liquid loadings within this range showed releases at 1.9 lb/in^2 for 15 minutes, confirming the previous findings.

RUGGEDNESS TESTING

The consolidation test was chosen for ruggedness evaluation, rather than the centrifuge test because the latter would require a large model centrifuge to accommodate the desired 100 grams of sample, and the smaller sample sizes, 7 to 10 grams, that could be used in table model centrifuges were considered too small to be representative of the sorbent materials to be tested.

RUGGEDNESS TEST DESIGN

The ruggedness testing was done principally to determine the procedure's sensitivity to minor reasonable variations in the different test conditions. These tests are necessary so that the procedure may be specified and controlled as closely as needed to avoid excessive variation among different laboratories. In addition, this ruggedness test also tested whether the storage of the sample would alter its liquid release characteristics. Some of the samples were stored for 15 days prior to testing, to provide for further equilibration of the mixture so that any need for such time extension between mixing of the materials and testing could be determined.

LIQUID RELEASE TEST PROTOCOL FOR RUGGEDNESS TEST

The ruggedness tests were run as described in this section, with changes in the procedure deliberately introduced at points indicated by an (*). Numbered subheadings 1.0 through 8.9 shown are those defining the test protocol.

1.0 SCOPE AND APPLICATION

1.1 The Liquid Release Test (LRT) is designed to indicate whether liquids can be released from sorbents when exposed to landfill pressures.

1.2 Any liquid-loaded sorbent which fails the EPA Paint Filter Free Liquid's Test (SW-846 Method 9095), shall be assumed to release liquids in this test. Analysts should make sure that material in question will pass the Paint Filter Free Liquid's Test.

2.0 SUMMARY OF METHOD

(*) 2.1 A 100 ± 0.1 gram representative sample of the liquid-loaded sorbent is placed between twin perforated Teflon disks in a device capable of simulating landfill pressures. Absorptive filter papers are placed against the opposite sides of these Teflon disks, and a compressive force of 310 kPa (45 lb/in^2) is applied. Release of liquid is indicated when a visible wet spot is observed on either filter paper, or distinct droplets of liquid are present on the inner surface of either Teflon disk.

3.0 INTERFERENCES

3.1 When testing sorbents loaded with liquids that are capable of rapidly evaporating (e.g., solvents), any liquid migrating to the filter paper may eventually evaporate. For this reason, all filter papers shall be examined immediately after the conduct of the test.

4.0 APPARATUS AND MATERIALS

4.1 Pressure Tester: For the purposes of this test, an acceptable pressure tester is one that is capable of accommodating a pressure of up to 414 kPa (60 lb/in^2), and which is capable of being quickly and easily dismantled for inspection of the filter papers. This pressure tester shall have an internal volume of 500 to 600 ml, and be equipped to accommodate fitted filter papers and Teflon disks (see Figures 1 and 2). Suitable apparatus known to EPA are identified in Table 2 The devices identified in Table 2 are known as Zero Headspace Extraction (ZHE) Vessels. The same device (with several minor modifications) is used in the Toxicity Characteristic Leaching Procedure (TCLP), for evaluating the potential leachability of volatile compounds. To avoid confusion, this method also refers to the device as the ZHE or ZHE vessel.

4.2 Pressure Source: The ZHE is pressurized using compressed gas (e.g., air, nitrogen.) This may be supplied from a compressed gas cylinder equipped with a suitable regulator, or may be supplied using a simple air pump, providing that such devices are capable of delivering the required pressures to the ZHE. The ZHE or the pressure source shall be equipped with a pressure gage accurate to within ± 7 kPa (1 lb/in^2), to indicate when the desired pressure has been attained.

(*) 4.3 Balance: A balance accurate to within ± 0.1 grams.

4.4 Teflon disks: Two 0.8 mm thick Teflon disks, perforated with 1 mm diameter holes, spaced approximately 5 mm apart (can be ordered with ZHE).

4.5 Filter papers: Two 90 mm absorptive filter papers (Whatman No. F2410-9, or Millipore No. 8P4004705, H5D75931A, or equivalent). One is cut to fit into the piston of the ZHE; the other fits without adjustment over the Teflon disk next to the ZHE end-piece.

5.0 REAGENTS

5.1 None required.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples shall be collected using a sampling plan that addresses the considerations discussed in "Test Methods for Evaluating Solid Wastes (SW-846)."

6.2 Preservatives shall not be added to samples, and samples shall not be kept at freezing temperatures.

(*) 6.3 Samples shall be tested as soon as possible after collection, but in no case after more than two days after collection. If samples must be stored, they shall be stored in sealed containers and maintained under dark, cool conditions.

7.0 PROCEDURE

7.1 Place the piston within the body of the ZHE such that it is approximately in the middle of the device. Secure the gas inlet/outlet flange to the device in accordance with the manufacturer's instructions.

TABLE 2. SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS

Company	Location	Model No.
Associated Design and Manufacturing Company	Alexandria, Virginia (703) 549-5999	3740-ZHB
Millipore Corporation	Bedford Massachusetts (800) 225-3384	SD1P581C5

7.2 Position the ZHE in an upright position, and place one of the filter papers against the piston and one of the Teflon disks on top of it.

(*) 7.3 Weigh out a representative sample of 100 ± 0.1 grams, and transfer it into the test unit on top of the Teflon disk.

7.4 Using a stirring rod, gently smooth the sample so that it is distributed evenly across the diameter of the test unit.

7.5 Place the other teflon disk on top of the sample, and the other filter paper on top of the Teflon disk. Assemble the liquid inlet/outlet flange to the device (with the stainless steel screen provided with the device set in place over the filter paper), in accordance with the manufacturer's instructions.

(*) 7.6 Tighten all fittings, make sure that the ZHE is in a vertical position, and open the liquid inlet/outlet valve.

> NOTE: Some samples, upon testing, may produce enough liquid in a strongly positive test such that it is capable of flowing out of the valve. To prevent any liquid flowing from this valve from contaminating the surrounding area, a liquid collection device (e.g., expandable sample bag, syringe) should be attached to the valve before proceeding to the next step.

(*) 7.7 Connect the pressure supply line to the gas inlet/outlet valve, and begin applying pressure, increasing the pressure to 69 kPa (10 lb/in^2) in 20 seconds. Slowly increase the pressure in 69 kPa (10 lb/in^2) increments, to a maximum of 310 kPa (45 lb/in^2). Allow 20 seconds to attain each 69 kPa increment of pressure.

> NOTE: Instantaneous application of high pressure can cause the filter paper to burst. If the filter bursts, the test must be redone using a fresh sample.

(*) 7.8 Let the test unit stand at 310 kPa (45 lb/in^2) for 30 minutes. Check the pressure at 5-minute intervals, and adjust as necessary. Very little adjustment should be necessary, unless the unit is leaking. If leaking is indicated, check and replace the ZHE O-rings, or other fittings, as necessary, and redo the test with a fresh sample.

(*) 7.9 After 30 minutes, turn off the compressed air supply, release the pressure from the unit, and immediately and carefully disassemble the device so that the filter papers may be inspected.

7.10 Examine the filters for the presence of any wet spots. The presence of a wet spot(s) indicates a positive test (i.e., liquid release). The presence of a distinct droplet of liquid on the inner surface of either Teflon disk also indicates a positive test.

8.0 QUALITY CONTROL REQUIREMENTS

8.1 Repeat any test twice, using fresh samples, whenever no liquid release is indicated in the first or second test (total of three tests), to insure that the test is negative. A release of liquid in any one or more of the three tests indicates a positive test result.

8.2 All data should be maintained for easy reference and inspection.

RUGGEDNESS TEST DESIGN

The ruggedness test requires an experimental design designating the total number of tests to be made, and indicating how the minor variations in the test procedure are to be applied throughout the tests to provide a set of data adequate for analysis. The analysis should provide measures of any excessive variations, and measures of within laboratory precision.

The test design is based on the use of a Plackett-Burman fractional factorial experimental design as prescribed by Youden and Steiner.[9] The test matrix is pictured in Table 3. Each row prescribes values of a test condition. Thus each column prescribes a set of conditions for each ruggedness test. Capital letters (A,B,...G) denote nominal values; small letters (a,b,...g) denote slightly altered values that might affect the test. Conditions altered included sample equilibration time, test pressure, sample size, test duration, pressure application mode, piston drive direction, and liquid loading.

During development of the test, samples were prepared and allowed to equilibrate for 24 hours before testing. The samples were kept sealed to prevent loss of liquid. In addition, the sealed containers were shaken periodically while equilibrating to keep the particles mixed and to insure that the liquid was distributed as evenly as possible among them. Nevertheless, it was felt that a further test of the adequacy of equilibration time should be made. For this reason, the samples tested for ruggedness were divided into two sets. One set was tested after the usual 24 h waiting time, the other set, after 360 h (15 days).

Pressure settings of 310 kPa (45 lb/in^2) are the usual level applied. To determine the sensitivity of the test to small

TABLE 3. RUGGEDNESS TEST DESIGN

Test Condition	Value of the Condition of Determination Number 1	2	3	4	5	6	7	8
1 Sample equilibrium time	A	A	A	A	a	a	a	a
2 Pressure	B	B	b	b	B	B	b	b
3 Sample Size	C	c	C	c	C	c	C	c
4 Duration	D	D	d	d	d	d	D	D
5 Pressure Application Mode	E	e	E	e	e	E	e	E
6 Piston Drive Direction	F	f	f	F	F	f	f	F
7 Liquid Loading	G	g	g	G	g	G	G	g

A: 24 h a: 360 h B: 310 kPa b: 345 kPa C: 100 g c: 105 g

D: 30 min d: 35 min E: Pressure raised to set point in 10 sec

e: Pressure to 69 kPa in 20 sec; 69 to 138 kPa in 20 sec; 138 to 207 kPa in 20 sec; 207 to 276 kPa in 20 sec; 276 to set point in 10 sec.

F: Piston presses down to test f Piston presses up to test

G: 96.5 w/w % (5 vol % acetone solution)

g: 95.5 w/w % (5 vol % acetone solution).

changes in the applied pressure, some of the tests were conducted at 345 kPa (50 lb/in^2).

Sample size was set at the usual 100 g and also at 105 g so that the sensitivity of the test to small changes in weighings of the sample might be determined.

The normal testing time, 30 min, was extended to 35 min for some of the tests in order to determine how critical exact timing of the test would be.

In other applications of the test vessels, other researchers had observed that the filters had become torn or ruptured by quick application of the pressure. Therefore two modes of raising the sample to test pressure were employed. The usual procedure of raising the pressure to set point in 10 seconds was used in half the tests; the gradual increase of applied pressure, reaching each additional 69 kPa (10 lb/in^2) in 20 seconds was used in the other half. All tests were observed for damage to the filters as well as for wetness.

The ADM tester can easily be used with the piston driven downward or upward during the application of test pressure. The Millipore vessel, however, cannot conveniently be used except in the upward driven position. Since all previous test data had been collected with the piston driven downward, both directions of drive were used in the ruggedness test to see if the direction changed the results significantly.

During the preparation of samples for the ruggedness test, a new lot of Floor Dry was used. It was found not to hold the expected amount of acetone solution that had been observed on previous tests of other lots of the material. Preliminary tests made with the new lot showed consistent liquid release at 105 w/w % liquid loading. Therefore a new search was made for the initial liquid release range of the new lot, and it was found to be between 95 w/w % and 98 w/w %. For this reason, the liquid loadings of 95.5 and 96.5 were adopted for the ruggedness test. These loadings were found to yield data within the range for which 1 to 2 releases in three tests were obtained. This range was necessary to make the data analyzable and the results interpretable.

Each column of Table 3 defines a set of conditions under which 9 tests were conducted. The total number of tests required for ruggedness determination was estimated 72. The estimate is based on the needs to have a high probability, P' = 0.9, of finding a difference as great as 0.33 in a one-tail statistical evaluation test at the 5 percent significance level of the proportion, p, of tests showing liquid release. The ruggedness test was conducted at a liquid loading for which the expected proportion of liquid releases was approximately 0.5. Accordingly, a difference of 0.33 would be found with a high degree of certainty. This difference would be critical, since it would lead to acceptance of loaded sorbent for landfill if the altered test condition showed no liquid releases for a material loaded to correspond with a 0.33 proportion of releases.

Applying these criteria, the number of tests, n, were estimated using the formula:

$$n = \frac{(t_{\alpha} + t_{\beta})^2 (p_1 q_1 + p_2 q_2)}{(p_1 - p_2)^2}$$

where:

t_{α} = the deviate of the "t" distribution corresponding to a one-tailed test at the 5 percent level;

t_{β} = the deviate of the "t" distribution corresponding to a one-tailed 0.9 probability level;

P1 = fraction of tests showing liquid release;

q_i = fraction of tests not showing liquid release;

n = tests required per condition i;

1 denotes standard condition;

2 denotes altered conditon.

Substituting the required values and solving for n gives:

$$(1.69 + 1.306)^2 \; (0.33 \times 0.66 + 0.66 \times 0.33)/0.33^2 = 36$$

The total number of tests is twice the number per condition (2 x 36 = 72).

This formula is based upon methodology described by G. W. Snedecor and William G. Cochran.[10] The original formula was based on the use of a test with known standard deviation. Since we are estimating the standard deviation from the test data, we have substituted values of deviates of the "t" distribution for those of the normal distribution.

With 72 tests required, the Plackett and Burman experimental design (Table 3) was repeated nine times.

RUGGEDNESS TEST RESULTS AND DATA ANALYSIS

The results of the ruggedness test are shown in Table 4. For each of the 8 sets of test conditions employed in the

TABLE 4. RUGGEDNESS TEST RESULTS

	Test Conditions							Test Results		
	A	B	C	D	E	F	G			
Test Set	Equilibrium time, h	Pressure kPa[a]	Sample Size, g	Test Duration min.	Pressurization Rate[b]	Piston Driven	Liquid Loading w/w%	Liquid Releases	Total Tests	Fraction Release, "p"
1	24	310	100	30	fast	down	96.5	4	9	0.4444
2	24	310	105	30	slow	up	95.5	6	9	0.6667
3	24	345	100	35	fast	up	95.5	5	9	0.5556
4	24	345	105	35	slow	down	96.5	6	9	0.6667
5	360	310	100	35	slow	down	95.5	7	9	0.7777
6	360	310	105	35	fast	up	96.5	4	9	0.4444
7	360	345	100	30	slow	up	96.5	2	9	0.2222
8	360	345	105	30	fast	down	95.5	3	9	0.3333
TOTAL								37	72	

[a] 310 kPa = 45 lb/in^2: 345 kPa = 50 lb/in^2

[b] fast = prescribed pressure reached in 10 sec.; slow = prescribed pressure reached in 90 sec.

TABLE 5. ANALYSIS OF RUGGEDNESS TEST RESULTS

Test Condition	Difference Tested	Difference in Proportion of Liquid Releases	Corresponding t_α	Statistical Significance
Test duration, min	35-30	0.6111-0.4167=0.1944	1.68	almost 0.05[a]
Equilibration time, h	24-360	0.5833-0.4444=0.1389	1.19	not signif. (0.10)
Liquid Loading, w/w%	95.5-96.5	0.5833-0.4444=0.1389	1.19	not signif. (0.10)
Pressure, kPa	310-345	0.5833-0.4444=0.1389	1.19	not signif. (0.10)
Pressure Application Mode	slow-fast	0.5833-0.4444=0.1389	1.19	not signif. (0.10)
Piston Drive Direction	down-up	0.5555-0.4722=0.0833	0.71	not signif. (0.25)
Sample Size, g	105-100	0.5278-0.5000=0.0278	0.236	not signif. (0.25)

[a] The t_α value for a significance level of 0.05 is 1.69.

ruggedness test, the table lists the number of liquid releases observed, the total number of tests conducted, and the fraction of them that showed liquid releases.

The effects of the changes in test conditions were calculated from the data of Table 4 by first computing the proportion of releases for each set of 36 tests obtained by summing the results over all sets that employed a particular level of each condition. These proportions were then compared by taking their differences. For example, test sets 1, 2, 3, and 4 were all made after 24 h equilibration time. These when combined showed a 0.5833 proportion of releases. Sets 5, 6, 7, and 8 showed a 0.4444 proportion of releases. The difference, 0.5833 - 0.4444 = 0.1389 is a measure of the effect of the change in equilibration time. In this comparison, all the other changes average out, since their levels both appear an equal number of times. The differences observed for each of the conditions tested are listed in descending order of magnitude in Table 5.

The statistical significance of these differences was tested using the Student "t" Test. The value of t_a was computed using the following formula:

$$t_{\propto} = \frac{6\ (P1 - P2)}{(P1q + P2q_2)^{0.5}} - 1.306$$

The values of "t" computed were compared with those for significance levels of p = 0.05, 0.10, and 0.25. This comparison is summarized in the Statistical Significance column of Table 5. In accordance with the planned decision to use the 0.05 level as the criterion for significance of an effect, none of the conditions tested showed a significant effect. The test method may be considered rugged with respect to these conditions. As noted in the table, however, the effect of test duration, 0.1944, was uncomfortably close to being significant. This differnce showed a "t" value of 1.68 versus a criterion value of 1.69. In view of this, it appears that the test time, 30 min, may not be sufficiently long to give proper indication of the release potential of loaded sorbents exposed to landfill pressures continuously. Further investigation of the effect of testing would be needed to determine whether, indeed, a 30 min test adequately distinguishes those sorbents which will release liquids in landfills.

The standard deviation of a single test series (3 tests) was determined by two methods. 1) Based on the average over the entire set of data for the ruggedness test, 37 liquid releases were obtained in 72 tests. The corresponding standard deviation of a test series is 0.2885 proportion releases, calculated by:

$$s.d. = (pq/n)^{0.5} = (0.5138 \times 0.4861)/3^{\ 0.5} = 0.2885$$

REFERENCES

1. Test Protocol for Free Liquids, FR 47,38, February 25, 1982, p. 8311.
2. Congressional Record, October 3, 1984.
3. Artiola, J.F.; K.W. Brown and D. C. Anderson, "Theoretical Evaluation of Gravitational Forces and Consolidation on the Behavior of Sorbents in Landfills.
4. Peirce, J. J. Soil Preparation and Permeability Testing with Consolidation Cell Apparatus, final report, EPA Contract 68-03-3149, 24-2, September 28, 1984.
5. Shah, S. I., letter of February 1, 1985, to David Friedman, Testing Criteria for Free Liquid Test, Task Group under ASTM Section 034.02.07, Physical Analytical Methods.
6. Artiola, J. C., letter of March 21, 1985, to Steve Piper, GCA Technology, concerning selection of sorbents and liquids for study.
7. Brown, K. W., and D. G. Anderson, "Effects of Organic Solvents on the Permeability of Clay Soils," EPA-600/2-83-016, U.S. EPA, 1983.
8. Carpenter, B. H.; J. J. Peirce; T. A. Peele, and K. A. Witter, "Liquid Release Test Development," Final Report, U.S. EPA Contracts 68-03-3149 and 68-01-7075, Task 38, March 7, 1986.
9. Youden, W. J. and E. H. Steiner, Statistical Manual of the Association of Official Analytical Chemists, A.O.A.C., Box 540, Benjamin Franklin Station, Washington, DC 40044, 1975.
10. Snedecor, G. W. and W. G. Cochran, Statistical Methods, 6th Ed., Iowa State University Press, Ames, Iowa, 1967.

EVALUATION OF METHODS FOR DETERMINING CHLORINE IN WASTE OILS

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ABSTRACT

The Environmental Protection Agency has issued a final rule prohibiting the sale for burning in non-industrial boilers of used oils contaminated above specified levels with certain metals and total chlorine. When burned as fuel in a small boiler, the contaminants may be emitted to the ambient air at hazardous levels. This regulation establishes a rebuttable presumption that used oil containing more than 1,000 ppm total chlorine has been mixed with halogenated solvents and is a hazardous waste. Rebutting the presumption requires the seller of the oil to prove that this chlorine is not due to halogenated solvents or other hazardous halogenated organics. If the rebuttal is successful, the oil can be sold as fuel up to a level of 4,000 ppm total chlorine.

To provide enforcement authorities and the regulated community with appropriate methods to meet the chlorine testing requirements of this regulation, an interlaboratory evaluation of test methods and instrumentation was conducted. The objectives were to assess the precision, accuracy, detection limit, matrix effects, interferences, field portabilities, and cost of this testing.

Methods and instrumentation evaluated included classical ASTM bomb oxidation followed by gravimetric, titrimetric or ion chromatographic analyses; instrumental microcoulometric titration using a chlorine analyzer; energy and wavelength dispersive x-ray fluorescence; a field kit based on a chemical colorimetric reaction; and a test device based on a flame photometric response.

The evaluation was carried out by nearly 20 cooperating laboratories who performed more than 120 analyses on around 40 samples of spiked virgin and waste oils. Spike constituents included water; volatile, semivolatile, and inorganic chlorine compounds. In addition, oil fuels and blends with waste oils were evaluated.

EVALUATION OF SELECTED DIGESTION METHODS FOR DETERMINING HEXAVALENT CHROMIUM IN SOLID WASTE MATRICES

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ABSTRACT

The analyses of solid waste materials for hexavalent chromium present formidable challenges to the analytical scientist. A metal speciation scheme such as the differentiation between trivalent and hexavalent chromium species, Cr(III) and Cr(VI), must address the capability to maintain the integrity of the individual species during all the sample manipulation phases of the overall analytical method. Whereas much reseach has focused on the separation and detection of dissolved chromium species in synthetic aqueous mixtures or relatively clean liquid environmental samples, the chemical solubilization and determination of insoluble chromates in solid waste materials have not been adquately addressed.

The present study has focused on an investigation of selected digestion methods for the chemical solubilization of insoluble Cr(VI) in barium chromate test compounds and in real environmental samples. An alkaline digestion medium, consisting of an aqueous solution of sodium carbonate and sodium hydroxide, and acid digestion media, consisting of nitric acid alone and in the presence of potassium persulfate, were studied. The digestion methods were evaluated in regard to their capabilities to solubilize solid test samples without reducing Cr(VI) or oxidizing Cr(III) species. A spectrophotometric method, specific for Cr(VI) using the diphenycarbazide (DPC) color reagent, was employed to measure concentration changes in hexavalent chromium for each test sample solution resulting from chromium redox phenomena occuring during the digestions. The relative merits of the digestion methods based on the analytical results and redox considerations of these experiments will be discussed in the present paper.

DEVELOPMENT OF A FIELD TEST FOR MONITORING ORGANIC HALIDES

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ABSTRACT

In the past, used oil has provided a valuable energy source in its use as a fuel for industrial and commercial boilers. There has been recent concern, however, as to the health risks involved in burning recycled oil containing halogenated compounds. As reported in the November 29, 1985 edition of the Federal Register, these health risks have prompted the EPA to impose new regulations involving the use and management of used oil. Specifically, levels for total halogen content have been set between 1000 ppm and 4000 ppm. Above this concentration range, the oil is considered to be a hazardous waste. Since about 500 million gallons of used oil are burned each year, an inexpensive and reliable test method is needed for determining the halogen content of a used oil at the site of its generator.

In response to this need, Auburn University, under sponsorship of the EPA, has been working on the development of a field test to determine halogen concentrations in waste oils. This test is an extension of the Beilstein flame emission test. The test is very inexpensive, easily performed and agrees with the standard ASTM oxygen bomb technique within ± 10 to 15 percent.

The test is a very simple procedure requiring only hydrogen and copper wool as replenishable materials. A copper probe is first burned to remove any oxidation which may interfere with the test. The clean probe is then dipped into the oil sample and placed in the flame. Copper halides radiate light at about 436 nm; therefore, the presence of halides is indicated by a blue-green emission. Since the intensity of the blue-green emission is a function of the halide concentration, this concentration can be determined by measuring the flame intensity using a photocell. The halide content of very non-volatile samples can be determined as low as 50 ppm. More volatile samples require dilution with a low volatile oil. For most waste oils, a dilution ratio of 10:1 diluent oil to waste oil is sufficient; this results in a lower threshold detection limit of 500 ppm halide.

The testing procedure works well for most waste oils. The reproducibility is poor for oils which contain significant amounts of water or for those that are highly volatile. With experience the test can be used to screen even these types of oil, but the results are not very quantitative.

This test has shown great promise for on-site determinations of halide concentrations in waste oils. Inconclusive tests are obtained for only a small percentage of oils, but even these samples can usually be screened qualitatively for the 1000 ppm limit. This test can be performed by waste oil users, dealers, and transporters as well as EPA enforcement personnel thus making the new regulations more easily met. This test represents a simple, inexpensive, and reliable method of screening waste oils for halide contamination in the field.

RCRA LABORATORY CERTIFICATION

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ABSTRACT

The Office of Quality Assurance (OQA) within the New Jersey Department of Environmental Protection develops laboratory standards for the Department's Safe Drinking Water and NPDES (NJPDES) programs, and administers a laboratory certification program. The existing certification program was first promulgated for drinking water in 1977. Certification for water and wastewater was offered beginning in 1981. The USEPA Region II RCRA staff incorporated a work output in the FY 1986 USEPA/NJDEP RCRA Interagency Agreement which requires the Department to begin evaluating compliance and performance of analytical laboratories which report measurement data to the Agency and the Department with respect to the RCRA program. OQA made a decision to develop a laboratory certification program for waste analyses (RCRA) and to incorporate such a program into its current regulations.

The RCRA laboratory certification program, as it is currently proposed, would provide laboratories with certification in four (4) major categories: waste characterization, inorganics, organics and miscellaneous analyses. Laboratories will be certified by individual parameter or analysis under the categories of waste characterization, inorganics (AAS), and miscellaneous analyses. For organics analyses, laboratories will be certified for entire analytical methods rather than by individual analytes (for example, a laboratory will be certified for all parameters covered under SW-846 Method 8240 rather than by each individual analyte listed in the method). Laboratories will be requested at the time they apply for certification to designate which matrices among (aqueous and/or nonaqueous) will be analyzed under their RCRA certification. The program will require, along with NJDEP's RCRA Regulations, that all laboratories which submit RCRA compliance data to the Department must be certified for the applicable parameters or methods.

The new regulations will cover administrative procedures for the program, such as annual fees for certification, laboratory personnel qualifications, proficiency evaluation, on-site inspections, and enforcement. Many new administrative proposals are incorporated into the proposed regulations, including a more efficient enforcement

procedure which will apply to drinking water, water/wastewater, and waste analysis certifications.

Development of the waste analysis certification program has also raised many other issues which are under review at OQA, such as development of performancce evaluation samples, analytical method development and validation, method equivalency procedures, and, in the long-term, establishment of laboratory performancce standards and uniform quality control procedures.

INTRODUCTION

Since its establishment in November, 1983, the Office of Quality Assurance has been the focal point within the New Jersey Department of Environmental Protection (NJDEP) for development of laboratory standards, quality assurance, and laboratory certification. The Office currently reviews quality assurance project plant and standard operating procedures for the Department's varied environmental monitoring programs, audits and advises NJDEP's divisional QA programs, administers the Department's contract for analytical services, and develops and administers the Department's regulations for certification of environmental testing laboratories.

The existing laboratory certification regulations were first promulgated by NJDEP for drinking water only in 1977. At that time, the program was based primarily upon the U.S. Environmental Protection Agency's certification program for the proposed National Interim Primary Drinking Water Regulations, 40 CFR Part 141. The State Department of Health, the agency delegated the authority for the certification program at that time, offered drinking water laboratory certification in five categories, microbiology, limited chemistry, atomic absorption, gas chromatography, and radiology. In 1978, the program was transferred to the Department of Environmental Protection, where it was expanded to include many parameters added by the passage of New Jersey's Safe Drinking Water Act by the State legislature. The additional parameters are referred to as the "secondary drinking water parameters."

Certification of laboratories reporting data to the Department for compliance with the National Pollutant Discharge Elimination System (NPDES, now called NJPDES after delegation to New Jersey by the USEPA) was offered beginning in 1981. This program for water and wastewater testing was divided into four categories: microbiology, limited chemistry, atomic absorption, and gas chromatography.

Soon after promulgation of the water/wastewater certification regulations, the Department's, as well as the USEPA's, emphasis on safe drinking water and controlled elimination of discharges was matched by the advent of the Federal CERCLA (Superfund) and RCRA programs. In addition, New Jersey enacted its own legislation which requires sellers of commercial and industrial properties to demonstrate that their sites are free from hazardous contamination. This bill, known as the Environmental Cleanup Responsibility Act (ECRA), combined with the Federal Acts, brought much attention to the analysis of multi-media environmental samples for organic and inorganic contaminants. CERCLA analytical work provided to the Department by contractors is generally performed in accordance with the USEPA Contract Laboratory Program's Information for Bid (IFB) documents. Use of the analytical methods in these documents, which are revised frequently, is made possible by the absence of legislation regarding analytical requirements such as those imposed by two 40 CFR Part 141 (drinking water), 40 CFR Part 136 (water/wastewater), and 40 CFR Part 261 (RCRA waste analysis). The Federal regulations compensate for their decreased flexibility by providing for standardization of analytical procedures over an extended period of time and, as a result, continous generation of additional data in support of the methods' validations from a growing nationwide pool of government, industrial, and commercial laboratories.

Because of the substantial need for analysis of multi-media samples for hazardous contaminants, the Office of Quality Assurance sought to improve and maintain the quality of data reported for compliance with the NJPDES, ECRA, and RCRA regulations. In late 1985, OQA began to study the feasibility of certifying laboratories for multi-media waste analysis. The release of 40 CFR Part 261 as final rule provided the impetus for the design of a new laboratory certification program for laboratories which report compliance or investigation data to the Department of RCRA. Also, because of the similarities and overlaps of some NJPDES and ECRA monitoring requirements with those of RCRA, OQA proposed to expand the applicability of the certification regulations to those programs. In January, 1986, the first draft of the new regulations was distributed for peer review within the Department. Many modifications were incorporated and a final proposal of the Regulations Governing Laboratory Certification and Standards of Performance (N.J.A.C. 7:18-1.1 et seq.) will be available for public comment through the <u>New Jersey Register</u> during the summer of 1986.

ORGANIZATION OF THE RCRA LABORATORY CERTIFICATION PROGRAM

The Laboratory Certification Program, as it is proposed, is made of up three major "categories". Each category is further divided into several "subcategories". The following outline of the program illustrates these categories and subcategories:

TABLE 1
ORGANIZATION OF THE LABORATORY CERTIFICATION PROGRAM

DRINKING WATER (including SDWA)

- Microbiology
- Limited Chemistry
- Inorganics (AAS and "wet chemistry" methods)
- Organics (THM's, pesticides, herbicides, and other organics)
- Radiology

WATER/WASTEWATER (including NJPDES)

- Microbiology (including recreational bathing water testing)
- Ames Testing
- Limited Chemistry
- Inorganics (AAS, ICP, and "wet chemistry" methods)
- Organics (priority pollutant organics)
- Radiology (including Radon)
- Bioassays

WASTE ANALYSIS (including RCRA, NJPDES, and ECRA)

- Waste Characterization
- Inorganics
- Organics
- Miscellaneous

Each subcategory contains numerous individual parameters and/or analytical methodologies for which certification is offered. Certification by parameter or by method is dependent upon practicality factors and instrumentation. Generally, inorganics certification for laboratories utilizing atomic absorption spectroscopy is issued by individual analyte because each analytical measurement is considered to be an individual analysis. On the other hand, analysis of inorganics by inductively coupled plasma (ICP) and organics by gas chromatography (GC or GC/MS) are handled as measurements of groups of analytes using one method at a time; thus, certification is issued by analytical method rather than by analyte.

The Waste Analysis category, which includes analyses for RCRA compliance and investigations, is illustrated in detail in Table 2 below. The category is organized to correspond directly with "Methods for Evaluation of Solid Waste," USEPA, SW-846. A system of offering combined sample preparation/extraction/analysis procedures was initially considered (e.g. combinations of 3000-series procedures with 7000- and 8000-series procedures). However, due to the overwhelming number of combinations possible, OQA decided to offer certification for the analytical procedures along with general certification for "aqueous" and "nonaqueous" matrices. At the time laboratories apply for certificaton in the Waste Analysis category, they will be required to specify one or both of the two general matrices for which they are requesting certification. For example, if a laboratory requests certification for halogenated volatile organics and specifies nonaqueous matricies on the application, and assuming that the laboratory has met all other conditions for certification, the laboratory will be certified for "Nonaqueous Halogenated Volatile Organics."

TABLE 2
WASTE ANALYSIS CERTIFICATION

WASTE CHARACTERIZATION

- Ignitability
- Corrosivity
- Reactivity
- EP Toxicity

INORGANICS

- Each 7000-series analyte by AAS

ORGANICS

- Halogenated volatile organics
- Nonhalogenated volatile organics
- Aromatic volatile organics
- Acrolein, acrylonitrile, and acetonitrile
- Phenols
- Phthalate esters
- Organochlorine pesticides/PCB's
- Nitroaromatics and cyclic ketones
- Polynuclear aromatic hydrocarbons
- Chlorinated hydrocarbons
- Organophosphorus pesticides
- Chlorinated herbicides
- Volatile organics (GC/MS)
- Semivolatile organics (GC/MS)

MISCELLAENOUS

- Total and amenable cyanide
- Total organic halides (TOX)
- Sulfides
- pH

APPLICABILITY OF THE RCA LABORATORY CERTIFICATION REGULATIONS

The proposed RCRA laboratory certification regulations were developed with specificity targeted toward compliance monitoring of New Jersey RCRA facilities. However, the current need for regulation of waste analysis points to a much broader scope of applicability. For example, the Department's NJPDES program administers permits and regulates the State's subsurface disposal facilities (such as leaking, underground storage tanks, groundwater injection, landfill leachates, etc.). The monitoring requirements for such facilities generally mandate collection and analysis of multi-media samples to demonstrate compliance with their permit requirements. The methodologies currently referenced by the Department's NJPDES regulations are the wastewater methods promulgated by 40 CFR Part 136 (October 26, 1984). These methods are not applicable to more complex matricies which may be encountered with monitoring of wastes. The NJPDES program will therefore benefit from being enabled to require that a laboratory reporting compliance data for these facilities be certified in the Waste Analysis category.

The New Jersey Environmental Cleanup Responsibility Act (ECRA) will also be able to mandate the use of certified "waste analysis" laboratories because of similar monitoring requirements.

ADMINISTRATION OF THE RCRA LABORATORY CERTIFICATION PROGRAM

The administration of the laboratory certification regulations in the Office of Quality Assurance is funded by annual fees which are assessed for each category. Since there are four subcategories under the Waste Analysis category, the proposed regulations provide for four distinct fees.

The laboratory certification program regulates education and experience requirements for laboratory managers, supervisors, and technical personnel. For example, those personnel directly involved with analysis of environmental analysis of environmental samples associated with RCRA must meet the following requirements:

1. GC operators must have at least nine (9) months experience in the operation of the GC on environmental samples. A formal training course in the operation of the GC may be substituted for three (3) months of experience.

2. GC/MS operators must have completed a formal training course in GC/MS operation and have at least nine (9) months experience in the operation of the GC/MS on environmental samples.

3. Extraction-concentration specialists must have at least one (1) year experience in the preparation of extracts from environmental samples.

4. Purge and trap specialists must have at least six (6) months experience using the purge and trap technique for volatile organics.

5. Pesticide and herbicide residue specialists must have at least two (2) years experience in organochlorine/organophosphorus pesticide, herbicide, and PCB analyses, including method-specified clean-up procedures on environmental samples.

6. Mass spectral interpretation specialists must have at least two (2) years experience in the interpretation of mass spectra generated from GC/MS analysis of environmental samples.

7. Atomic absorption spectrometer operators must have at least six months experience in the operation of atomic absorption equipment or have completed a formal training course in the operation of atomic absorption equipment.

Until such time that proficiency evaluation samples for RCRA are validated, the certification program will base a laboratory's eligibility for certification in the Waste Analysis category on the information submitted with the application and on its findings from on-site evaluations of the laboratory. These on-site inspections of the laboratory cover all areas regulated by the Department and generally include audits of actual data reports submitted to the Department by RCRA facilities. The laboratories are afforded thirty (30) days from notification of deficiencies in which to correct those deficiencies and notify OQA of such. OQA plans to conduct annual announced on-site evaluations of "waste analysis" laboratories. The Office has also begun to conduct unannounced inspections of laboratories, especially if a problem is exhibited by the data reported to the Department.

The regulations provide for broader, more defined enforcement of the regulations than in the past. The Office of Quality Assurance may suspend a laboratory's "waste analysis" certificaton indefinitely for such infractions as unsatisfactory performance (when PE samples become readily available), data reporting deficiencies, failure to respond to deficiencies noted by OQA, and noncompliance with any requirements of the regulations. OQA may also decertify a laboratory for serious violations of the regulations including, but not limited to, direct or indirect misrepresentations to the Department and falsification of records. In addition to the above, OQA may assess deficient laboratories for fines of fifty (50) dollars to five thousand (5,000) dollars for each deficiency or violation. The enforcement process has been streamlined to permit rapid turnaround for handling of deficiencies and violations, and to expedite the corrective action process.

FUTURE DIRECTION OF THE RCRA LABORATORY CERTIFICATION PROGRAM

As mentioned earlier, the Office of Quality Assurance does not currently evaluate the performance of RCRA laboratories. NJDEP's needs for validated multi-media performance evaluation samples cannot be over-emphasized. The Office is eager to participate in the development of these samples and has documented proposals for such.

The agencies within the NJDEP which administer the RCRA program have established certain deliverables requirements which, in addition to being used for validation of sample results, are being stored in a database. OQA plans to use the database to develop uniform laboratory performance standards for such things as surrogates, matrix spikes (accuracy), and matrix spike replicates (precision).

The Office of Quality Assurance advocates the development of performancce standards, along with standardized test procedures, as vital steps in achieving data comparability, which is of great importance to any long-term monitoring program. Although the Office receives numerous requests for alternative test procedures, each proposal is assessed against the existing methodologies. It is far more important to a program such as RCRA to maintain consistency in test procedures than to continually update "state of the art" procedures, which damages data comparability. The RCRA Laboratory Certification Program is designed to assure data comparability and to control the approval of alternate test procedures.

U.S. EPA REFERENCE STANDARDS AND QUALITY ASSURANCE MATERIALS FOR THE ANALYSIS OF ENVIRONMENTAL CONTAMINANTS

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ABSTRACT

To support the need for a certified, quality-contolled, common database in the analysis of contaminating chemical agents in environmental substrates, U.S. EPA's Environmental Monitoring Systems Laboratory (Las Vegas) and Environmental Monitoring and Support Laboratory (Cincinnati) jointly maintain several repositories of analytical grade refernece materials under the Agency's quality Assurance Reference Materials (QARM) Project. Operated under contract by Northrop Services, Inc. in Research Triangle Park, NC, the project currently offers standards of over 2000 compounds of environmental concern including pesticides and their metabolites and degredation products, PCBs and other halogenated organics, plasticizers, nitrosamines, polynuclear aromatics, and heavy metals. Included amongst these are those Agency-identified compounds commonly known as the "priority pollutants," materials regulated under Appendix VIII (RCRA) and CERCLA (Superfund) legislation, and groundwater monitoring compounds.

The program is currently being supplied by over 180 chemical manufacturing companies and 23 chemical supply houses. Additional compounds, especially select environmental reaction and degradation products, are synthesized and purified in-house. The program currently offers standards of over 2000 compounds of environmental concern. During 1985, more than 100,000 standards were distributed in response to some 6000 requests.

Maintenance of such a repository for both neat (essentially pure) materials and certified solutions necessitates a comprehensive analytical quality assurance (QA) program. The analytical QA support includes component identification, purity assays, concentration verifications, and stability studies using a variety of instrumental methods, for most reference materials, QA protocol comprises identification by mass spectrometry or IR, with subsequent purity assay by GC, HPLC, DSC, or elemental analysis. Additionally, isotopic purity of compounds enriched with stable isotopes (^{13}C, ^{37}Cl, ^{2}H) is established by mass spectrometry. Typical purity of materials distributed exceeds 99%. Prepared solutions of single and multiple components (in sealed ampuls) are analyzed (by GC, HPLC, UV-Vis) to verify concentration immediately after preparation and again at established time intervals to assess stability.

The program supports laboratory quality assurance efforts with standardized column packings and spiked media reference materials. Technical manuals on analytical methods, analytical quality control, standards preparation, and related topics are also available. In addition, the project staff operates a technical information and assistance service, providing chemical/physical/toxicological information, literature searches, methodology, instrumental troubleshooting, and a wide variety of other types of technical information. More than 4000 monitoring, enforcement, and research laboratories in 92 countries are currently utilizing these services, all of which are provided by the Agency without charge.

THE QUANTITATION OF PCB'S AND PCDD'S BY ELECTRON IMPACT GC/MS USING RESPONSE FACTOR ESTIMATION

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ABSTRACT

U.S. EPA methods for the determination of polychlorinated dibenzofurans (PCDF's) and polychlorinted dibenzodioxins (PCDD's) in hazardous wastes (1) and for the determination of polychlorinated biphenyls (PCB's) in samples originating at Superfund hazardous sites (2) require the determination of the concentration of all isomers of a given compound class. For technical, practical, and economic reasons, it is effectively impossible to standardize a GC/MS system for all analytes of interest in such applications of GC/MS. Therefore response factor estimation procedures are required for the quantitation of these important environmental pollutants when various isomers are identified in samples, but standards are not available. The approach currently proposed for the quantitation of PCB's in Superfund analyses utilizes the concept of "isomer group" quantitation. This procedure employs a mean response factor for congeners of the various degrees of chlorination to quantitate "unknown" species. Likewise, the RCRA method for the quantitation of PCDD's and PCDF's also employs mean response factors for quantitation of various tetra, penta, hexa, hepta and octa species. Obviously, the accuracy of "statistical" approaches to RF value estimation depends on how well the RF values utilized to estabish the mean values. Clearly, a formalism which could provide RF value estimates for the quantitation of various "unknowns" would be preferred from a technical accuracy and a QA/QC standpoint, as "The object of all science, whether natural science or psychology, is to co-ordinate our experiences and to bring them into a logical system"(3).

Recently, we have published a model for the estimation of electron impact GC/MS RF values (4). In this work, we have applied our model to estimating RF values for various PCB's, PCDF's and PCDD's with good results. For the thirty compounds listed in Table 1, the average estimated/observed response factor was found at 1.07 ±0.114. These data included 25 RF values determined using full scan data at nanogram levels and 5 RF values determined at picogram levels in the selected ion monitoring mode. While the application of the model is limited to situations where mass and/or chromatographic discrimination are not severe, properly applied, our model provides a formalism which can yield estimated RF values with an average accuracy of

approximately ± 10 percent at one standard deviation. Within a proper QA/QC context, we assert that similar accuracy can be expected for quantitation of various PCB's, PCDD's and PCDF's for which standards are not available. We show how our model can be employed to this effect, and we demonstrate how our model could unify the environmental Quality Control and Quality Assurancce of the GC/MS determination of PCB's, PCDD's and PCDF's.

REFERENCES

(1) RCRA Method 8280, Draft, May 12, 1986.

(2) Proposed Analytical Method for Pesticides and PCB's, Exhibit D, presented at CLP Method Review Conference, Atlanta, Ga, March 1985.

(3) Einstein, A., The Meaning of Relativity, Princeton University Press, Princeton, N.J.

(4) Sauter, A. D., Downs, J. J., Buchner, J. D., Ringo, N. T., Shaw, D. L., and Dulak, J. G., Model for the Estimation of Electron Impact Gas Chromatography/Mass Spectrometry Response Factors for Quadrupole Mass Spectrometers, Analytical Chemistry, in press.

Table 1

Estimated/Observed Response Factors for Selected PCB's, PCDD's and PCDF's

PCB's	Estimated/Observed
2	1.13
3,3'	1.02
2,4,5	1.09
2,2'4,4'	0.974
2,3'4,5',6	0.961
a pentachlorobiphenyl	0.866
2,2'3,4,5,5',6	1.08
2,2'3,3',4,4',5,5'	1.10
2,2',3,3',4,4',5,5',6	1.10
2,2',3,3',4,4',5,5',6,6'	1.13
PCDD's[a]	
2,3,7,8	0.950
1,2,3,7,8	0.925
1,2,3,4,7,8	1.00
1,2,3,4,6,7,8	1.19
1,2,3,4,5,6,7,8	1.08
PCDD's	
2,3,7,8	1.10
1,2,3,7,8	1.10
1,2,3,6,7,8	1.04
1,2,3,4,6,7,8	0.975
1,2,3,4,5,6,7,8	0.925
TCDD's	
2,3,7,8	1.25
1,2,3,8	0.983
1,2,3,4	0.953
1,2,7,8	1.16
1,2,8,9	1.29
PCDF's	
2,3,7,8	1.14
1,2,3,7,8	1.09
1,2,3,4,7,8	1.01
1,2,3,4,6,7,8	1.32
1,2,3,4,5,6,7,8	1.29

$$\frac{X}{E/O} = 1.07 \pm 0.114$$

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[a] SIM RF values provided by D. Catalano, IT Corp., Knoxville, TN.

HAZARDOUS WASTE REGULATIONS IN CANADA

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ABSTRACT

The Constitutions of Canada and the United States contain similar provisions which divide legislative powers between federal and state or provincial governments. Canadian provinces however, have a great deal more autonomy and authority over many affairs than do their American counterparts. In Canada, the provinces exercise considerable control over land and natural resources and thus, their role in environmental matters is extensive. They have significant environmental responsibility and use several legislative and regulatory instruments to carry out that responsibility.

The Canadian Council of Resource and Environment Ministers (CCREM), is composed of federal and provincial Ministers of the environment and natural resources. CCREM meets regularly to discuss the state of the environment and to reach consensus on those areas affecting both levels of government. It reflects the division of powers governing environmental legislation in Canada and the need for cooperative action.

In 1978, in response to growing concern over the potential environmental damage posed by uncontrolled disposal of hazardous waste, CCREM recommended that the federal government, in consultation with the provinces, initiate a program to develop a transboundary control system to track hazardous waste movements. Transborder environmental matters are clearly federal jurisdiction and hence, the only appropriate source of regulation was the federal government.

Accordingly, the Canadian government has developed legislation to control the international and interprovincial movements of wastes. This has been done under the authority of the Transportation of Dangerous Goods Act, 1980. After extensive federal/provincial consultation, the regulations implementing the Act finally came into force July 1, 1985.

Two key areas covered are hazardous waste listing and "cradle to grave" tracking (manifesting) for hazardous waste movements. The hazardous waste listing system is based on a combination of the existing hazard identification procedures

and lists of hazardous and/or toxic substances, currently widely used to describe hazardous materials in the transportation field. The addition of other criteria/lists that ensures appropriate and complete identification of all environmentally hazardous properties of wastes completes the system. Once listed or caught by a characteristic described by the Transportation of Dangerous Goods Regulations, the waste is defined as hazardous and becomes subject to the prenotification (international only) and manifest controls accordingly. Provincial legislation regulates the management options at the waste's ultimate destination.

At the present time there are four provincial control systems for chemical wastes in Canada, which are for the most part complementary to the national system. Some provinces are maintaining their own systems in the interim, others have already or will soon be adopting the national approach. All provinces agree that the ultimate goal is to refine the existing and proposed system, and attain one nation-wide system which will effectively address all hazardous waste movements.

METHODOLOGY FOR THE DETERMINATION OF PRENALYTICAL HOLDING TIMES

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ABSTRACT

Because of the importance of analytical methodology to public decision making in the environmental area, it has become necessary to apply strict quality control and quality assurance precedures to all aspects of the aspects of the process, background data or valid statistical procedures are available to assist in the development of appropriate quality control procedures. However, the period of time from which the sample is collected until it is analyzed has largely been left to empiricism, particularly with respect to organic analysis. This paper is a discussion of the experiments ongoing in an attempt to clarify and document the preanalytical holding time associated with the analysis of organic compounds in water and soil. The experimental design consists of the analysis (by USEPA methods) of volatile organic compounds and semivolatile nitroorganic compounds in three water and three soil matrices under three storage conditions until all analytes fall outside the 90% confidence limit of the analysis of the original sample.

In order to perform this experiment, methods have to be developed for the preparation of a large, homogeneous volume of original sample which can be aliquotted into individual storage containers with a precision of less than 5%. For volatile organic compounds in water, a method has been developed which consists of filling a Tedlar gas sampling bag with water, adding a methanolic solution of volatiles, mixing, and aliquotting into standard VOA vials. This procedure produces aliquots which are about ± 3% by analysis. The method for soil sample preparation involves precise weighing of a dried soil sample, and addition of a known volume of water prepared in the manner described above. For the semivolatiles, ethanolic solutions of the compounds are added to volumetric flasks containing the water and aliquotted directly. Soil samples are prepared using a solution of the semivolatiles in diethyl ether, with the ether being allowed to evaporate.

Preliminary data on the holding time of various analytes will be presented, as will the complete experimental design. Precision and accuracy data for the various preparation methods will be presented.

Analysis of Non-Homogeneous Mixtures

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The New Jersey Department of Environmental Protection, Office of Quality Assurance has administered a laboratory certification program for the Safe Drinking Water Act and the Clean Water Act (New Jersey's Pollutant Discharge Elimination System) for many years. As new programs were enacted by the various state agencies they required that the monitoring data reported for compliance must be produced by laboratories certified by the Office of Quality Assurance. These programs have required the analysis of more complex samples and the development of new methods in cases where methods were not available. To accomplish this task, the Office of Quality Assurance has increased the number of categories for which laboratories can be certified, and the analytical procedures that are required in the analysis of the samples, by promulgating these procedures in the Regulations Governing Laboratory Certification and Standards of Performance. Some programs required the analysis of substances that did not have validated methods while others required methods specific to a certain matrix. The Department has resolved these issues in several ways.

Our first example is New Jersey's RCRA program. The requirements for the analysis of these samples were quite simply solved by the department by promulgating the USEPA's Test methods for

Evaluation of Solid Waste (SW846) and by providing for certification of laboratories for RCRA analysis in the New Jersey Laboratory Certification Regulations.

The second example is a program created by an amendment to the New Jersey Safe Drinking Water Act; known as Assembly Bill A-280. This program requires the owner or operator of each potable water supply to undertake the periodic testing of the water provided to its customers for various hazardous contaminants which include purgeable organics, certain aromatic and aliphatic hydrocarbons, a pesticide, PCB's an aldehyde, a ketone and a glycol. Again it was necessary to identify appropriate laboratory methods. The initial solution to this problem was amendment of the Laboratory Certification Regulations to include EPA methods 601, 602, 608, 612, 624, 625 and 503.1 to cover the halogenated aliphatics and aromatics, chlordane, the arochlors, benzene and the xylenes. Development of methods for analysis of the remaining chemicals (ethylene glycol, kerosene, formaldehyde, n-hexane and methyl ethyl ketone) was contracted to a research laboratory and will be validated as they become available.

This Bill also established the New Jersey Drinking Water Quality Institute which is mandated to establish MCL's for compounds listed in the act at levels based on a cancer risk of no more than one in a million for a lifetime of ingestion. To accomplish this, several committees have been activated. The first committee will determine the risk for each of the chemicals listed in the act.

The second groups will then use these risk factors to set the maximum contaminant levels. Unfortunately the method detection levels for the 600 series methods are generally above the projected maxium contaminant levels. A third work group has been assembled to modify methods 502.1 and 503.1 to obtain lower detection levels. These levels should lower the Practical Quantitation level to a point that will satisfy the intent of the act. If the modifications proves successful, the A-280 approved laboratories will gather data to validate this procedure.

Since this act also gives the Drinking Water Quality Institute the power to include other substances in the list of analytes, an additional research project has been started for the analysis of asbestos in water. Initial results of this project indicate that this method will require less analysis time and therefore be less costly than the present electron microscopy method. New Jersey does not have a sufficient number of laboratories to validate this method so it will be presented to EPA when it is ready for validation.

Our next example is the Sludge Management Program, part of which is regulated through the Sludge Quality Assurance Regulations (SQAR). These regulations require sewage treatment plants to analyze sludge periodically for selected chemical parameters and certain physical properties. The reporting frequency is dependent upon the total flow entering the sewage treatment plant. At the time of SQAR promulgation there were no standardized methods for the analysis of sludge and a lack of control over the laboratory performing the sludge analysis. As a result, the data submitted to the Department was difficult to interpet and was difficult to use in the broad sense as was originally intended.

Hence the Sludge Methods Task Force was formed to evaluate and establish the methods and QC procedures needed for the analysis of sludge as required by SQAR. The task force is composed of individuals chosen from industry, sewage treatment plants, acedemic and state and federal governments. This Task Force has developed a general procedure for the adoption of stardarized methodologies. This procedure consists of five steps. The first step is a literature review and a survey of laboratories to identify candidate procedures. Step two of the procedures is task force evaluation of each candidate method including rewriting into a standardized format. After the method is given tentative approval by the Task Force, step three of the procedure is circulation of the methods to a panel of laboratories for their review and comment. During step four each laboratory comment is reviewed by the Task Force and appropriate changes are made to the method. In step five the methods are subject to inter and intra laboratory validation. Once the Task Force is satisfied with the validation results, the methods will be recommended to the department for use in sludge analysis. Presently, there are six methods ready for validation. These methods are for the analysis of pH, total residue, volatile and ash of total residue, oil and grease, phenols, and metals. The validation study will consist of the collection of liquid and solid sludges at two concentrations, homogenizing each batch, and delivering samples to participating laboratories for replicate analysis. A local laboratory will be employed for the homogenization process and for referee analysis. Prior to initiation of the study, the laboratories will participate in a symposium where the methods and validation procedure will be discussed to assure that all the methods are clearly understood and uniformly applied.

Our next example is the Environmental Cleanup Responsibility Act (ECRA) which was signed into law in September of 1983. This act provides the Department with the statutory ability to ensure that industrial establishments involved with hazardous substance and waste are not sold, transfered or closed without proper cleanup. The Department conducts a review of the facility including an on-site inspection. If DEP finds that the site is not environmentally acceptable the company must develop and implement a DEP approved cleanup plan. The company must also provide financial assistance for the full estimated cost of the cleanup. Thus this program requires the analysis for every conceivable compound in any matrix. At present we have used SW846 as the major source of methodologies and any other EPA Method available.

To Summarize

The NJPDES requires that all analytical data submitted to DEP within the NPDES and the SDWA programs be from state certified labs. The State Lab Certification Regulations were recently revised to upgrade and extend the coverage of the Lab Certification Program to include RCRA and various State Program. Provision was made within the new Certification Program to initiate implementation of the recommended sludge methods and to further validate the procedures. Laboratories performing sludge analyses will have to be certified within the Certification Program. The Program certifies by category of analysis:

Category 1- Drinking Water (SDWA)
Category 2- Water/Wastewater/Sludge (NJPDES)
Category 3- Waste Analysis (RCRA,NJPDES)

Within each category, a lab is certified by methods (appropriate for subcategories of inorganics, organics, limited chemistry, etc.)

Laboratories conducting these analyses will be required to use recommended procedures and submit results to the State with specific data deliverables requirements. This specific QA/QC data will be incorporated into a data base to establish yearly statistical acceptance parameters for the methods. During this process, we will also initiate establishment of sludge solid waste and A280 analytical performance evaluation samples to survey the performance or participating laboratories and enforce Department standards.

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