First Annual

United States
Environmental Protection Agency
Symposium
on

Solid Waste Testing and Quality Assurance

PROCEEDINGS

July 23-26, 1985
Washington, D.C.
Vista International Hotel

Symposium managed by
The American Public Works Association

FIRST ANNUAL

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

SYMPOSIUM

on

SOLID WASTE TESTING
AND
QUALITY ASSURANCE

PROCEEDINGS

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The American Public Works Association

Proceedings Edited By
William S. Forester
Director
ISW/ISWA Secretariat
American Public Works Association
Chicago, Illinois

FIRST ANNUAL UNITED STATES ENVIRONMENTAL PROTECTION AGENCY SYMPOSIUM

on

SOLID WASTE TESTING AND QUALITY ASSURANCE

PROGRAM

Vista International Hotel — Washington, D.C.

July 24-26, 1985

Wednesday, July 24, 1985

7:00 am - 8:30 am	REGISTRATION
8:30 am - 8:50 am	OPENING SESSION Opening presentation given by Dr. John H. Skinner, Director, Office of Solid Waste, U. S. EPA, Washington, DC 20460
8:50 am - 9:15 am	CONFERENCE OVERVIEW Overview presented by David Friedman, Manager, Methods Program, Office of Solid Waste, U. S. EPA, Washington, DC 20460
9:15 am - Noon	SESSION I, ANALYSIS OF INORGANICS Chairperson: Douglas Gillard, Methods Program, Office of Solid Waste (WH-562B), U. S. EPA, Washington, DC 20460
9:15 am - 10:15 am	"Comparative Performances of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS)" Speaker: Barton P. Simmons, Hazardous Materials Laboratory, California Department of Health Services, 2151 Berkeley Way, Berkeley, CA 94720; and "Comparative Performance of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP) and Atomic Absorption Spectroscopy (AAS)" Speaker: Thomas A. Hinners, Hazardous Waste Methods Evaluation Branch, U.S. EPA-EMSL, P.O. Box 15027, Las Vegas, NV 89114
10:15 am - 10:30 am	BREAK
10:30 am - 11:00 am	"Evaluation of SW-846 Methods for Metal

	Extraction/Disolution of Aqueous, Oil, and Solid Waste Matrices" Speaker: Dr. Mirtha Umana, Analytical and Chemical Sciences, Research Triangle Institute, P. O. Box 12194, Research Triangle Park, NC 27709
11:00 am - 11:30 am	"Interference Reduction Studies Involving Hydride Generation Arsenic and Selenium Determinations Utilizing Atomic Absorption and Plasma Emission Spectrometry" Speaker: Dr. J. Wilson Hershey, Lancaster Laboratories, Inc., Lancaster, PA 17601
11:30 am - Noon	"Employment of Alkaline Digestion Procedures for Determination of Metals in Industrial Wastes" Speaker: Joseph Lowry, Chief, Inorganic Analytical Section, U. S. EPA-NEIC, Box 25227, Denver Federal Center, Denver, CO 80225
Noon - 1:30 pm	LUNCH BREAK
1:30 pm - 5:00 pm	SESSION II, METHODS FOR IDENTIFYING HAZARDOUS WASTE CHARACTERISTICS Chairperson: Todd A. Kimmell, Methods Program, Office of Solid Waste (WH-562B), U.S. EPA, Washington, DC 20460
1:30 pm - 2:00 pm	"Performance of Ignitable Solids Methods for Characterizing Hazardous Wastes" Speaker: Florence Richardson, Office of Solid Waste (WH-562B), U.S. EPA, Washington, DC 20460
2:00 pm - 2:30 pm	"Reactive Sulfides and Cyanides: Test Methods and Regulatory Threshold Setting Models" Paul H. Friedman, Studies and Methods Branch,. Office of Solid Waste (WH-562B), U. S. EPA, Washington, DC 20460
2:30 pm - 3:00 pm	"Mobility of Toxic Compounds from Hazardous Wastes: Comparison of Three Test Methods to a Lysimeter Model" Speaker: Michael Maskarinec, Chemistry Division (Building 1505), Oak Ridge National Laboratory, P. O. Box 10, Oak Ridge, TN 37830
3:00 pm - 3:30 pm	COFFEE BREAK
3:30 pm - 4:00 pm	"Application of the Toxicity Characteristic Leaching Procedure (TCLP) to Industrial Wastes: A Single Laboratory Evaluation" Speaker: L. R. Williams, U. S. EPA-EMSL, BOX 15027, Las Vegas, NV 89114
4:00 pm - 5:00 pm	PANEL DISCUSSION - Overview of the EPA Program to Define the Characteristics of Hazardous Wastes Chairperson: Todd A. Kimmell, OSW, U. S. EPA Participants: David Friedman, Paul H. Friedman,

	Douglas Gillard, and Florence Richardson, OSW, U. S. EPA
6:00 pm - 7:30 pm	RECEPTION - For All Symposium Speakers and Attendees

Thursday, July 25, 1985

8:00 am - Noon	SESSION III, ANALYZING FOR ORGANICS Chairperson: Dr. Paul H. Friedman, Methods Program, Office of Solid Waste (WH-502B), U. S. EPA, Washington, DC 20460
8:00 am - 8:30 am	"Application of SW-846 Methods to Groundwater Monitoring Programs: Experiences of Two Contract Laboratories" Speaker: Dr. Denis Lin, ETC, 284 Raritan Center Parkway, CN 3154, Edison, NJ 08818
8:30 AM - 9:00 am	"Quantitive Analytical Screen for the Determination of the Appendix VIII Hazardous Constituents" Speaker: Dr. Mark J. Carter, Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, CO 80002
9:00 am - 9:30 am	"The Use of SW-846 Cleanup and Mass Spectroscopy Methods to Identify and Quantify Compounds in Complex Industrial Wastes: Petroleum Industry Case Histories" Speaker: Alice Boomhower, Radia Corporation, 7655 Old Springhouse Road, McLean, VA 22102
9:30 am - 10:00 am	"Methodology for the Analysis of Organic Chemicals in Petroleum Refining Wastes to Support RCRA Waste Listing and Delisting and Land Treatment Demonstration Programs" Speakers: Dr. Mark J. Carter, Dr. Michael P. Phillips, and Jerry L. Parr, Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, CO 80002
10:00 am - 10:15 am	BREAK
10:15 am - 10:45 am	"Development of Groundwater Screening Procedures for Use in Monitoring Programs: Objectives and Experiment Progress at Battelle Columbus Laboratories" Speaker: S. V. Lucas, Battelle Columbus Laboratories, 505 King Street, Columbus, OH 43201
10:45 am - 11:30 am	EPA/INDUSTRY PANEL DISCUSSION - The Need for Standard Laboratory Procedures and EPA's "Methods for Evaluating Solid Wastes" (SW-846) Chairperson: Dr. Paul H. Friedman, OSW, U. S. EPA

	Participants: Session Speakers (see names above); Al Verstuyft, Chevron Oil Company, 576 Standard Avenue, Richmond, CA 94802; and Ronald Mitchum, U. S. EPA-EMSL, P. O. Box 15027, Las Vegas, NV 89114
11:30 am - 1:00 pm	LUNCH BREAK
1:00 pm - 4:30 pm	SESSION IV, SAMPLING UNDER RCRA Chairperson: Martin Myers, Methods Program, Office of Solid Waste (WH-562B), U. S. EPA, Washington, DC 20460
1:00 pm - 1:30 pm	"Volatile Organic Sampling Trains for Hazardous Waste Incinerators: Laboratory Validation" Speaker: Thomas Logan, U. S. EPA-EMSL, Research Triangle Park, NC 27711
1:30 pm - 2:00 pm	"Practical Considerations for Improving Sampling Accuracy at Groundwater Test Wells" Speaker: Douglas Richardson, Geo-Research, 2001 Wisconsin Avenue, NW, Suite 200, Washington, DC 20007
2:00 pm - 2:30 pm	"The Relationship Between the Design of Wells and Sampling in Compliance Monitoring for Groundwater Under RCRA" Speaker: Roy Murphy, U. S. EPA (WH-527), Washington, DC 20460
2:30 pm - 2:45 pm	BREAK
2:45 pm - 3:15 pm	"Sampling Techniques for Risk Management: A Dioxin Case History" Speaker: Mark Haulenbeek, Affiliated Engineering Laboratories, 1095 Amboy Arena, Edison, NJ 08837
3:15 pm - 3:45 pm	"Design and Implementation of Sampling Plans for RCRA Listing and Delisting Programs" Speaker: John Maney, Vice President, ERCO, 205 Alewife Brook Parkway, Cambridge, MA 01238
3:45 pm - 4:15 pm	"Practical Statistical Considerations in Designing a Sampling Plan" Speaker: John Warren, U. S. EPA (PM-223), Washington, DC 20460
4:15 pm - 4:30 pm	DISCUSSION
7:30 pm - 9:30 pm	EVENING WORKSHOP - For Federal and State Agency Attendees Chairperson: Michael Barclay, Office of Waste Program Enforcement, U. S. EPA, Washington, DC 20460
7:30 pm - 8:00 pm	"Evaluation of Laboratories Performing Analyses for the RCRA Program" Speaker: Alexis Taylor, Technology Applications,

	5201 Leesburg Pike, Suite 800, Falls Church, VA 22041
8:00 pm - 9:30 pm	"Test Method Support for Enforcement Programs: Current Applications, Problems, and Experiences" Participants: Kenneth Jennings, OWPE, U. S. EPA; and Roy Murphy, GWTF, U. S. EPA
	Friday, July 26, 1985
8:00 am - Noon	SESSION V, QUALITY ASSURANCE ISSUES Chairperson: Florence Richardson, Quality Assurance Officer, Methods Program, Office of Solid Waste, U. S. EPA, Washington, DC 20460
8:00 am - 8:30 am	"Documenting the Equivalency of Proposed Methods to Approved Test Methods for Evaluating Solid Waste" Speaker: L. R. Williams, U. S. EPA-EMSL, P. O. Box 15027, Las Vegas, NV 89114
8:30 am - 9:00 am	"Use of Performance Based Quality Control Criteria in the Superfund Contract Laboratory Program" Speaker: Gareth Pearson, U. S. EPA-EMSL, P. O. Box 15027, Las Vegas, NV 89114
9:00 am - 9:30 am	"A National Voluntary Laboratory Accreditation Program for Environmental Measurements" Speaker: Peter Unger, National Bureau of Standards, U. S. Department of Commerce, ADMIN A-531, Gaithersburg, MD 20899
9:30 am - 9:45 am	DISCUSSION
9:45 am - 10:00 am	BREAK
10:00 am - 10:30 am	"Controlling and Coping with Unwanted Variance in Groundwater Monitoring Data: Quality Control and Statistics" Speaker: Burnell Vincent, Groundwater Program, Office of Solid Waste (WH-565E), U. S. EPA, Washington, DC 20460
10:30 am - 11:00 am	"Sources and Means of Obtaining Compounds for the Quality Analysis Materials Bank" Speaker: Edward Kantor, U. S. EPA-EMSL, P. O. Box 15027, Las Vegas, NV 89114
11:00 am - Noon	PANEL DISCUSSION: Analytical Standards and the Regulatyed Community Chairperson: John Winter, U. S. EPA-EMSL, 26 West St. Clair Street, Cincinnati, OH 45268 Participants: Edward Berg, U. S. EPA-EMSL; Michael Bolgar, Foxboro/Analabs; Henrie Garie, New Jersey Department of Environmental Protection; and Thomas

	Gills, National Bureau of Standards
Noon	ADJOURN

FIRST SESSION

ANALYSIS OF INORGANICS

9:15 am - Noon

Wednesday, July 24, 1985

Chairperson: Douglas Gillard
Methods Program
Office of Solid Waste
U. S. Environmental
Protection Agency
Washington, D. C.

COMPARATIVE PERFORMANCE OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES) AND ATOMIC ABSORPTION SPECTROSCOPY (AAS)

BARTON P. SIMMONS, MILAD S. ISKANDER, AND ROBERT D. STEPHENS, HAZARDOUS MATERIALS LABORATORY, CALIFORNIA DEPARTMENT OF HEALTH SERVICES, BERKELEY, CALIFORNIA

ABSTRACT

ICP-AES has rapidly emerged as a powerful tool for the elemental analysis of hazardous wastes. Comparisons of ICP-AES with the established AAS techniques has provided data on the relative precision, accuracy and ruggedness of the technique. Comparative studies have been completed with contaminated soil, waste oil, baghouse dust from waste solvent incineration, auto shredder waste, and fly ash. Good agreement was generally found between ICP-AES, AAS, and X-ray Fluorescence Spectroscopy (XRF). Exceptions are discussed. The precision of ICP-AES was determined and compared with the precision of sampling and extraction.

Particular problems for ICP-AES include the effects of variable chemical composition and physical properties of hazardous waste samples. Solutions include the prudent choice of emission lines, use of an internal standard, choice of digestion technique, and choice of sample introduction technique.

INTRODUCTION

The growth in concern about hazardous waste has produced a massive response by both government and the private sector. This response has been directed at improved methods of management of these materials as they are generated by today's modern industry as well as efforts to identify and correct problems caused by improper practices of the past.

A principal component of both government and private sector programs to address hazardous waste problems is to characterize these complex materials sufficiently to allow for assessment of public health and environmental impacts, to determine appropriate approaches for assessing the extent of contaminated land, and to determine the effectiveness and impacts of a wide variety of treatment technologies. This requirement for characterization in light of the considerable complexity of waste and environmental samples places an unusual demand on the analytical laboratory. New methods must be developed to determine efficiently and accurately many analytes on one prepared sample. A necessary requirement of such multi-parameter analysis must be, in addition, the ability to give reliable results for a wide variety of matrices.

Several basic technologies currently are available for

multi-elemental analysis. Among those available are automated, multi-lamp atomic absorption spectroscopy (MLAA); x-ray fluorescence spectroscopy (both wavelength and energy dispersive) (XRF); and inductively coupled plasma emission spectroscopy (ICF). Each one of these technologies has its characteristic strengths and weaknesses. This laboratory has developed a considerable data base utilizing all three technologies on a wide variety of waste and environmental samples. This has allowed us to make direct comparisons between the technologies and to make evaluations as to the appropriate use of each. As a result of this evaluation, our laboratory has chosen to rely heavily on ICP as the backbone of our multi-elemental analysis program. For selected elements, when very low detection limits are required, atomic absorption is employed.

This paper presents the consideration of, and the procedures for, analyzing waste and environmental samples by ICP. In addition, results of comparative studies are presented for three very different waste types using XRF, MLAA, and ICP.

PREVIOUS STUDIES

While AAS and ICP have been extensively studied, relatively little has been published on the comparison on the two techniques in hazardous waste analysis.

AAS and ICP have compared favorably for the analysis of 25 elements in fly ash water extracts (Drenski) and eight elements in Extraction Procedure (EP) extracts (King, 1984). The latter study noted poor recovery of silver for both AAS and ICP.

ICP and AAS have been compared with NAA and XRF in the analysis of biological materials and soils (Dahlquist, 1978). FAA and ICP compared favorably for the diethyltriaminepentaacetate (DTPA), exchangeable elements Mn, Fe, Zn, and Cu, and ammonium acetate exchangeable elements CA, Mg, K, No, and Mn in soil. The authors concluded that ICP random and systematic errors were generally smaller than or equivalent to those for single element techniques such as AAS.

A comparison of ICP and FAAS for wear metals in lubricating oils was reported with good correlation of results from ICP and FAAS for oil samples and NBS Standard Reference Materials (SRMs) 1084 and 1085 (Rains, 1985; King, 1984a).

ICP has been evaluated for the screening of hazardous materials and hazardous waste samples by comparison with AAS (Leighty, 1983; Tzavaras, 1984).

A literature review of multi-elemental analytical techniques for hazardous waste analysis was recently published (Oppenheimer, 1984). The literature review considered Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn analysis by several techniques.

It concluded that ICP, XRF, and Instrumental Neutron Activation Analysis (INAA) were the most amenable to development as techniques. The report also recommended additional comparative studies of the three techniques on samples of hazardous waste.

METHODS AND MATERIALS

Sample Preparation for ICP Analysis

Many hazardous materials samples contain large amounts of organic matter for which the sample preparation steps are often long and involved and sometimes a major source of analytical error. This includes solid samples such as soil, sludge, auto shredder waste, and synthetic organic materials; plus liquid samples such as oil, wastewater and solvent. Nitric acid is used widely for oxidizing both organic and inorganic substances prior to measurement. Previous studies have discussed the effects of acid digestion on ICP performance (for example, McQuaker, 1979). A 20-minute HNO_3 digestion was previously compared with more comprehensive digestion (Tzavaras, 1984).

The HNO_3 method (Method A), for digestion and destruction of organic matter used in this work was a wet digestion in which the sample was treated with concentrated HNO_3, the mixture heated to 100 C-200 C to aid the digestion process, and H_2O_2 occasionally employed in addition to HNO_3 as oxidizing agent. Method B was EPA Method 2050 from SW-846 (EPA, 1984). Method C was similar to Method 3050 but used a twofold excess of nitric acid in the initial digestion step. Wet digestion is much less troubled with volatilization losses because of the lower temperature compared to dry ashing methods, particularly for Hg and Se. Using dry ashing techniques under certain conditions, As, Cd, Cr, Pb, V and Zn have also been reported to be lost.

The major disadvantage to wet ashing is the possibility of contamination from the large excess of reagents employed. A number of precautions can be taken to minimize the difficulties associated with dissolution in nitric acid. A major problem associated with HNO_3 acid involves samples containing high levels of total dissolved solids and suspended solids. In such cases, the dissolved salts in the sample digest is near saturation. This leads to erratic nebulizer behavior during aspiration of the solution into the ICP and can eventually lead to total clogging of the nebulizer due to formation of a deposit inside the glass capillary of a Meinhard nebulizer. The use of a 0.45 micrometer filter cartridge with a 20 cc syringe to filter the digest solution will eliminate most insoluble particles and give a clear and homogeneous solution. Extending the time for the tip washer will help to wash any deposits or buildup of the salts on the nebulizer tip. The use of a peristaltic pump and dilution of the solution reduces the effect and keeps a constant flow of solution into the plasma without frequent clogging of the nebulizer.

Figure I shows a comparison of the three digestion methods for a contaminated soil. Method B gave consistently lower results than the other two methods. For contaminated soils, of course, none of these methods are truly total digestion techniques since they are inefficient at removing elements from silicate minerals. For regulatory purposes, any of these techniques could be acceptable provided that they are sufficiently reproducible.

Selection of Analytical Emission Lines for ICP

Routine ICP analysis requires information on the chemical and physical characteristics of the samples, the lowest quantitative determinable concentration (detection limit), the analytical concentration range and the expected potential major spectral interferences.

Based on this information, the ICP user can consult several references for selecting the proper spectral lines to be used under compromise conditions. There are many sources for selecting the most useful emission lines such as,m "An Atlas of Spectral Interferences in ICP Spectroscopy," by M.L. Parsons, et al.

The most widely used wave length tables are commonly referred to as (NBS) Tables of Spectral Line Intensities and "MIT".

All wavelengths to be used in the analytical tasks must be stored for future use. These spectral lines must follow the criteria used by the majority of published wavelength tables whereby wavelengths < 200 nm are determined in vacuum and those greater than 200 nm obtained in air. To adjust for wavelength shift occurring when lines > 200 nm are measured on a vacuum instrument, each data acquisition program applies the formula by Meggers and Peters relating the shift to refractive index of air (at 760 mm pressure and 30 C) to correct each wavelength before performing analyses.

The ICP-ARL 35000 system contains a special program for wave length Correction Data (#Elin) and Linearization Correction which allows the analyst to evaluate the magnitude and rate of change of correction to be applied within a given segment as shown in Tables I and II.

Prior to performing the multi-element analysis on hazardous materials samples, substantial data must be collected to determine the major interferences.

These interferences were examined when wave length scans for 17 elements were programmed into the system.

The scans were measured around the selected analyte lines on different complex matrices of samples, standards and blank.

Detailed examination of the scan data used to characterize the

background and off-peak technique was applied by selecting accordant regions of background on either or both sides of the spectral lines.

A significantly improved understanding of the sample spectrum came about when the major spectral interferences were evaluated from the scan data and different techniques were applied to eliminate or minimize the spectral interferences. Selected lines and comparison between selected lines and major interferences are shown in Table III.

Effect of Organics

Organic material can often be destroyed prior to analysis by wet digestion using nitric acid and hydrogen peroxide. The resulting solution contains the inorganics in acid solution free from organics and ready for analysis. Any possible effects of residual organics on the analysis can generally be ignored. Organic matrices, e.g. solvent extracts, are problematic because the rate of vaporization cannot be easily controlled with an organic matrix.

The California waste extraction for hazardous wastes uses a 0.2M citrate buffer (Calif. Admin. Code). Subsequent metal analysis by ICP could result in a change in the nebulization process causing shifts in the slopes of the calibration curve; the organic content also causes matrix interferences in ICP from differences in surface tension and/or viscosity. This can be compensated for by calibration with standards in the citrate buffer, use of an internal standard and the use of a peristaltic pump to maintain a constant flow of sample extract to the plasma. Dilution was used in some samples to reduce the effect of organics, provided that resulting detection limits were acceptable.

Instrumentation

Sequential Inductively Coupled Plasma Atomic Emission Spectrometer Applied Research Laboratories Model 35000:

Grating: Bausch and Lomb diffraction grating
Focal length 1 meter
Blazed at 2400l/mm
Computer readout: DPC PDP 11/03L
Rx02 dual floppy disk
Generator: 2.5 KW continuous
Frequency: 27.12 MHz, quartz stabilized
Power: 1200 watts (3 turn coil)
Torch: Quartz, 18 mm
Argon flow: plasma 0.8 L/min
coolant 12 L/min
carrier 1 L/min
Meinhard nebulizer: 2.1 mL/min flow rate
Observation height: 15 mm above rf coil

SOLID WASTE STUDIES

Auto Shredder Waste

Samples were mixtures of soil and auto shredder waste from a California facility. Each sample was dried, mixed, ground with mortar and pestle, and sieved through a 16 mesh sieve. For "total" analysis 10 g of each sample was digested with concentrated nitric acid until brown fumes were no longer evolved, cooled, filtered, and diluted to 100 mLs with 5% nitric acid.

Analysis--Each sample was digested and extracted in triplicate. Each digest or extract was then analyzed in duplicate, yielding six measurements for each sample.

The results in Table IV show that the measurement level precision, as determined by the average CV for replicate measurements, is consistently better than the overall method precision. Since the difference is not consistent, i.e., element specific, sample heterogeneity is the likely major source of variability.

Incinerator Dust

As part of an evaluation of cement kiln incineration of hazardous wastes, baghouse dust was analyzed for total and extractable lead by three laboratories. Initial comparison of interlaboratory ICP and AAS results revealed serious systematic discrepancies. However, the discrepancy also existed with interlaboratory AA results, as shown by the initial results in Figure II. The discrepancy was found to be due to not spectral interferences, but to the failure of one laboratory to acidify waste extracts prior to AA analysis. The results after modification of technique are shown as final results in Figure II.

The comparison of AA and ICP results for routine analysis of baghouse dust over several months is shown in Figure III.

Surface Soil--XRF vs. ICP

As part of a remedial investigation of a site in Richmond, California, a comparison of ICP and XRF was made. Samples were digested with nitric acid according to Method A. XRF analysis was performed at the Lawrence Berkeley Laboratory. Results are shown in Figure IV.

Waste Oil Analysis

ICP, AAS, and XRF were used in an evaluation of metals in waste oil. Samples were digested by nitric acid according to Method A

for analysis by ICP at the Hazardous Materials Laboratory (HML) and the Air and Industrial Hygiene Laboratory (AIHL). Split samples were dry ashed and analyzed by ICP at Chevron, Inc. Results are shown in Figures V-X.

DISCUSSION AND CONCLUSIONS

For the routine analysis of solid waste samples with concentrations above the upper limit of the range of the method, the possibility of interelement interference is high. For those samples, either interelement correction is required or analysis by AAS using method of additions, or both. For the work reported here, AAS was generally used for high level samples. Samples with a novel matrix should be analyzed by one of the above procedures.

The analysis for arsenic and selenium at trace levels should be done by GFAA or hydride generation AAS.

Mercury analysis should be done by cold vapor AAS rather than ICPAES due to the superior sensitivity and accuracy of the cold vapor technique.

Whenever feasible, standards should be prepared in the same matrix as samples, particularly for waste extracts with significant concentrations of organics.

ICP analysis of hazardous waste samples must be conducted by or supervised closely by experienced operators who are able to recognize samples with high potential for spectral overlap or other chemical or physical interference. QC samples should be developed for each major matrix which is to be analyzed.

A consensus still needs to be reached on determining method detection limits and quantification limits for multi-element analysis. In particular, LODs and LOQs should be developed which account for variable sample matrix.

Interlaboratory precision and accuracy for ICP are generally equivalent to or better than those for AAS.

As with industrial waste analysis in general, sampling and sample preparation is generally a source of greater error than the analytical measurement.

In general, interlaboratory precision and accuracy are highly variable and dependent on the experience of the participating laboratories. ICP requires more training of operators than AA for production of consistently high quality data (Oppenheimer). Laboratory certification or a similar program would help to establish standards for laboratories involved in RCRA and CERCLA work by ICP.

REFERENCES

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(a) King, Alan D., "Comparison of Results for Determination of Wear Metals in Used Lubricating Oil by Flame Atomic Absorption Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry", Atomic Spectros., Vol 5, No. 4, July-Aug., 1984, pp. 181-191.

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Figure I

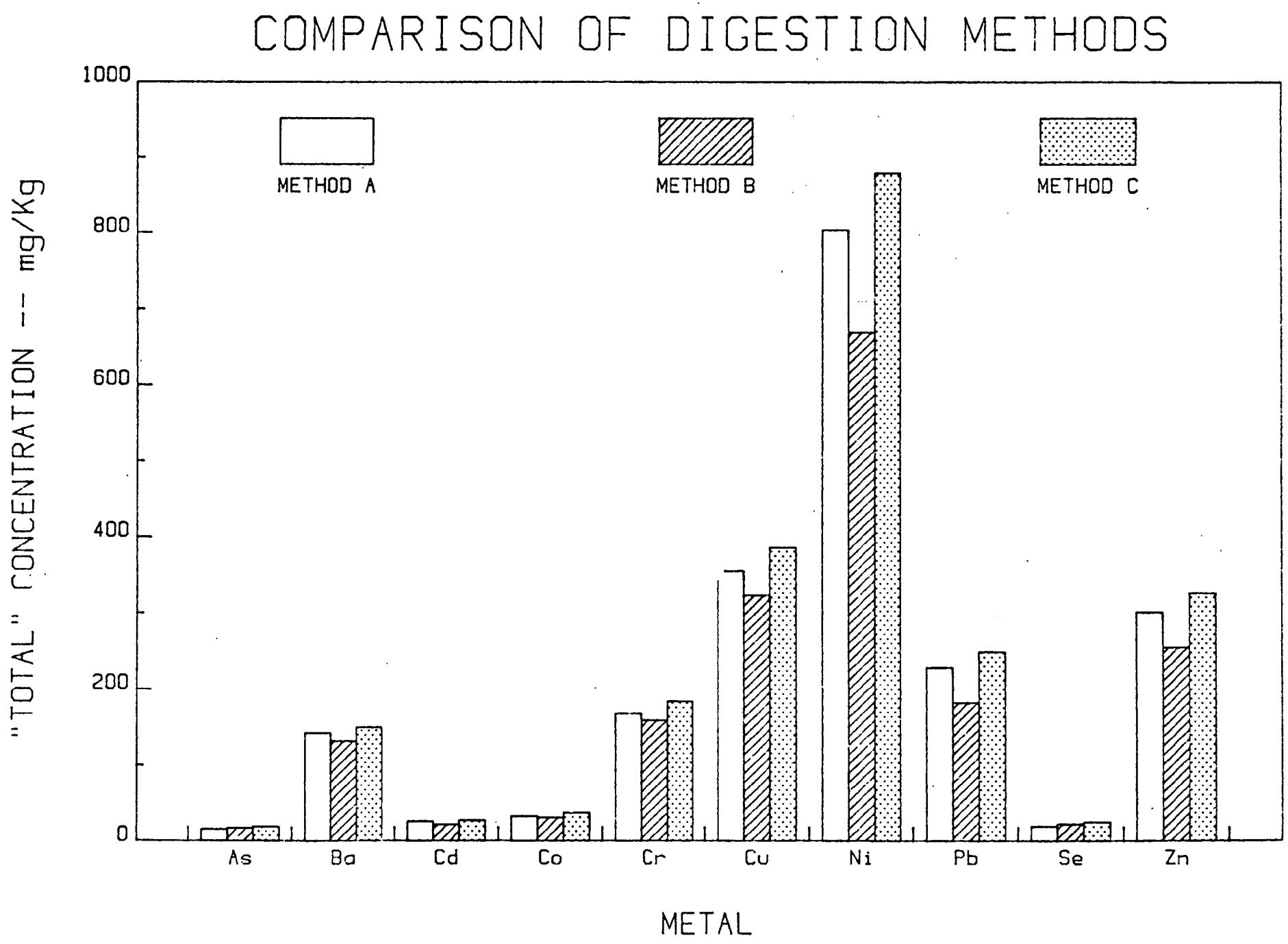
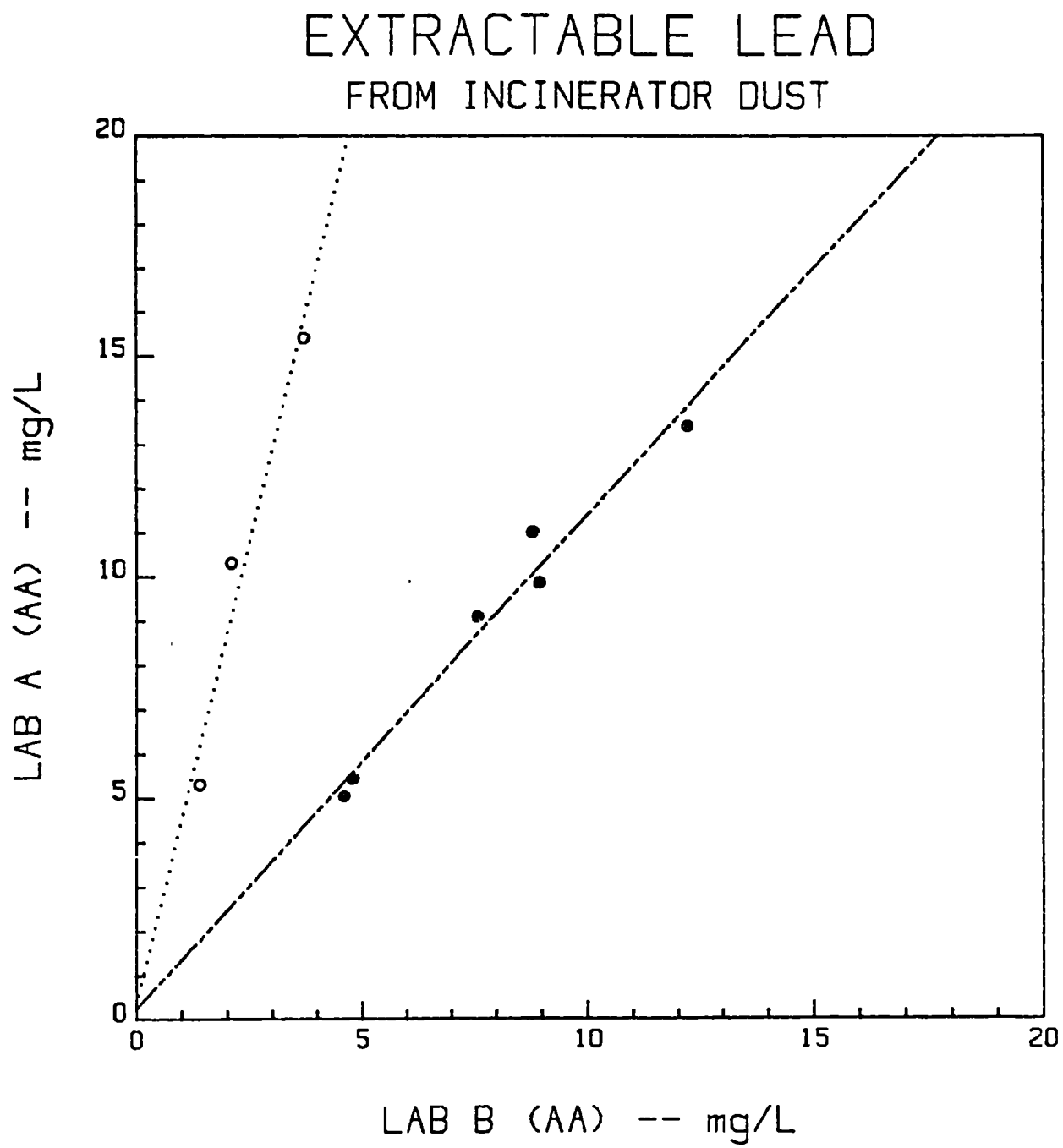

COMPARISON OF DIGESTION METHODS
METHOD A
METHOD B
METHOD C
"TOTAL" CONCENTRATION -- mg/Kg
1000
800
600
400
200
0
As
Ba
Cd
Co
Cr
Cu
Ni
Pb
Se
Zn
METAL

Figure II



INITIAL RESULT
SYMBOL=o
LINETYPE=.....
y=a+b*x
n=3
a=0.2930 s_a=2.3790
b=4.1835 s_b=0.9200
$s_{y.x}$=1.5340 r=0.9767

FINAL RESULT
SYMBOL=●
LINETYPE=——————
y=a+b*x
n=6
a=0.2342 s_a=0.7893
b=1.1160 s_b=0.0957
$s_{y.x}$=0.6123 r=0.9856

Figure III

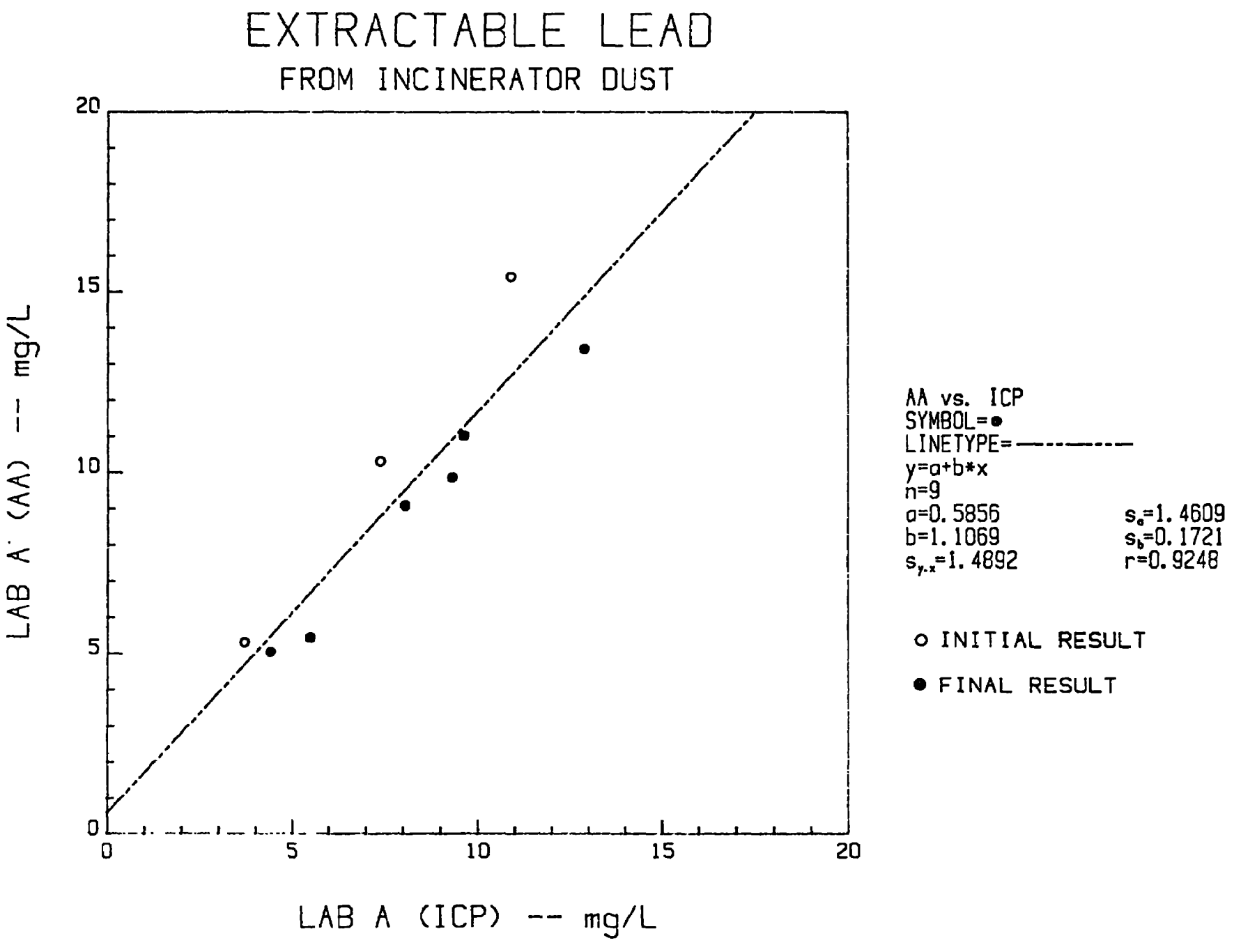

EXTRACTABLE LEAD
FROM INCINERATOR DUST
LAB A (AA) -- mg/L
LAB A (ICP) -- mg/L
0
5
10
15
20
AA vs. ICP
SYMBOL=●
LINETYPE=————————
y=a+b*x
n=9
a=0.5856
b=1.1069
$s_{y.x}$=1.4892
s_a=1.4609
s_b=0.1721
r=0.9248
INITIAL RESULT
FINAL RESULT

Figure IV

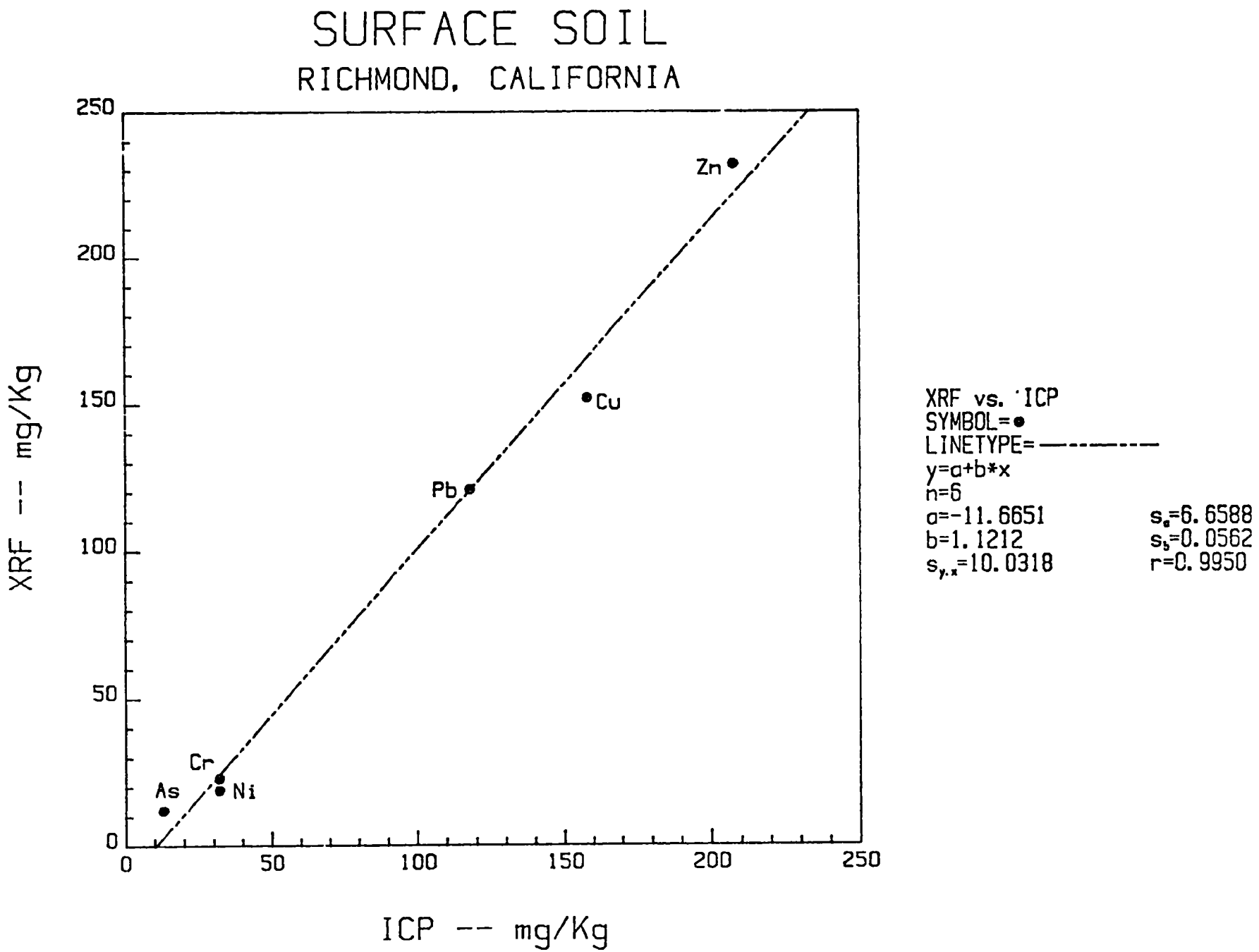

SURFACE SOIL
RICHMOND, CALIFORNIA
XRF -- mg/Kg
ICP -- mg/Kg
0
50
100
150
200
250
Zn
Cu
Pb
Cr
Ni
As
XRF vs. ICP
SYMBOL=●
LINETYPE=——————
y=a+b*x
n=6
a=-11.6651
b=1.1212
$s_{y.x}$=10.0318
s_a=6.6588
s_b=0.0562
r=0.9950

Figure V

LEAD IN WASTE OIL SAMPLES

Maximum value: 800 ug/g
Interval : 80 ug/g

AIHL-XRF	:	602
AIHL-AAS	:	578.5
HML-ICP	:	578.6
CHEVRON-ICP	:	561.6

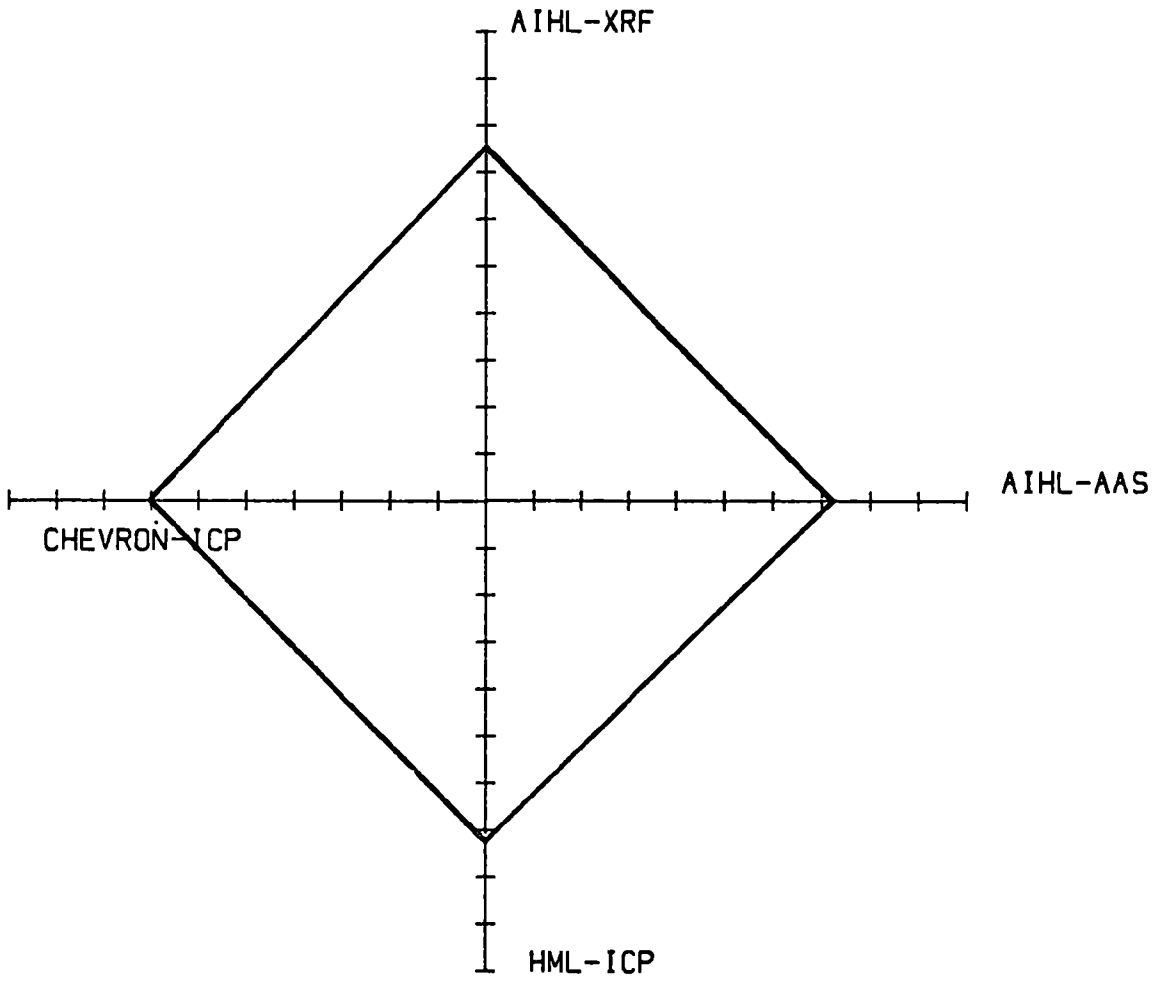


Figure VI

ZINC IN WASTE OIL SAMPLES

Maximum value: 1000 ug/g
Interval : 100 ug/g

AIHL-AAS : 846.4
HML-ICP : 809.5
CHEVRON-ICP : 786.7

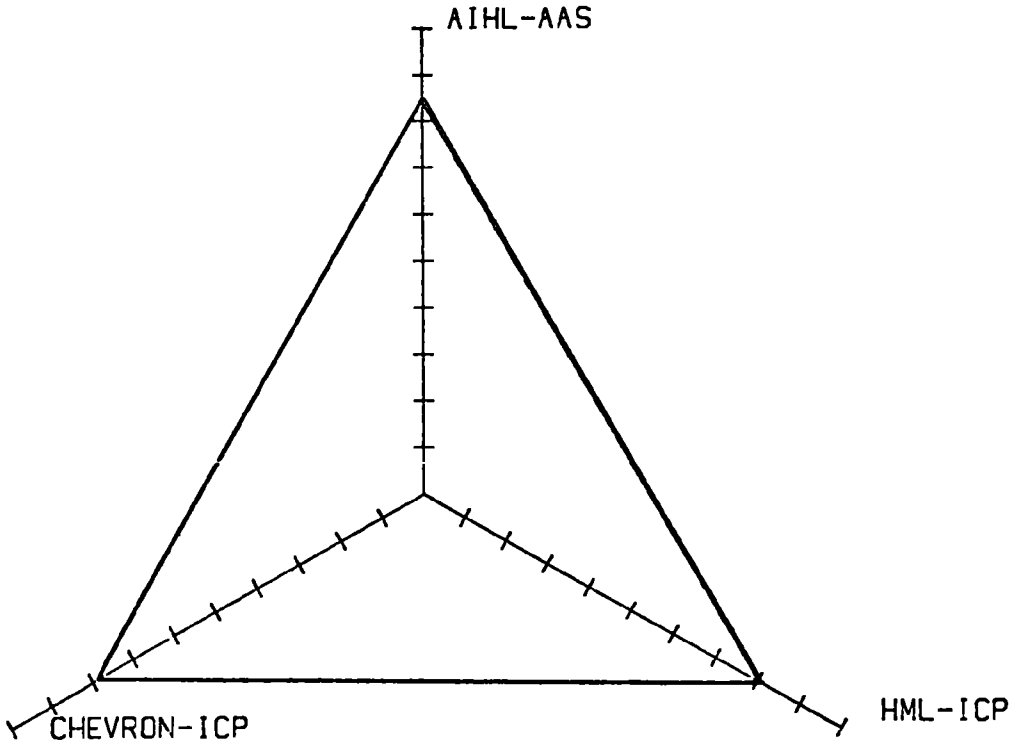


Figure VII

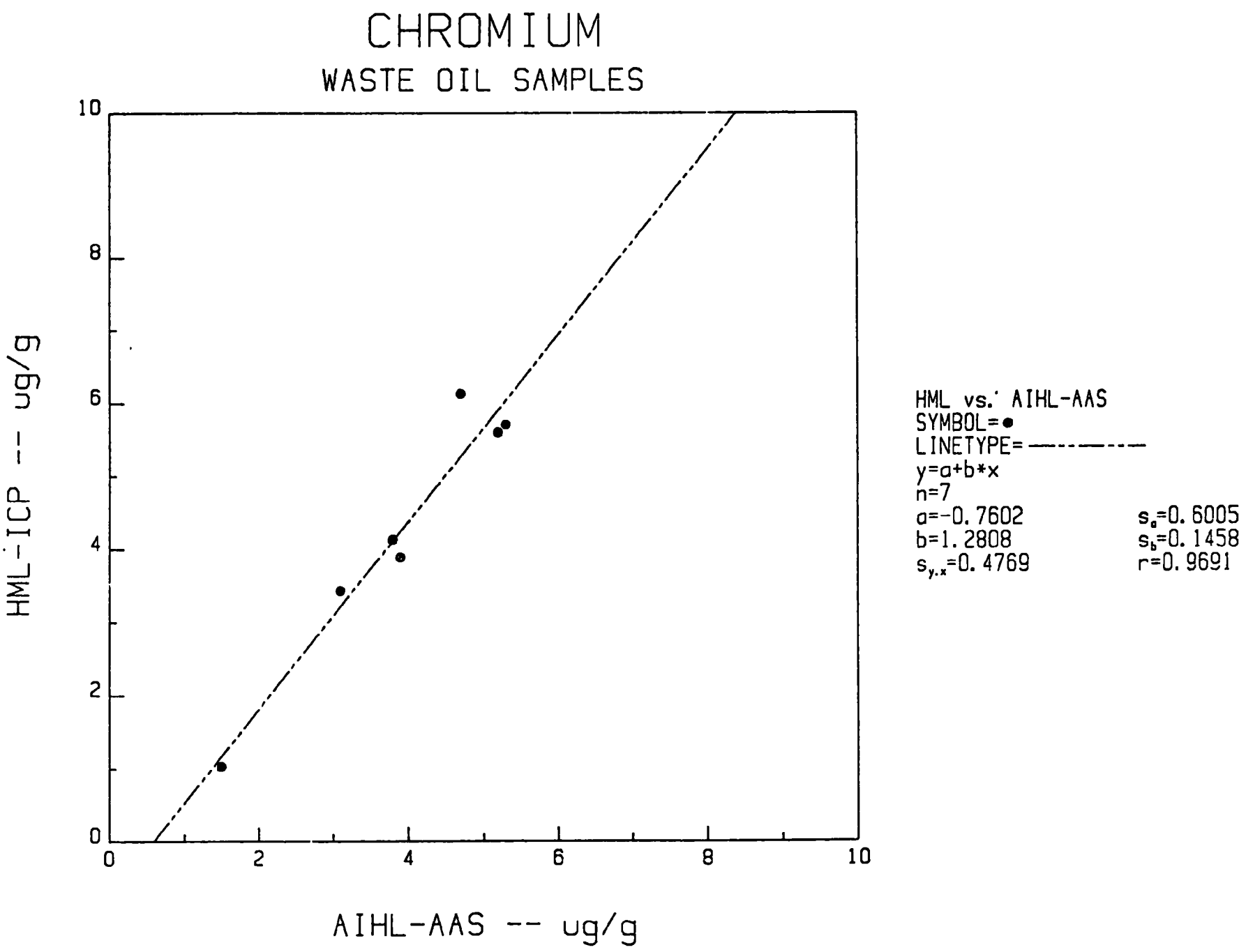

CHROMIUM
WASTE OIL SAMPLES
HML-ICP -- ug/g
AIHL-AAS -- ug/g
0
2
4
6
8
10
HML vs. AIHL-AAS
SYMBOL=●
LINETYPE= —·—·—
y=a+b*x
n=7
a=-0.7602
b=1.2808
$s_{y.x}$=0.4769
s_a=0.6005
s_b=0.1458
r=0.9691

Figure VIII

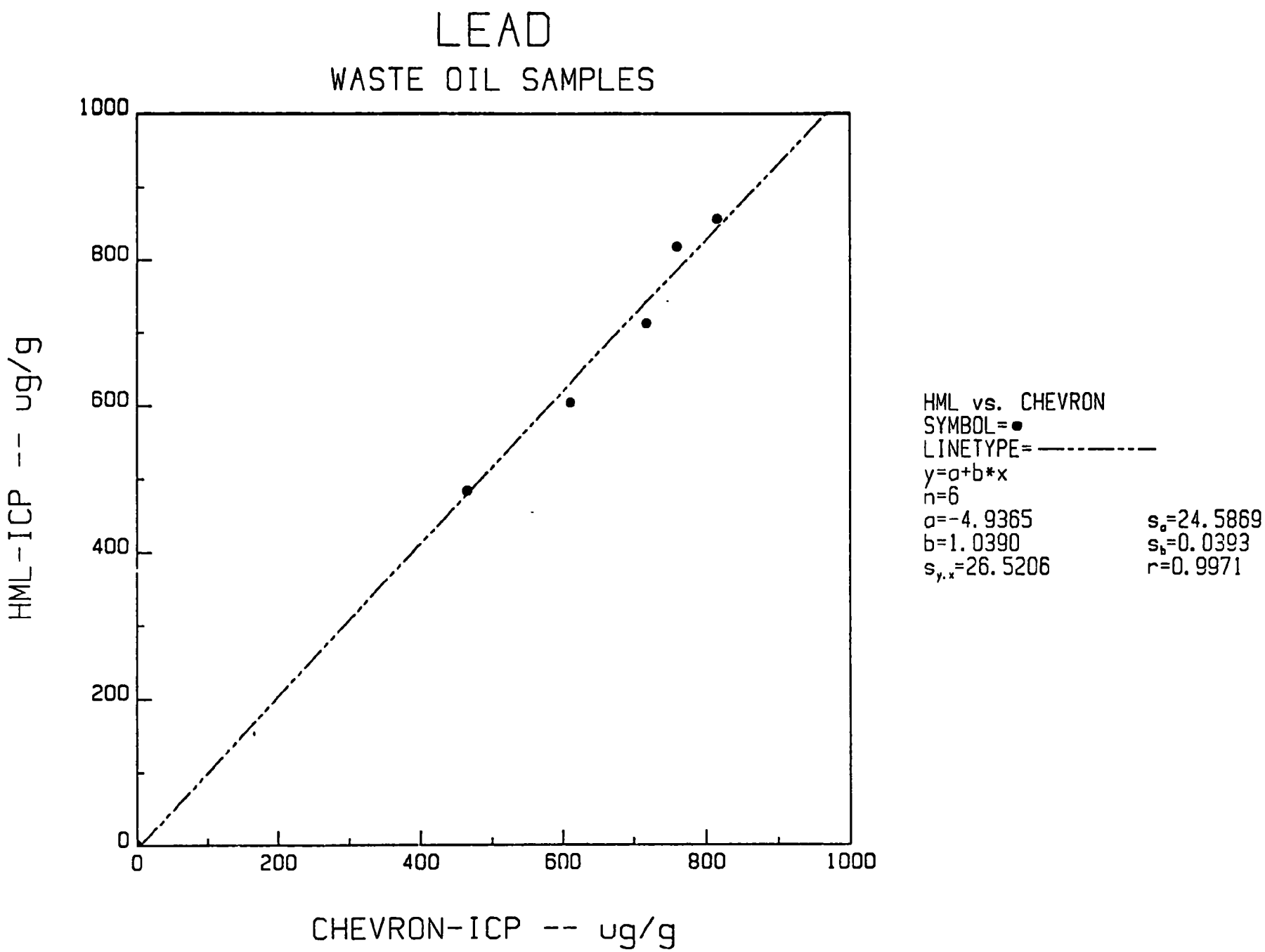

LEAD
WASTE OIL SAMPLES
HML-ICP -- ug/g
CHEVRON-ICP -- ug/g
0
200
400
600
800
1000
HML vs. CHEVRON
SYMBOL=●
LINETYPE=
y=a+b*x
n=6
a=-4.9365
b=1.0390
$s_{y.x}$=26.5206
s_a=24.5869
s_b=0.0393
r=0.9971

Figure IX

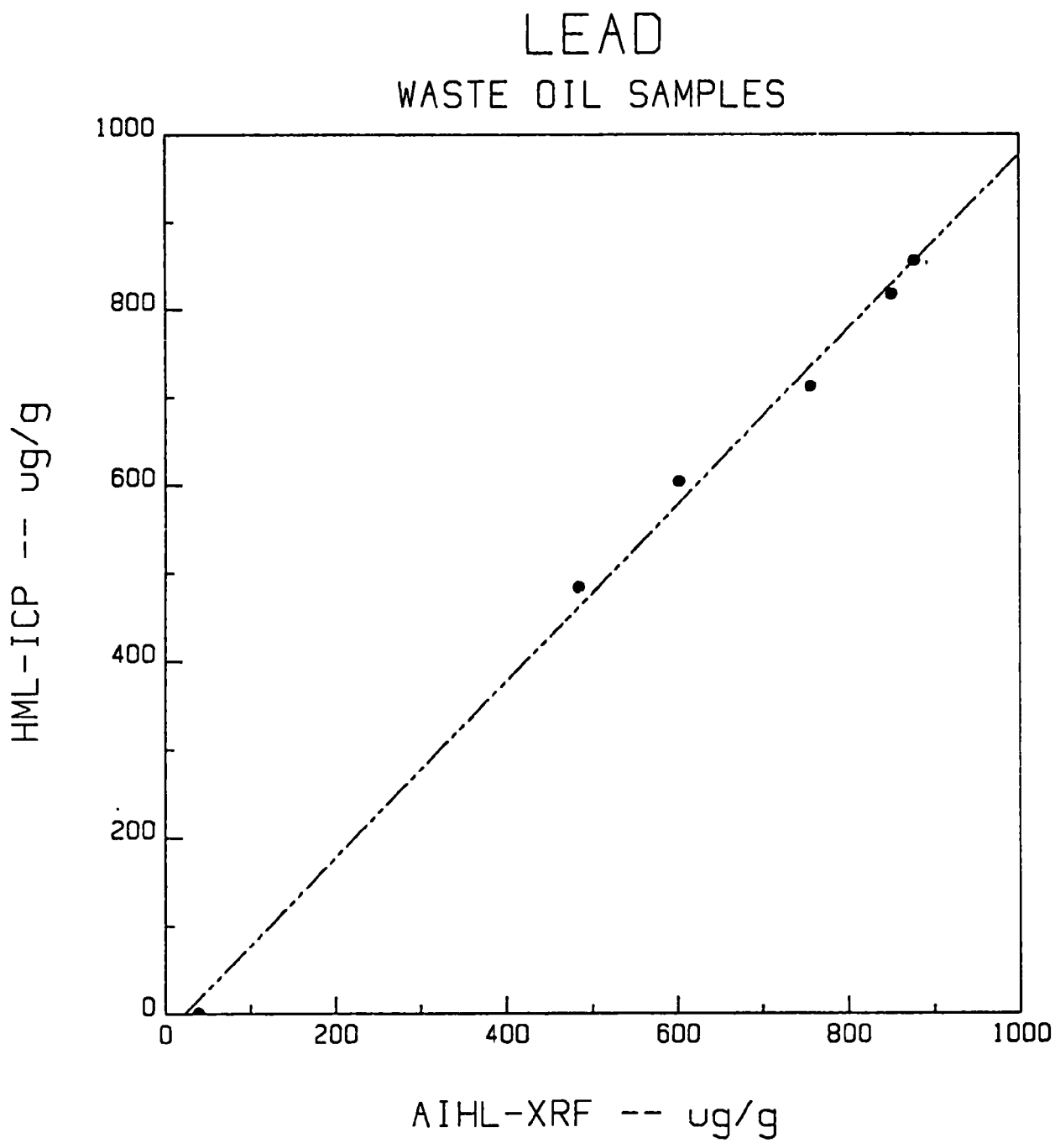

LEAD
WASTE OIL SAMPLES
HML-ICP -- ug/g
AIHL-XRF -- ug/g
0
200
400
600
800
1000
HML vs. AIHL-XRF
SYMBOL=●
LINETYPE=
y=a+b*x
n=6
a=-22.6291
b=0.9987
$s_{y.x}$=22.1830
s_a=21.0549
s_b=0.0316
r=0.9980

Figure X

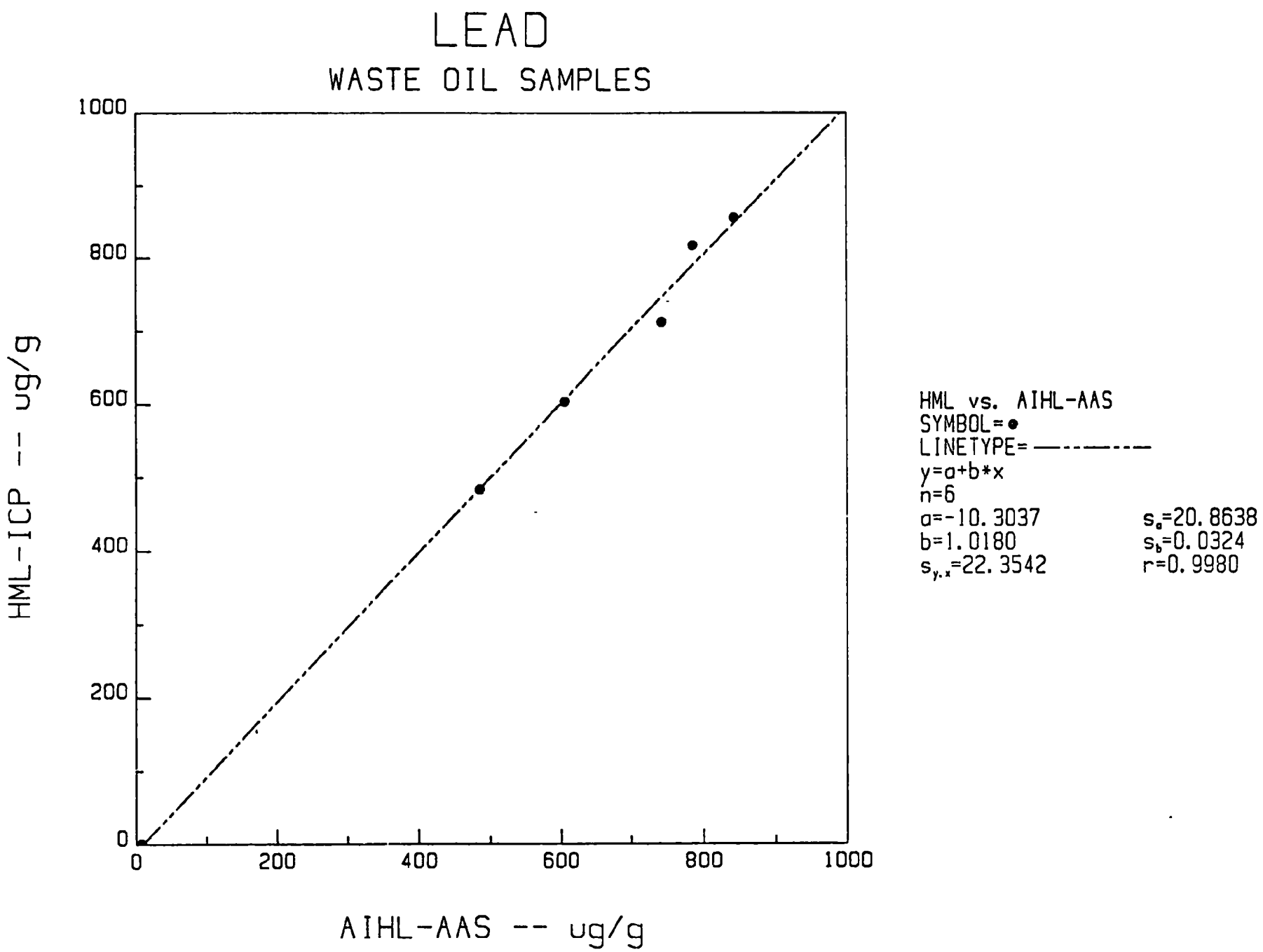

LEAD
WASTE OIL SAMPLES
HML-ICP -- ug/g
AIHL-AAS -- ug/g
0
200
400
600
800
1000
HML vs. AIHL-AAS
SYMBOL=●
LINETYPE= —-——-—
y=a+b*x
n=6
a=-10.3037
b=1.0180
$s_{y.x}$=22.3542
s_a=20.8638
s_b=0.0324
r=0.9980

Table I TABLE OF WAVELENGTH CORRECTION DATA #ELIN

NO.	WAVE	ELEM		DELTA 1	DELTA 2	DELTA 3
1	1849.57	HG	7	0.138	0.136	0.129
2	1890.5	AS	12	0.113	0.123	0.127
3	1899.8	SN	12	0.241	0.241	0.246
4	1908.64	TL	8	-0.247	-0.260	-0.265
5	1937.6	AS	12	0.139	0.141	0.147
6	1942.27	HG	8	0.147	0.149	0.158
7	1960.9	SE	11	0.193	0.181	0.190
8	2020.3	MO	4	0.240	0.226	0.239
9	2039.85	SE	12	0.237	0.231	0.231
10	2055.52	CR	7	0.265	0.260	0.266
11	2061.91	ZN	5	0.301	0.301	0.302
12	2068.33	SB	8	0.218	0.207	0.211
13	2138.56	ZN	4	0.202	0.196	0.194
14	2144.38	CD	4	0.202	0.201	0.205
15	2169.99	PB	12	0.205	0.206	0.198
16	2175.9	SB	9	0.109	0.092	0.090
17	2203.53	PB	9	0.165	0.164	0.159
18	2216.5	NI	5	0.140	0.147	0.145
19	2247	CU	7	0.163	0.153	0.156
20	2265.02	CD	4	0.167	0.169	0.167
21	2286.16	CO	5	0.171	0.161	0.169
22	2289.02	CD	4	0.170	0.167	0.172
23	2316.04	NI	6	0.147	0.141	0.142
24	2335.27	BA	4	0.176	0.170	0.176
25	2348.61	BE	1	0.130	0.135	0.133
26	2378.62	CO	6	0.136	0.128	0.132
27	2382.04	FE	4	0.133	0.117	0.128
28	2536 5	HG	8	0.137	0.139	0.124
29	2576.1	MN	1	0.103	0.097	0.102
30	2599.4	FE	3	0.129	0.125	0.131
31	2677.16	CR	4	0.125	0.120	0.115
32	2767.87	TL	10	0.087	0.080	0.086
33	2795.53	MG	1	0.064	0.062	0.063
34	2816.15	MO	3	0.073	0.085	0.090
35	2924.02	V	5	0.067	0.066	0.067
36	3082.15	AL	8	0.037	0.045	0.049
37	3130.416	BE	1	0.032	0.035	0.045
38	3247.54	CU	3	0.039	0.028	0.035
39	3280.68	AG	4	0.027	0.029	0.007
40	3372.8	TI	2	0.002	-0.002	0.002
41	3382.89	AG	4	0.013	0.008	0.023
42	3578.69	CR	5	-0.047	-0.046	-0.045
43	3710.3	Y	2	-0.084	-0.085	-0.074
44	3891.78	BA	5	-0.087	-0.078	-0.078

Table II

TABLE OF LINEARIZATION CORRECTIONS IN #COLI

WAVELENGTH MINIMUM	WAVELENGTH MAXIMUM	INTCPT	SLOPE	DELTA AT MIN.	DELTA AT MAX.
0.00	1849.57	0.000	0.0000725	0.000	0.134
1849.57	1890.50	0.735	-0.0003249	0.134	0.121
1890.50	1899.80	-24.654	0.0131049	0.121	0.243
1899.80	1908.64	107.654	-0.0565381	0.243	-0.257
1908.64	1937.60	-26.578	0.0137905	-0.257	0.142
1937.60	1942.27	-3.592	0.0019275	0.142	0.151
1942.27	1960.90	-3.709	0.0019874	0.151	0.188
1960.90	2020.30	-1.351	0.0007850	0.188	0.235
2020.30	2038.85	0.433	-0.0000982	0.235	0.233
2039.85	2055.52	-3.770	0.0019625	0.233	0.264
2055.52	2061.91	-11.818	0.0058775	0.264	0.301
2061.91	2068.33	29.056	-0.0139454	0.301	0.212
2068.33	2138.56	0.647	-0.0002102	0.212	0.197
2138.56	2144.38	-1.772	0.0009207	0.197	0.202
2144.38	2169.99	0.179	0.0000108	0.202	0.203
2169.99	2175.90	38.982	-0.0178706	0.203	0.097
2175.90	2203.53	-5.091	0.0023844	0.097	0.163
2203.53	2216.50	3.408	-0.0014726	0.163	0.144
2216.50	2247.00	-0.823	0.0004363	0.144	0.157
2247.00	2265.02	-1.144	0.0005792	0.157	0.168
2265.02	2286.16	0.269	-0.0000449	0.168	0.167
2286.16	2288.02	-3.489	0.0015990	0.167	0.170
2288.02	2316.04	2.298	-0.0009301	0.170	0.143
2316.04	2335.27	-3.534	0.0015879	0.143	0.174
2335.27	2348.61	7.364	-0.0030787	0.174	0.133
2348.61	2378.62	0.197	-0.0000274	0.133	0.132
2378.62	2382.04	4.538	-0.0018523	0.132	0.126
2382.04	2536.50	0.007	0.0000499	0.126	0.134
2536.50	2576.10	2.230	-0.0008266	0.134	0.101
2576.10	2599.40	-2.953	0.0011853	0.101	0.128
2599.40	2677.16	0.408	-0.0001075	0.128	0.120
2677.16	2767.87	1.181	-0.0003963	0.120	0.084
2767.87	2795.53	2.205	-0.0007663	0.084	0.063
2795.53	2816.15	-2.639	0.0009666	0.063	0.083
2816.15	2924.02	0.506	-0.0001502	0.083	0.067
2924.02	3082.15	0.496	-0.0001467	0.067	0.043
3082.15	3130.42	0.431	-0.0001256	0.043	0.037
3130.42	3247.54	0.127	-0.0000288	0.037	0.034
3247.54	3280.68	1.320	-0.0003961	0.034	0.021
3280.68	3372.80	0.745	-0.0002206	0.021	0.001
3372.80	3382.89	-4.661	0.0013821	0.001	0.014
3382.89	3578.69	1.062	-0.0003095	0.014	-0.046
3578.69	3710.30	0.904	-0.0002655	-0.046	-0.081
3710.30	3891.78	-0.084	0.0000008	-0.081	-0.091
3891.78	9999.00	-0.132	0.0000132	-0.081	0.000

Table III

ICP Spectral Information and Comparison

Element	SW -846 (EPA, 1984) Wavelength	Note and Major Interferences	Solid Waste HML Wavelength	Note and Major Interferences
Antimony	206.833	Bad spectral interferences Cr - Mo	Same	Correction for background should be selected very carefully
Arsenic	193.696	Very bad background	189.05	Clean line- good background Detection limit 0.035 PPM
Barium	455.403	Outside range of ARL-35000 Mo	233.527	Detection limit 0.0015 PPM
Beryllium	313.042		Same	Clean line- good background Detection limit 0.001 PPM
Cadmium	226.502	Ni - Fe - Mo	214.438	Pt - W - Pd Detection limit 0.002 PPM
Chromium	267.716	Pt - Fe - Mn	205.552	Good detection limit Detection limit 0.005 PPM
Cobalt	228.616		Same	Detection limit 0.004 PPM
Copper	324.754		Same	Clean line- good background Detection limit 0.003 PPM
Lead	220.353 *	Background from Al	Same	Detection limit 0.015 PPM
Mercury	NA	xxxxxxxxxxxxxxxxxxxxxxxxxx	NA	xxxxxxxxxxxxxxxxxxxxxxxxx
Molybdenum	202.030	Fe	Same	Detection limit 0.008 PPM
Nickel	231.604		Same	Detection limit 0.006 PPM
Selenium	196.026	Weak Fe interference Mn - Fe - Co	196.09	Good background Detection limit 0.06 PPM
Silver	328.068	Mo	Same	Detection limit 0.002 PPM
Thallium	190.864	Mo - V	Same	Detection limit 0.19 PPM
Vanadium	292.402	Weak Fe interference	Same	Detection limit 0.005 PPM
Zinc	213.856	Ni - V	Same	Detection limit 0.002 PPM

NA = Not Analyzed

High level of Ca may present line broading interferences between 3900-4000 A due to two primary calcium ion line at 3933.7 and 3968.5.

*High level of Al presents a high background on Pb line at 2203.5 that should be corrected.

Table IV Precision of Auto Shredder Analysis

	Mean Conc mg/kg	Method Level Precision, % CV	Measurement Level Precision, % CV
Ag	0.0777	53	35.1
As	< 0.35	ND	ND
Ba	118	4.5	1.0
Be	0.505	2.4	0.90
Cd	4.4	6.8	2.1
Co	8.3	10.8	1.5
Cr	44.0	7.7	0.9
Cu	196	37	1.2
Mo	5.8	1.7	1.5
Ni	51.6	16	1.3
Pb	131	6.4	0.9
Sb	3.3	6	6.2
Se	< 0.610	ND	ND
Ti	< 1.87	ND	ND
V	19.4	2	1.0
Zn	694	4.3	0.9

COMPARATIVE PERFORMANCE OF INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP) AND ATOMIC ABSORPTION SPECTROSCOPY (AAS) IN WASTE ANALYSES

THOMAS A. HINNERS, U. S. ENVIRONMENTAL PROTECTION AGENCY - EMSL, LAS VEGAS, NEVADA

The performance of analytical techniques can vary for different sample matrices. The analysis of solid samples presents complications of analyte heterogeneity, digestion inefficiency, and the potential for more interferences than the analysis of water samples. For example, only 2 of 10 elements exceeded a relative standard deviation (RSD) of 20% in an AAS collaborative study of water by Temperley (New Zealand J. Sci. 21:557-564, 1978, whereas 8 of 19 elements exceeded a 20% RSD in an AAS interlaboratory study (Amer. Lab. 13:31-35, 1981) on sewage sludge digested with nitric acid and hydrogen peroxide. Even for water samples the performance of ICP and AAS can differ. Garbarino et al. at the U.S. Geological Survey recently reported (Applied Spectros. 39(3):535-541, 1985) better correlation coefficients between 2 labs for cadmium and lead by ICP (0.9997 and 0.9916) than by AAS (0.8227 & 0.9495).

In this talk, data obtained by inductively coupled plasma optical emission spectroscopy (ICP) and atomic absorption spectroscopy (AAS) will be presented for waste digests and for extracts produced by Method 1310, the official Extraction Procedure (EP) specified in the Federal Register. The ICP abbreviation will be used in this talk to refer to ICP/optical emission spectroscopy, and should not be confused with ICP/atomic fluorescence or ICP/mass spectrometry.

Applying different analytical techniques to the same samples provides the means to evaluate the accuracy of methods. In a study conducted for the EPA office in Las Vegas by Dr. Eaton at Montgomery Engineers, five wastes were analyzed not only by AAS and ICP but also by neutron activation analysis (NAA) and x-ray fluorescence (XRF). Since these latter 2 techniques are applied to undigested solids while the other 2 are typically applied to liquids, sample homogeneity and rigorous digestion were critical concerns for this multi-method comparison. The wastes examined were sludges from electroplating, paint production and a drying-bed process plus 2 soil samples from a disposal site. The wastes were air dried and ground (with an agate mortar and pestle) before the fraction passing a 325-um sieve was distributed for analysis by the 4 techniques. Particles smaller than 326 um are classified as "fine sand" by geologists, and allow even the 0.1-gram aliquots used for NAA to be homogeneous.

The NAA and XRF analyses were conducted at the Lawrence Berkeley Laboratory, and the AAS and ICP analyses were conducted at the Montgomery Engineers' facility in Pasadena, California. The NAA analyses involved compressing the samples with cellulose into pellets, a 10-minute irradiation at 11 kW for the short-lived isotopes (followed by two counting periods on intrinsic germanium detectors) and an 8-hour irradiation at 1,000 kW for longer-lived isotopes

(followed by three counting periods). The XRF analyses involved measuring the pulverized samples directly and after dilution with sulfur powder (to minimize matrix effects) in an energy-dispersive system designed and built at the Lawrence Berkeley Laboratory. This XRF system uses a low power tungsten x-ray tube, a molybdenum secondary target for some analytes (As, Cr, Cu, Hg, Ni, Pb, Se & Zn), a terbium secondary target for other elements (Ag, Ba, Cd & Sb), a 1,024-channel pulse-height analyzer and a CDC 6600 computer (as described in Anal. Chem 49:62-67, 1977).

Since the sample digestion procedure must solubilize all analytes completely in order for conventional ICP and AAS analyses to agree with XRF and NAA analyses, the adequacy of several digestion procedures were evaluated using two NBS SRMs (River Sediment and Urban Particulates). The final digestion procedure selected for use on seven aliquots of each waste sample involved nitric, perchloric and hydrofluoric acids and a teflon-lined bomb (Table 1). Table 2 shows results obtained for the NBS SRMs using this digestion procedure.

The elements and analysis wavelengths for the ICP and AAS measurements are shown in Tables 3 & 4. The AAS and ICP measurements were obtained with a Perkin-Elmer 5500 system. Figure 1 shows a graphic comparison of data for the electroplating waste by the 4 techniques. The ICP data is indicated by the solid white area and the AAS data by the area with horizontal lines. The average values by AAS and ICP are not statistically different for Cd, Cr, Cu, Ni and Zn in the electroplating waste, but the AAS silver value is 50% lower than the ICP average. The ICP Ag value is consistent with the values obtained by XRF and NAA. The low Ag value obtained with AAS may have resulted from the extensive dilution used to bring the Ag concentration into the linear range for AAS analysis. Figure 2 shows arsenic results for samples where high variability for ICP and NAA values is apparent. Difficulties in measuring arsenic in complex samples by conventional ICP have induced some investigators, including Dr. Lowry at the National Enforcement Investigations Center (NEIC) in Denver, to develop systems to generate and to deliver the gaseous hydride of inorganic arsenic (and other hydride-forming elements) into ICP instruments, which serves to separate arsenic from interferences and to improve the detection limit. Dr. Lowry is scheduled to discuss sample preparation at the symposium this afternoon. High lead concentrations in the drying-bed sludge and the paint waste prevented accurate arsenic determinations by XRF so no XRF values for these wastes are shown in Figure 2. Figure 3 shows the cadmium results for the samples and demonstrates an unusually high measurement variability for the paint waste by NAA. This serves to illustrate that measurement precision can differ drastically for different matrices. Figure 4 shows the chromium data where a high bias by XRF is indicated for soil but not for the paint waste. Figure 5 illustrates high variability for copper measurements by NAA, which has a poor sensitivity for copper. Figure 6 shows agreement among the 4 techniques for nickel except for a high value by XRF for the drying-bed sludge. This illustrates that accuracy obtained with a technique on one matrix does not ensure accuracy for a different matrix. Figures 7 & 8 show the agreement among three of the

techniques for lead. NAA is too insensitive for lead measurements below the percentage level, so no NAA lead values are shown in Figures 7 & 8. Agreement between ICP and AAS is shown for all samples for manganese in Figure 9. Figure 10 shows that the ICP Sb data for the paint waste is consistent with NAA and XRF data while the AAS (furnace) data for Sb is inconsistent with the other 3 techniques. Loss of Sb by premature volatilization in the AAS furnace is probably involved in the low AAS values. Figure 11 shows zinc results for the samples and demonstrates general agreement. The ICP and AAS precision obtained in this study is generally in the range of 3 to 10% RSD, and typically half of the RSD value is attributable to the measurement process while the majority of variation is ascribable to sample heterogeneity and sample preparation. For example, the RSD is 3% for repeated ICP analyses of one of the 7 digests of the electroplating waste, whereas the RSD for all 7 electroplating digests is 8.4%.

Six of the elements included in this study were not detected in more than one sample by more than one of the multielemental techniques. A blend of cellulose containing Ag, Cd, Hg, Sb, Se and Tl was mixed with the waste and ICP analysis revealed recoveries as shown in Figures 12 & 13. Added mercury could be measured in these matrices at the 100-ug/g level by ICP. Lead interference prevented reliable thallium measurements by XRF so no Tl values are shown in Figure 13 for XRF.

In another study conducted under contract at the EPA's Las Vegas facility, the official Extraction Procedure (EP) was applied to 6 wastes and the resulting extracts were analyzed by ICP and AAS for barium, cadmium, chromium, lead and silver. Although arsenic, mercury and selenium are also EP Toxicity elements, they are not currently included in the elements specified in ICP Method 6010. The inorganic EP-criterion centrations for classifying a waste as hazardous are listed in Table 5. AAS measurements were obtained with a Perkin-Elmer Model 5000, and ICP measurements were obtained with a Spectrametrics echelle spectrometer (Spectraspan IIIA). Analytical conditions for both techniques are indicated in Tables 6 & 7. The wastes examined in this study are identified in Table 8. The EP extracts of these wastes were spiked at 20% and 100% of the EP-toxicity criterion levels in an effort to provide two measurable concentrations for the AAS and ICP measurements. ICP Method 6010 requires that EP extracts be digested prior to analysis and that the method of standard additions be used for quantitation. Measurements were also conducted to evaluate the need for digestion of the EP extracts and for the use of the method of standard additions. ICP and AAS results obtained by the method of additions for the spiked extracts are shown in Tables 9-13. Table 9 shows the chromium data and includes the RPD (relative percent difference) for the average concentrations by the two techniques for the six samples. For chromium the ICP average concentration exceeded the AAS Cr average by more than 10% only for the lower-spike level (1 ppm) for the plating waste and the storage tank wastewater. The average Cr RSD was 7% by ICP and 9% by AAS for these waste extracts. Data for digested and undigested extracts are included in Tables 9-13, but are summarized on Tables to be shown later. Table 10 shows that the average RSD for Cd is 8.3% by ICP and 7.1% by AAS and the relative percent difference (RPD) only exceeded 10% for the sulfuric acid waste

(where the ICP values are 0.2 mg/L higher than the AAS values). Table 11 shows several RPD values above 10%, but the AAS Ba detection limit is near 2 mg/L and precision is expected to be poor near the detection limit. With the exception of the plating and sulfuric acid wastes (#1 & #5 in Table 11), Ba in digested extracts was much higher than the Ba in the undigested extracts. While digestion of the EP extracts does not always seem necessary, it does in the case of Ba for many wastes. As expected, Ba added to the sulfuric acid waste (#5) was lost as $BaSO_4$, and soluble Ba was below both AAS and ICP detection limits. Ba recovery was low for the 2 mercury wastes (#4 & #6 in Table 11) even with digestion of the extracts.

Table 12 shows the AAC/ICP comparison for Pb in the waste extracts. Precision was worse by ICP than AAS and undigested extract concentrations were frequently much lower than the concentrations in the digested extracts. Table 13 shows the comparison for Ag and is complicated by instability in the concentrations in the undigested extracts (except for wastes #4 & #5).

Although digestion of EP extracts did not always produce a significant difference, an extensive difference was observed for Ag, Ba & Pb in several (but not all) of the wastes examined (Tables 14 & 15). While Ba & Pb concentrations are higher in digested extracts than in undigested extracts, the opposite pattern was observed for Ag. The silver concentrations were low but stable in digested extracts, but unstable in undigested extracts.

Use of the method of standard additions increases the time and cost of analyses. Measurements conducted to determine the benefit obtained using the method of additions (Table 16) for these EP extracts revealed that a difference of more than 6% for Cr and 7% for Ba & Cd were only obtained for the storage tank wastewater (1 of the 6 wastes). Poor precision and instability made conclusions on Ag & Pb uncertain. Time and cost can be minimized if the method of standard additions is only used when "recovery" of a spike added to a prepared sample indicates a significant interference.

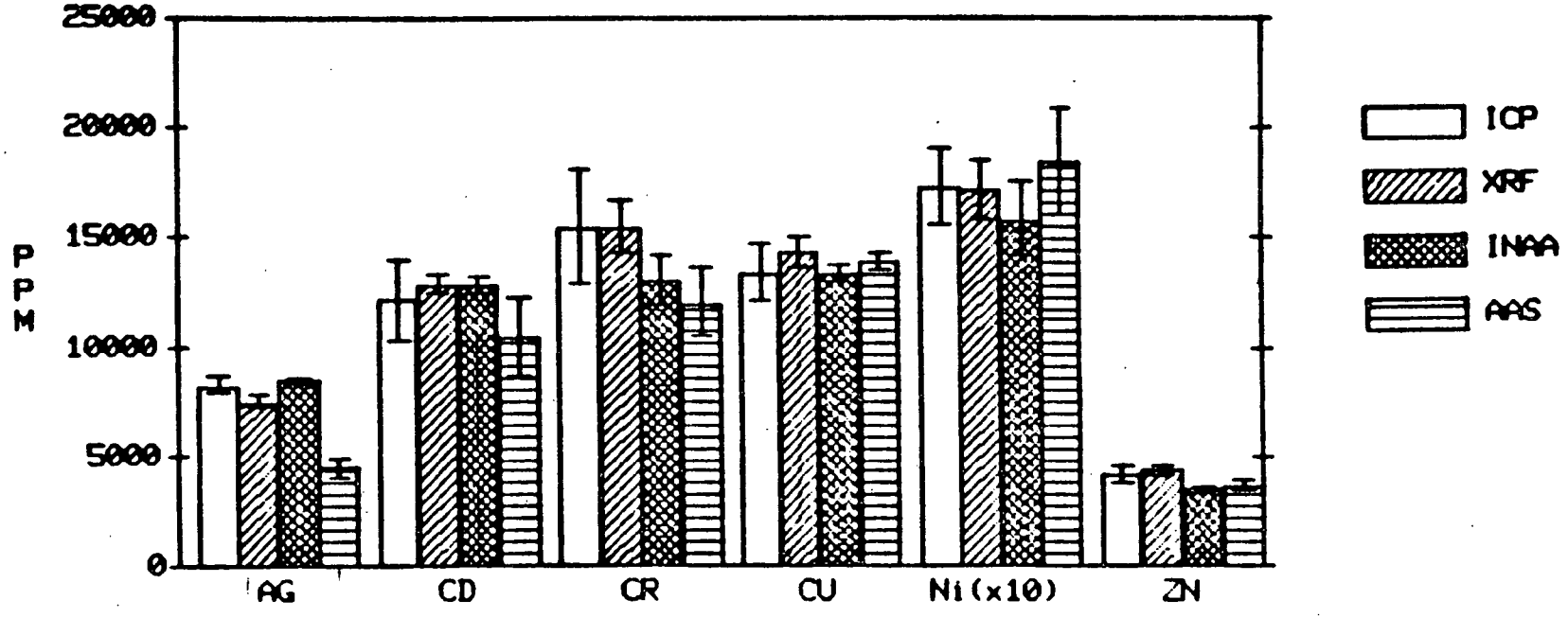


Figure 1. Results for the electroplating waste (mean values and 95% confidence intervals in µg/g).

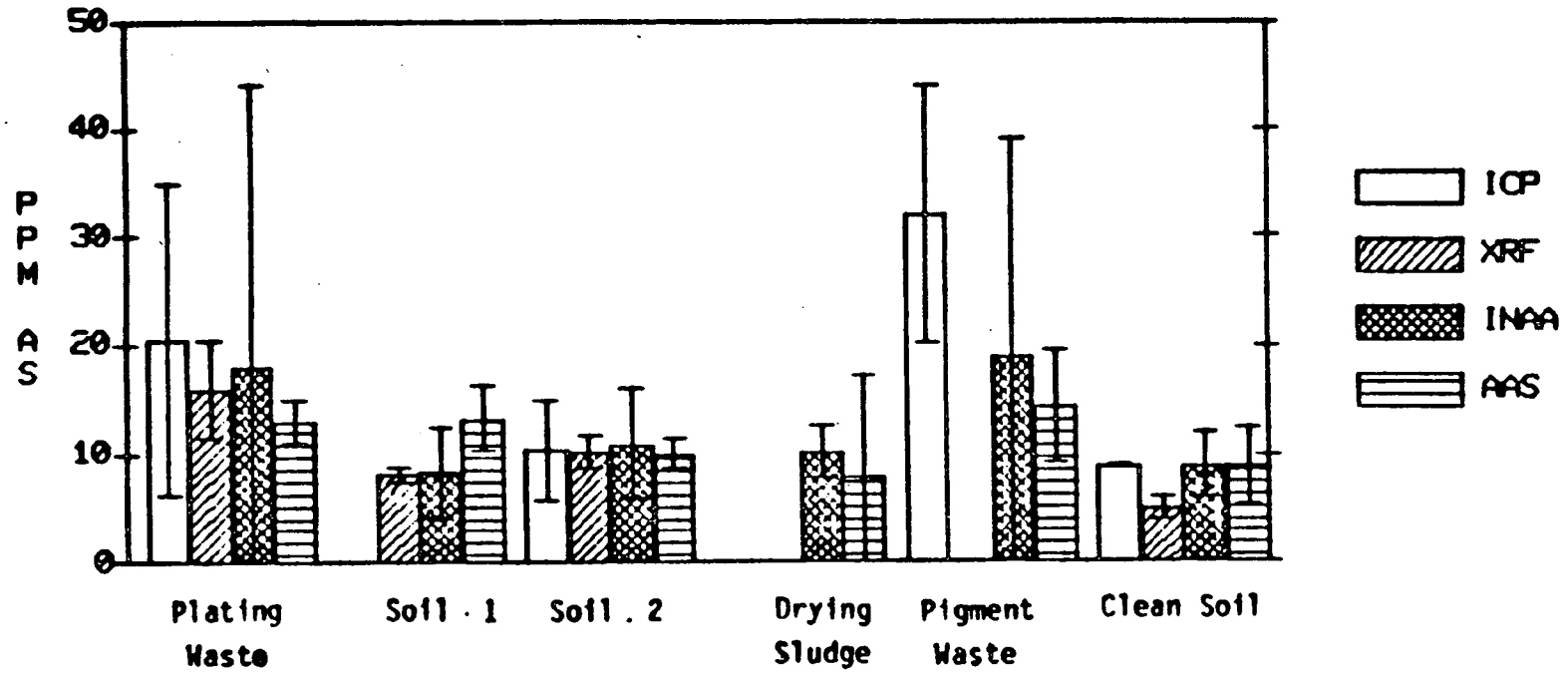


Figure 2. Arsenic results for the samples (mean values and 95% confidence intervals in µg/g).

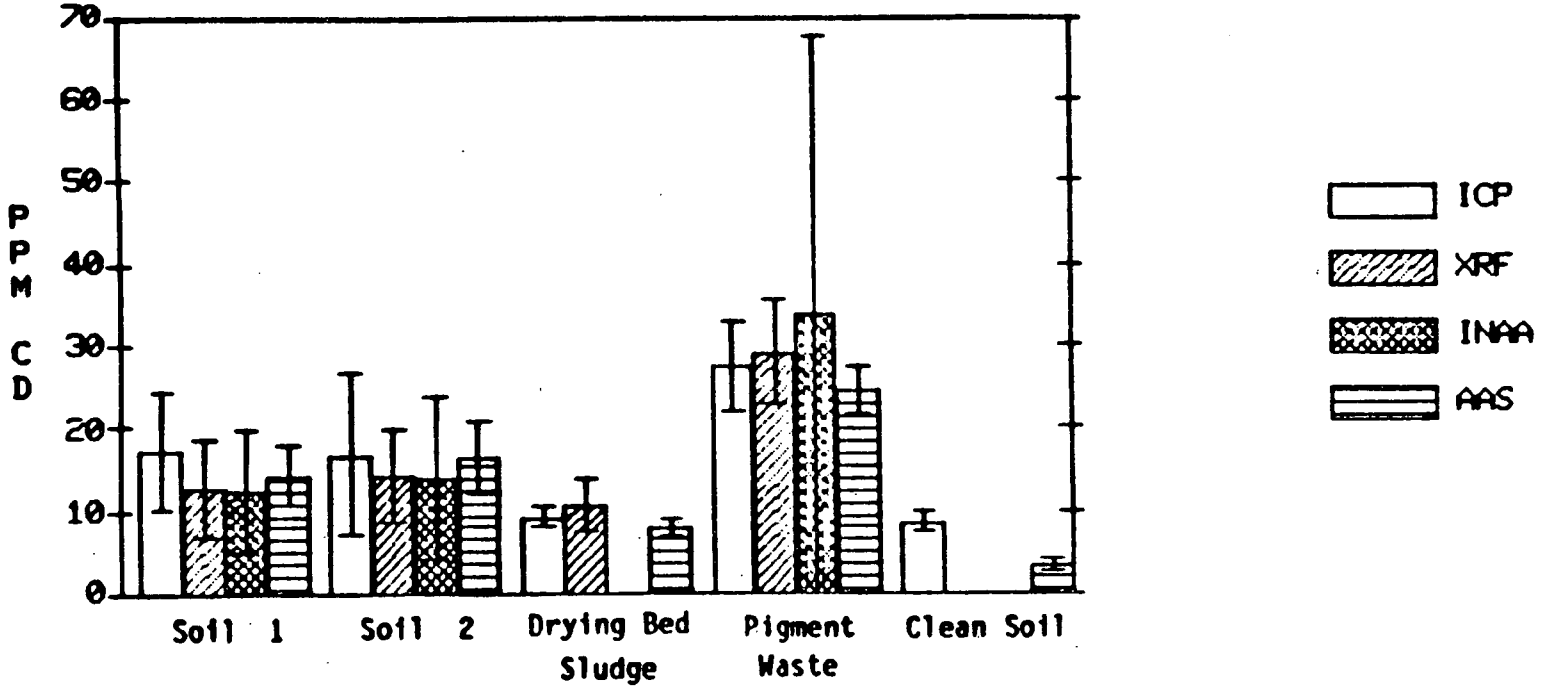


Figure 3. Cd results for the samples (mean values and 95% confidence intervals in µg/g).

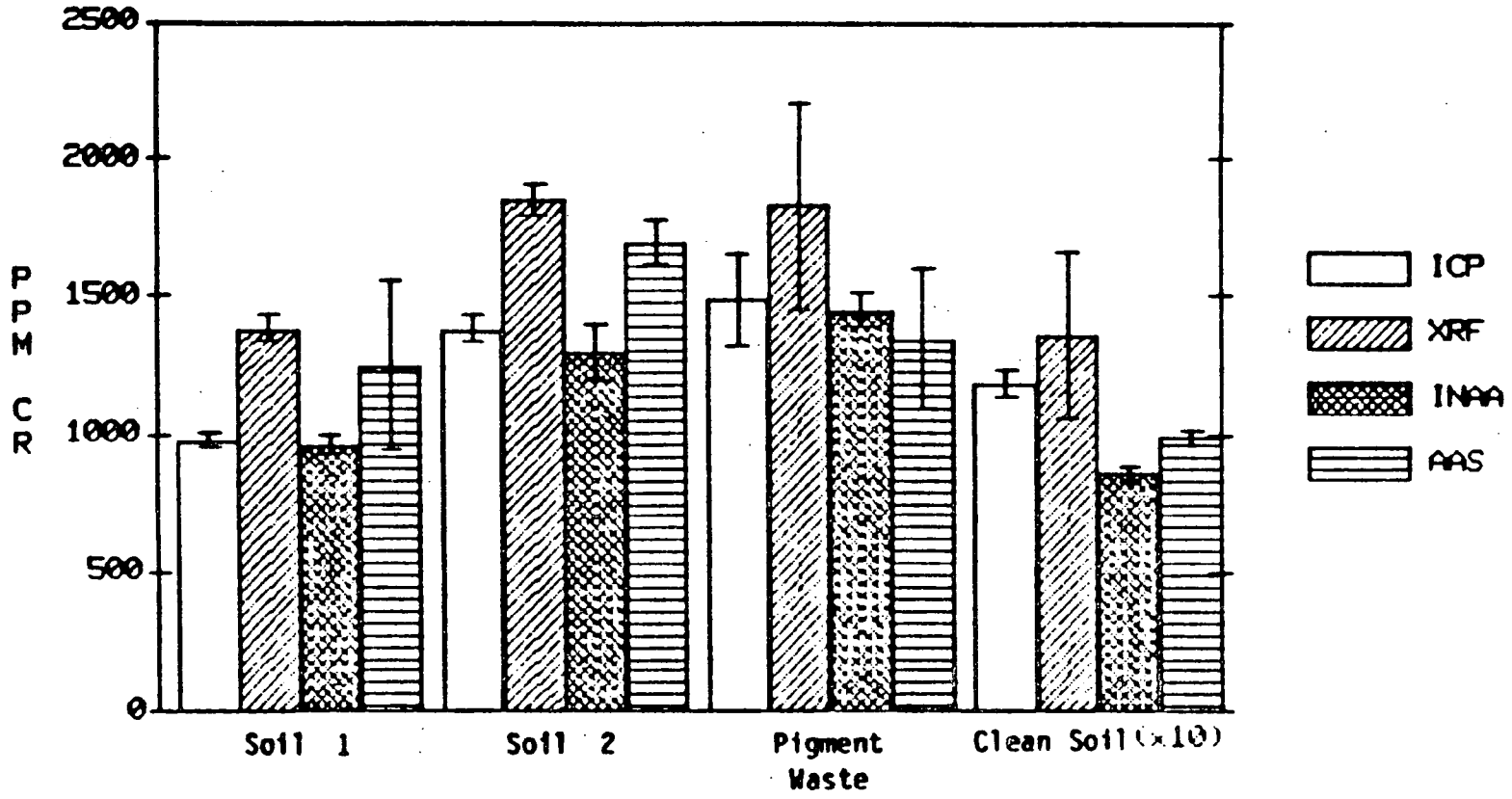


Figure 4. Cr results for selected waste samples (mean values and 95% confidence intervals in µg/g).

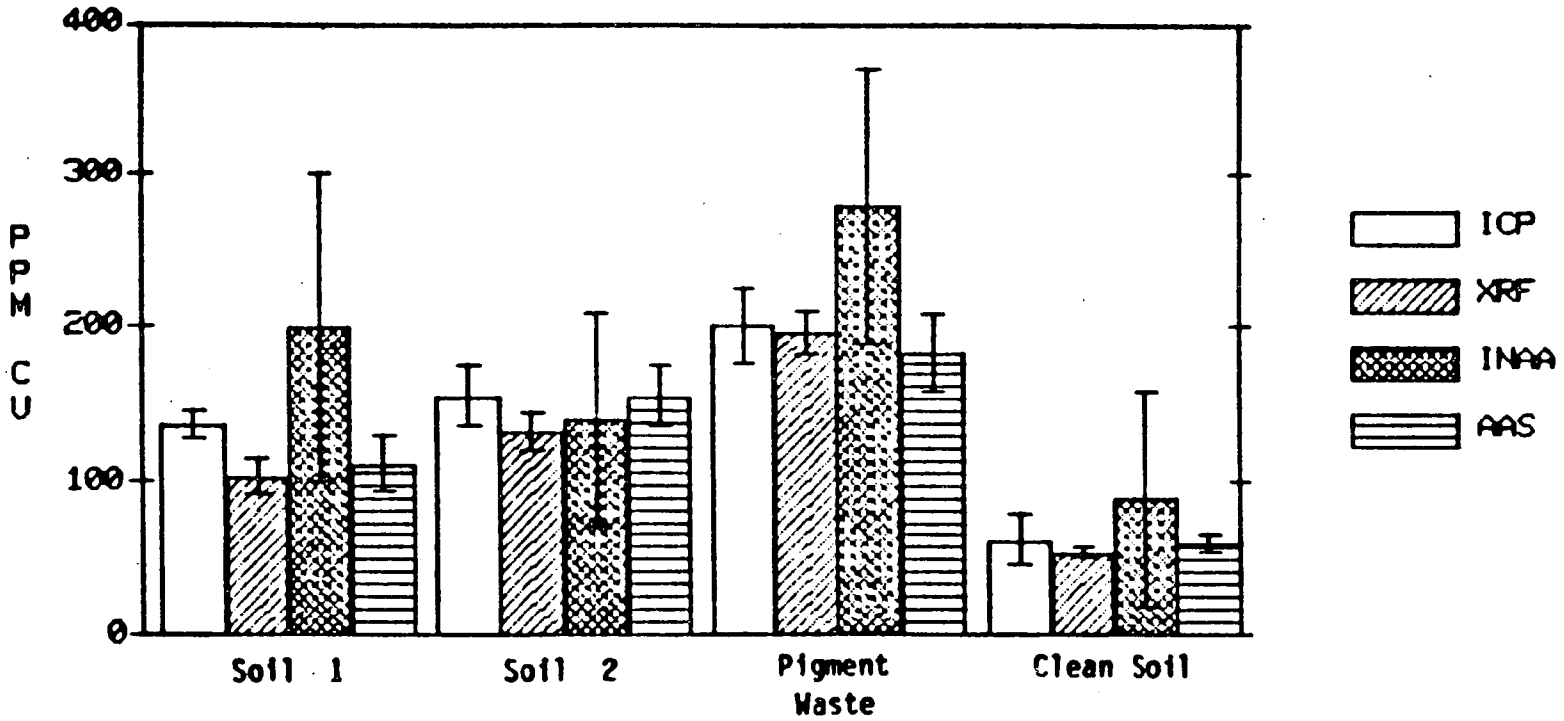


Figure 5. Cu results for selected waste samples (mean values and 95% confidence intervals in µg/g).

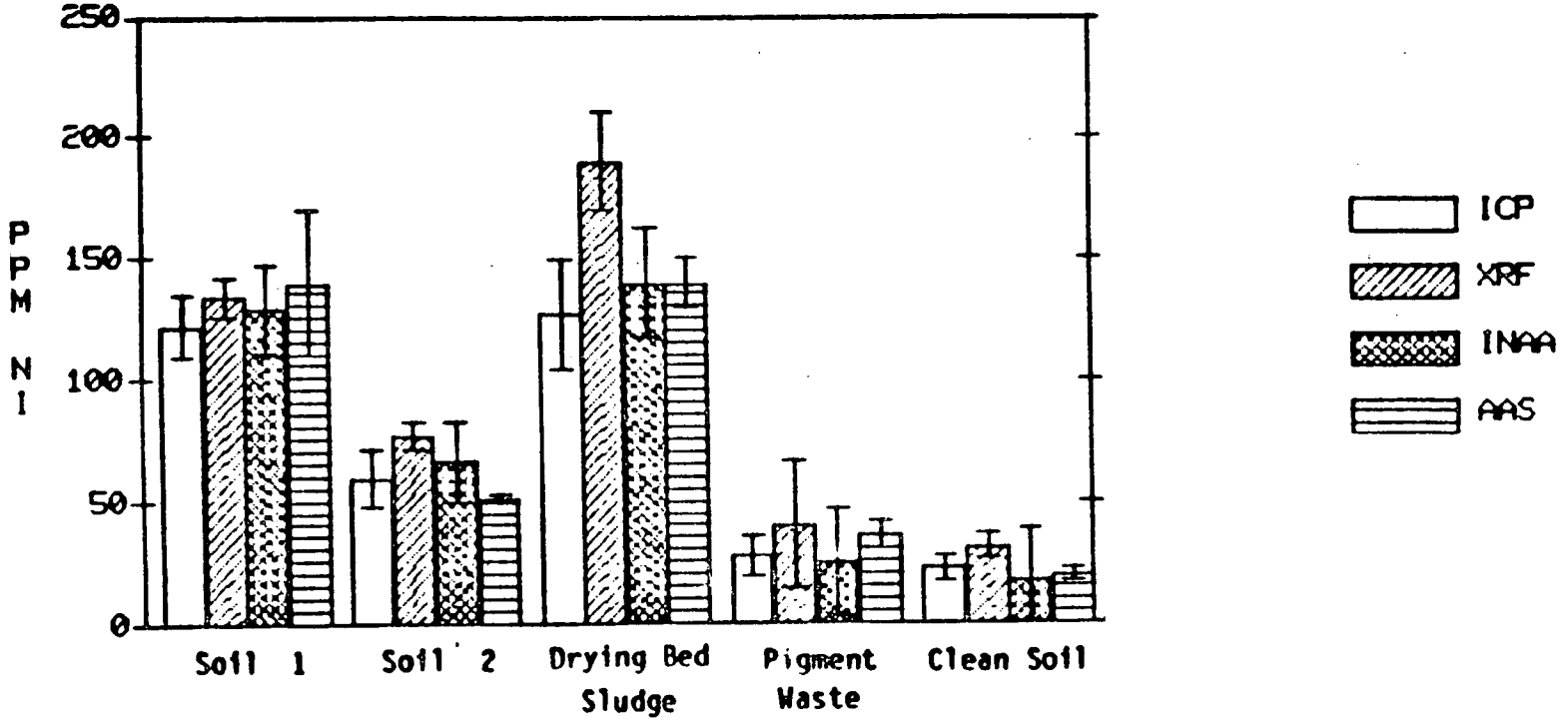


Figure 6. Ni results for selected waste samples (mean values and 95% confidence intervals in µg/g).

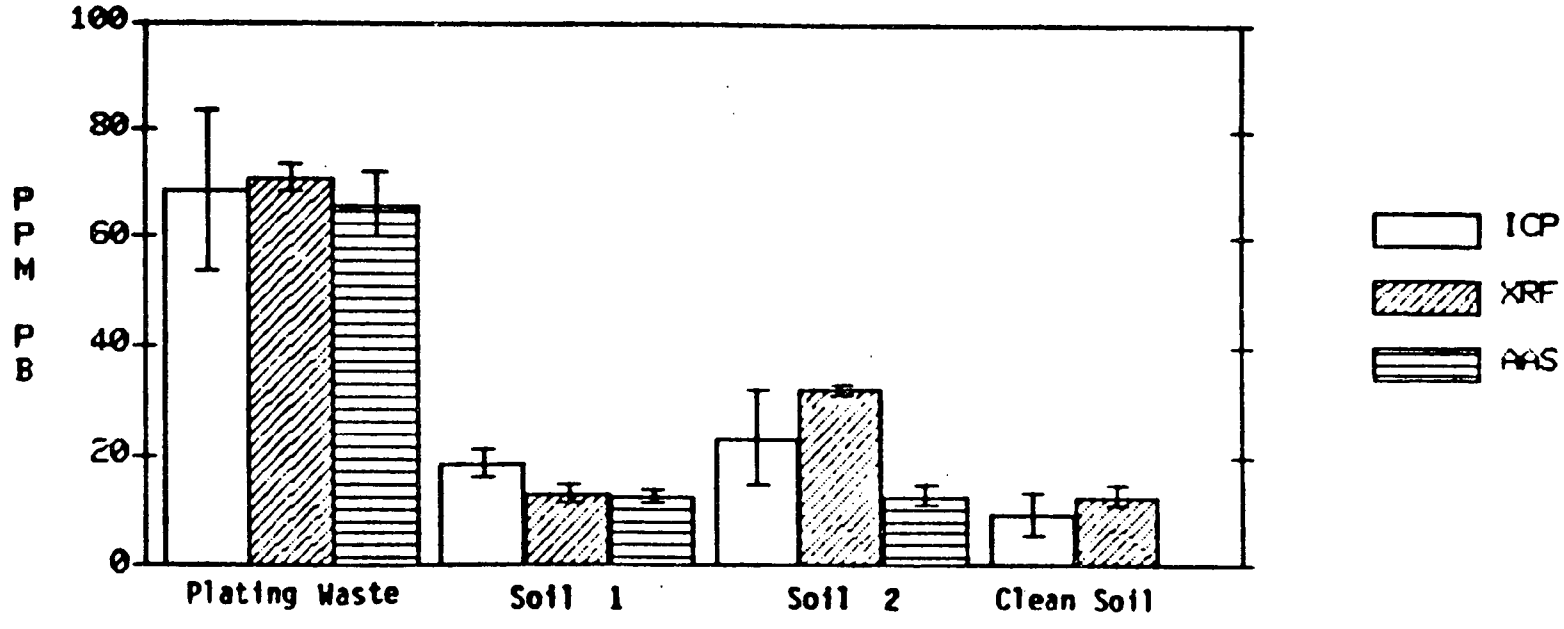


Figure 7. Pb results for the low concentration samples (mean values and 95% confidence intervals in µg/g).

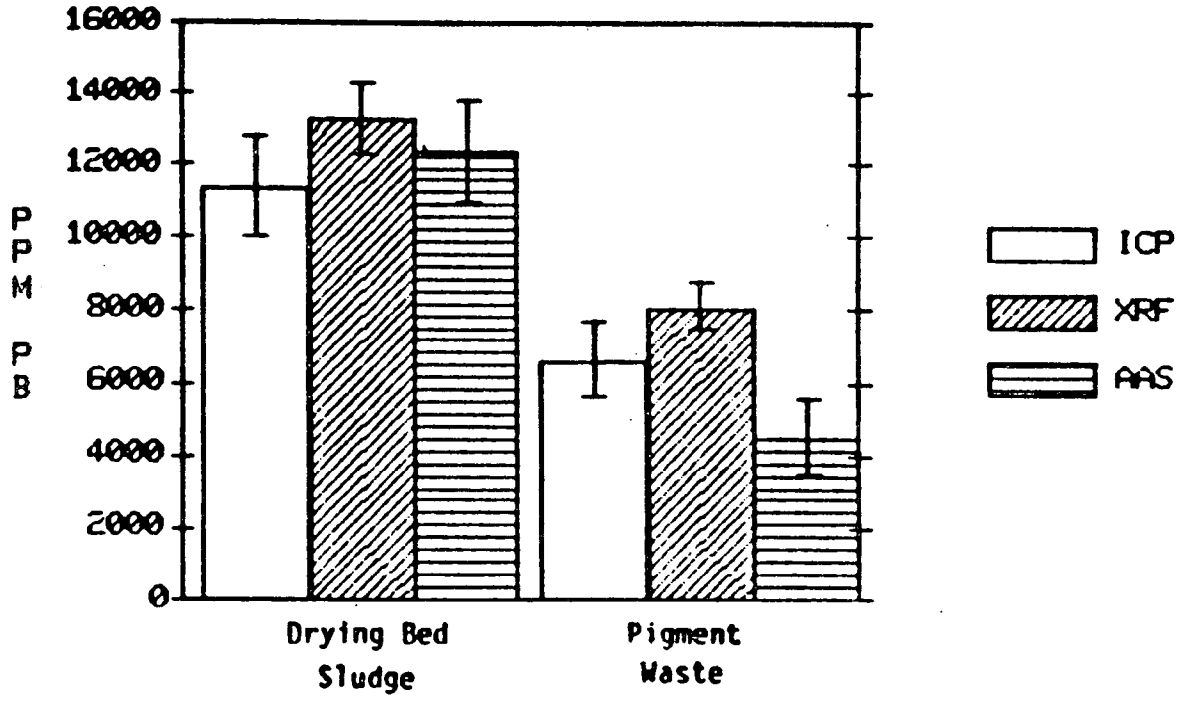


Figure 8. Pb results for the high concentration samples (mean values and 95% confidence intervals in µg/g).

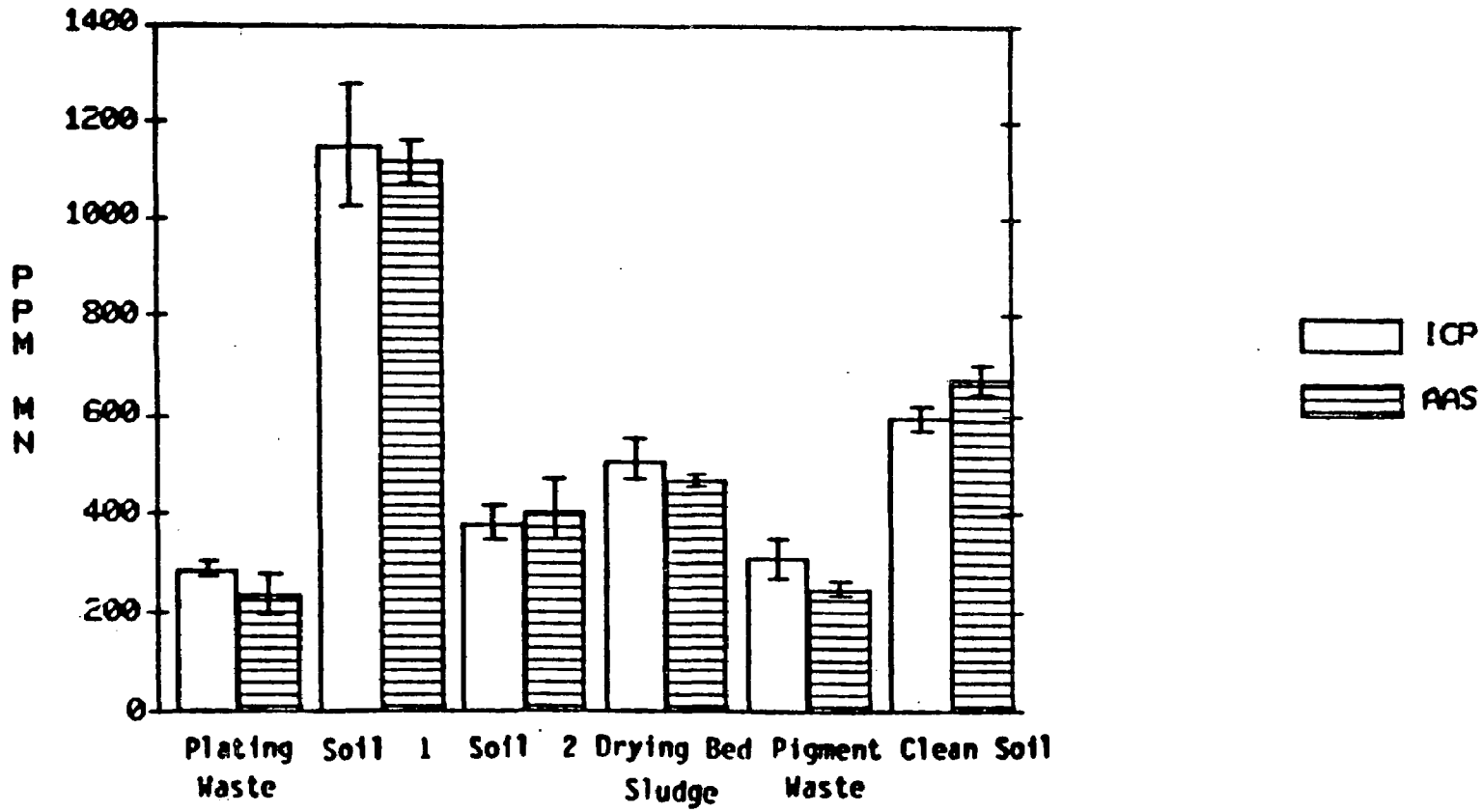


Figure 9. Mn results by ICP-OES and AAS (mean values and 95% confidence intervals in µg/g).

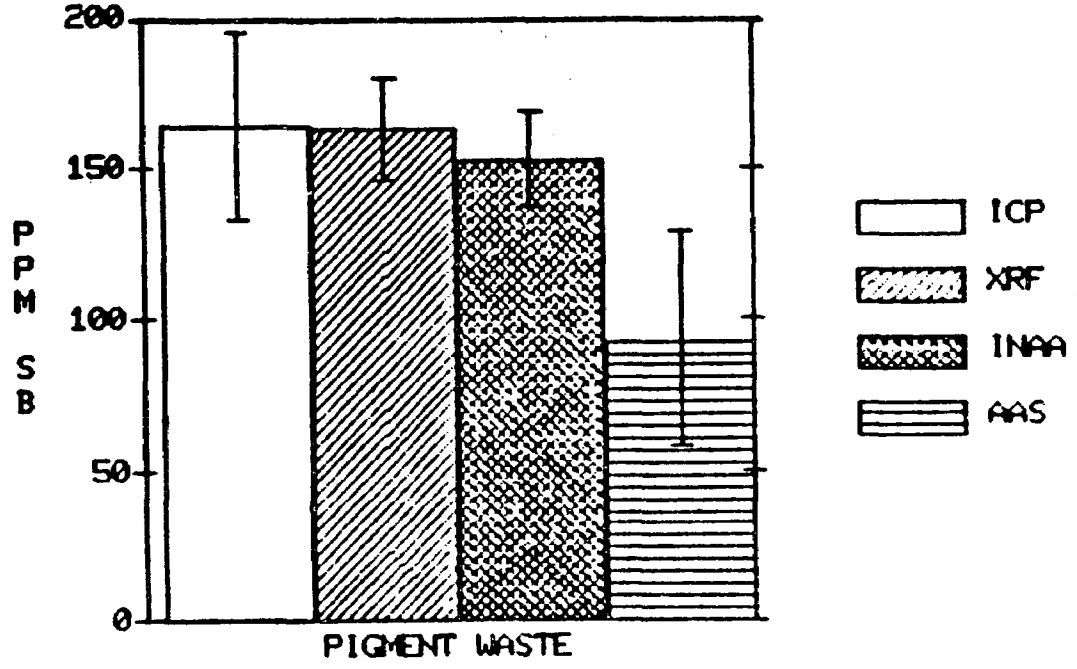


Figure 10. Sb results for the paint pigment sample (mean values and 95% confidence intervals in µg/g).

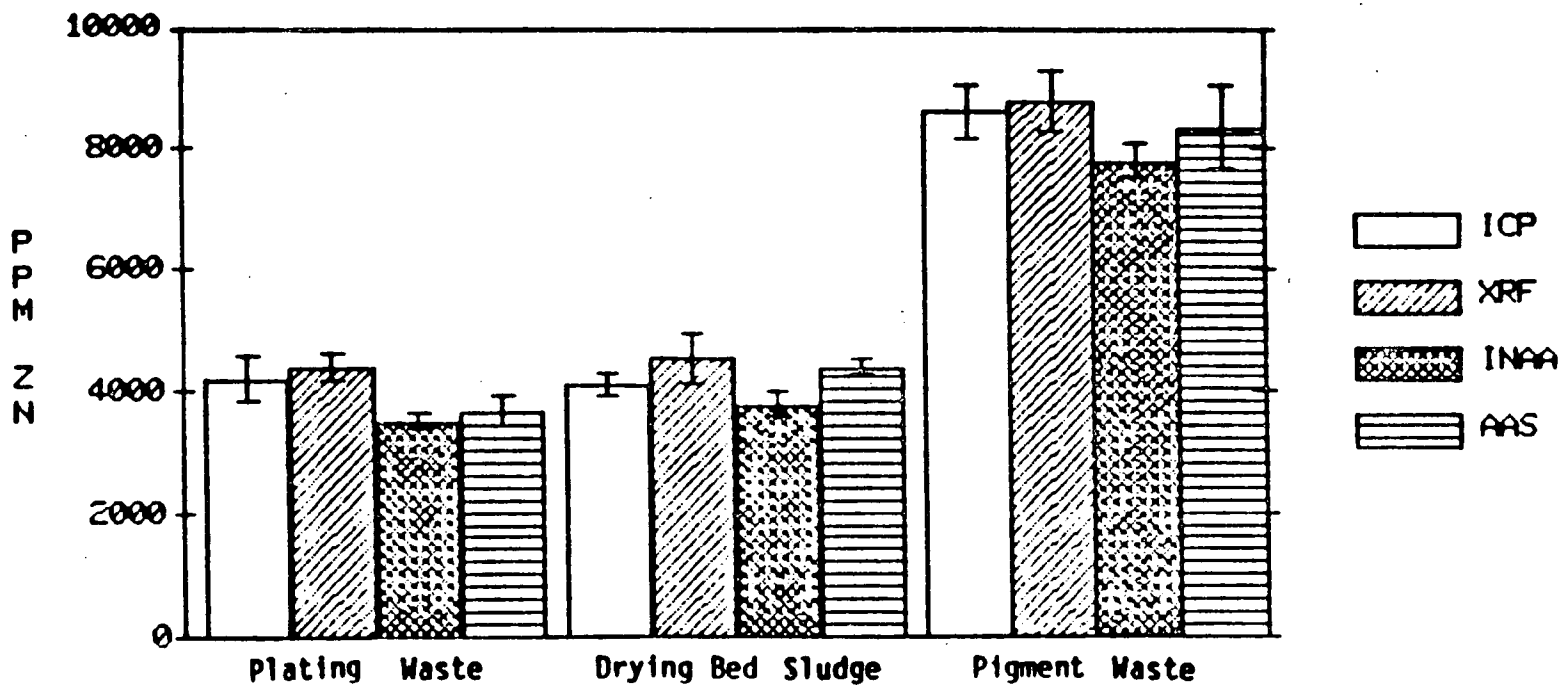


Figure 11. Zn results for high concentration samples (mean values and 95% confidence intervals in µg/g).

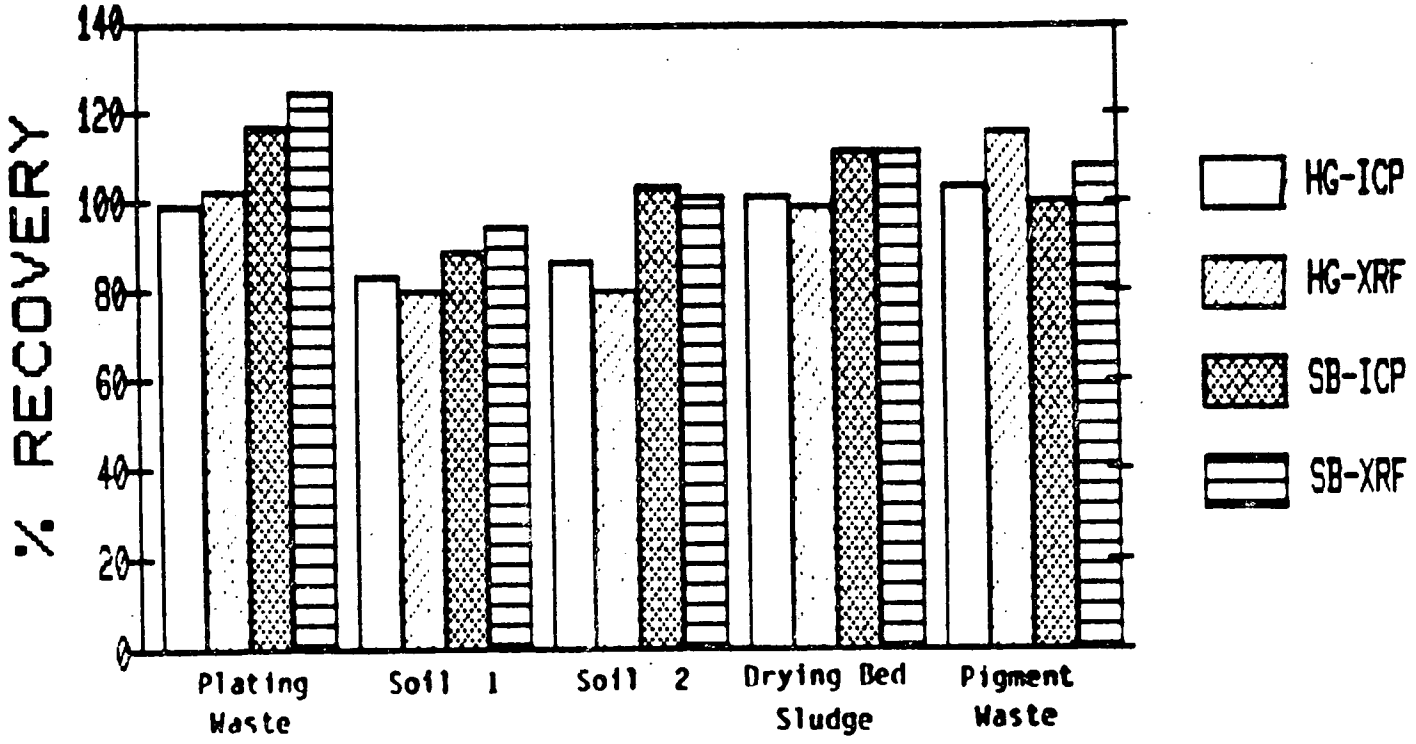


Figure 12. Percent recovery for Hg and Sb added to the wastes.

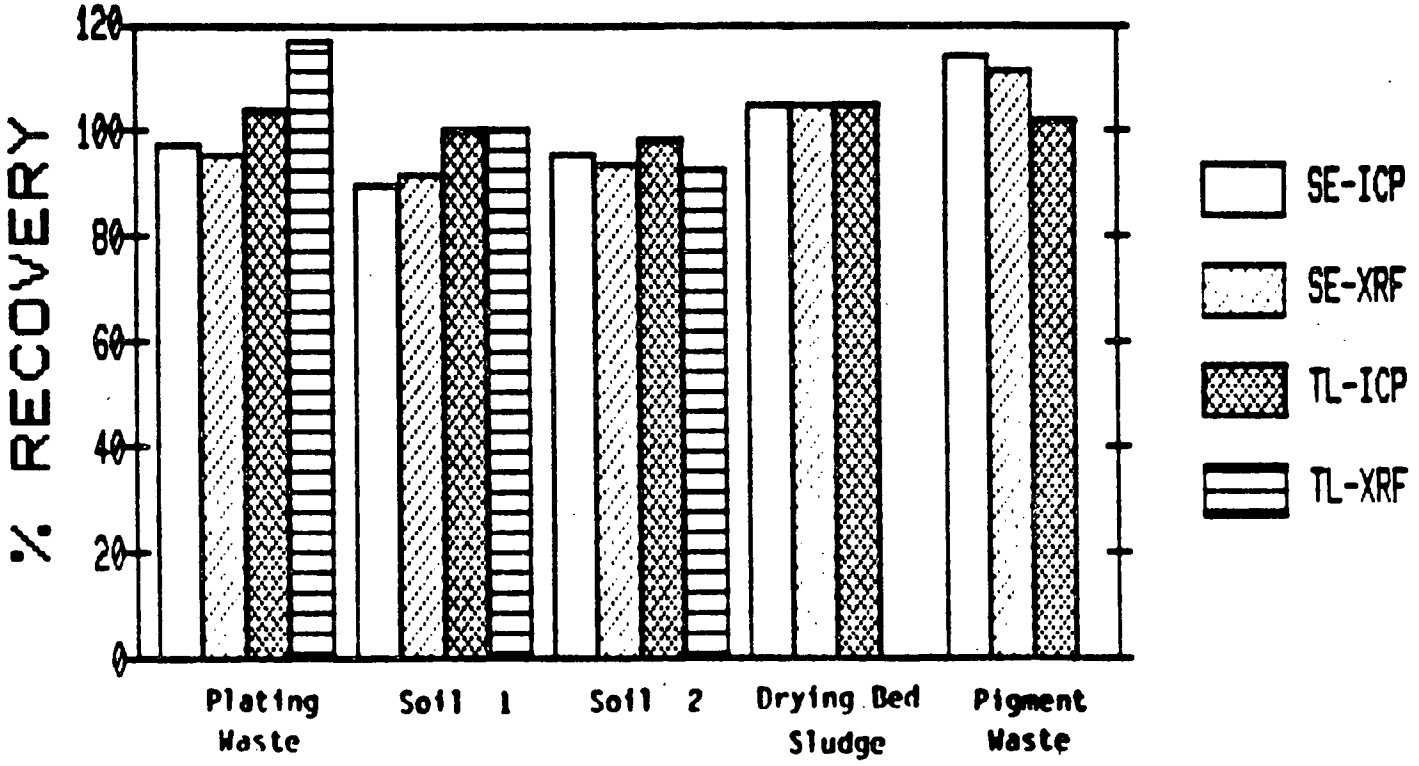


Figure 13. Percent recovery for Se and Tl added to the wastes.

Table 1. Sample Digestion Procedure

Teflon-lined Digestion Bomb
500 mg sample
4 mL HF, 2 mL HNO_3, 2 mL $HClO_4$ (Ultrex grade)
120° C for 8 hours
Cool 1 hour
Add 1 g H_3BO_3 (Ultrex grade)
Dilute to 50 mL with DI water

Table 2. ICP-OES Results for NBS SRMs*

Element	Urban-Particulates (1648)			River Sediment (1645)			
	Set 1	Set 2	True	Set 1	Set 2	Set 3	True
Ag	6.3	6.5	(6)	3	1	1	no value
As	96	98	115	65	63	62	66
Ba	700	720	(737)	360	340	340	no value
Be	5.3	4.2	no value	2	1	1	no value
Cd	68	69	75	10	9.8	9.8	10.2
Cr	400	380	403	2.7%	2.6%	2.6%	2.96%
Cu	620	630	609	110	102	105	109
Fe	3.9%	3.7%	3.9%	10.1%	9.9%	9.7%	11.3%
Hg	6	8	no value	14	5	3	1.1
Mn	750	790	(860)	750	720	710	785
Ni	76	73	82	32	31	30	45.8
Pb	6600	6500	6550	680	670	670	714
Sb	43	41	(45)	28	10	6	(51)
Se	23	20	(24)	25	9	5	no value
Tl	7.1	6.7	no value	5	2	2	1.44
Zn	4600	4520	4760	1710	1680	1650	1720

*Data in ug/g, except where noted otherwise
Parenthese = uncertified NBS value

Table 3. ICP-OES Conditions Used For Analyses Of Waste Samples

Element	Wavelength (nm)	Background Measurements Distance from Analytical Wavelength (nm)	Detection Limit (ug/g)
Ag	328.07	0.08 Below	1
As	197.20	0.10 Below	9
Ba	455.40	0.09 Above	0.2
Be	313.04	0.06 Below	0.3
Cd	226.50	0.06 Below; 0.10 Above	0.4
Cr	205.55	0.08 Below; 0.15 Above	0.7
Cu	324.75	0.12 Below	0.6
Fe	259.94	0.10 Above	0.7
Hg	194.23	0.11 Above	3
Mn	257.61	0.12 Above	0.2
Ni	231.60	0.06 Above	2
Pb	220.35	0.10 Below; 0.05 Above	6
Sb	206.83	0.05 Below; 0.12 Above	7
Se	190.03	0.14 Below	9
Tl	190.86	0.10 Below	5
Zn	213.86	0.05 Below; 0.05 Above	0.2

Plasma Gas Flow	12.1/min.
Aux Gas Flow	0.1/min.
Nebulizer Gas Pressure	36 psi (2.5 kg/cm^2)
Forward RF Power	1.2 kW
Viewing Height	16 mm above load coil

Table 4. Analytical Conditions For AAS Analysis Of Waste Samples

Element	Wavelength nm	Slit Width nm	Bkg Correction (W, D_2, None)	Method
Ag	328.1	0.7	D_2	Flame
As	193.7	0.7	D_2	Furnace
Ba	553.6	0.4	W	Flame
Be	234.9	0.7	D_2	Flame
Cd	228.9	0.7	D_2	Flame
Cr	357.9	0.7	W	Flame
Cu	324.8	0.7	D_2	Flame
Hg	253.7	0.7	None	Cold Vapor
Ni	232.0	0.2	D_2	Flame
Pb	283.3	0.7	D_2	Flame
Sb	217.6	0.2	D_2	Furnace
Se	196.0	2.0	D_2	Furnace
Tl	276.8	0.7	D_2	Furnace
Zn	213.9	0.7	D_2	Flame

D_2= Deuterium Lamp
W = Tungsten Lamp

Table 5. EP Toxicity Concentrations

Element	EP-Criterion Concentration (mg/L)
Ag	5.0
As	5.0
Ba	100
Cd	1.0
Cr	5.0
Hg	0.2
Pb	5.0
Se	1.0

Table 6. ICP Analytical Conditions

Instrument: Spectrametrics SpectraSpan III A ICP-DCP Emission Spectrometer capable of operating in a manual sequential single-element mode or simultaneous multi-element mode. The Monochromator is a modified Czerny-Turner using an Echelle grating with 30° prism for order separation.

Entrance slit size:	50 um by 200 um
Background Correction:	High 8 and Low 6
Source:	Argon ICP
Source Power:	1200 W
Plasma Gas Flow:	16 L/min
Auxiliary Gas Flow:	0.2 - 0.4 L/min
Nebulizer:	GMK Babington Nebulizer
Nebulizer Gas Flow:	0.3 L/min at 22 psi
Sample Uptake Rate:	1.5 mL/min using a Gilson Minipuls 2 Peristalic Pump
Plasma Viewing Height:	15 mm above the load coil

Table 7. Instrumental Detections Limits

	AAS		ICP	
Element	WL (nm)	Detection Limit (mg/L)	WL (nm)	Detection Limit (mg/L)
Ag	328.1	0.02	328.068	0.02
Ba	553.6	0.2	455.403	0.04
Cd	228.8	0.01	214.438	0.003
Cr	357.9	0.08	267.716	0.008
Pb	283.3	0.3	283.306	0.5
Pb			220.353	0.1

Table 8. Description of Hazardous Waste Samples

Waste Number	Description
1	Plating waste sludge
2	Drying bed solids
3	NBS QA sludge
4	Mercury storage tank wastewater
5	Sulfuric acid scrubber waste solution
6	Mercury settling basin sludge

TABLE 9. COMPARISON OF ICP AND AAS RESULTS FOR Cr

Sample	Spike Level[a]	Digest[b]	ICP[c] n	ICP[c] $\bar{x} \pm s$	ICP[c] RSD (%)	AAS[c] n	AAS[c] $\bar{x} \pm s$	AAS[c] RSD (%)	RPD[d]
1	1	1	4	1.05 ± 0.12	11	6	0.88 ± 0.19	22	+18
	2	1	4	4.55 ± 0.09	2.0	6	4.27 ± 0.20	4.7	+6.4
	2	2	6	4.57 ± 0.19	4.2	6	4.47 ± 0.34	7.6	+2.2
2	1	1	4	0.90 ± 0.10	11	6	0.85 ± 0.14	16	+5.5
	2	1	6	4.87 ± 0.72	15	6	5.00 ± 0.37	7.4	-2.6
	2	2	6	3.97 ± 0.06	1.5	6	3.93 ± 0.38	9.7	+1.0
3	1	1	4	1.01 ± 0.08	8.0	6	0.92 ± 0.13	14	+8.9
	2	1	6	4.85 ± 0.45	9.3	6	4.65 ± 0.22	4.7	+4.2
	2	2	6	4.55 ± 0.25	5.5	6	4.59 ± 0.31	6.8	-0.9
4	1	1	4	1.14 ± 0.23	20	6	1.01 ± 0.24	24	+12
	2	1	6	4.77 ± 0.38	8.0	6	4.87 ± 0.36	7.4	-2.1
	2	2	6	3.71 ± 0.22	5.9	6	3.43 ± 0.23	6.7	+7.8
5	1	1	4	388 ± 24	6.2	6	405 ± 29	7.2	-4.3
	2	1	6	384 ± 3	0.9	5	422 ± 12	2.8	-9.3
	2	2	6	365 ± 11	3.0	6	381 ± 18	4.7	-4.3
6	1	1	6	27.1 ± 0.9	3.3	6	27.1 ± 0.6	2.4	0
	2	1	6	30.0 ± 1.4	4.7	6	31.1 ± 1.4	4.5	-3.6
	2	2	6	28.6 ± 2.0	7.0	6	28.8 ± 1.6	5.6	-0.7

[a] Spike 1 = 20% of the EP toxicity concentration.
Spike 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] Results are expressed in mg/L.

[d] $$\text{RPD} = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

TABLE 10. COMPARISON OF ICP AND AAS RESULTS FOR Cd

Sample	Spike Level[a]	Digest[b]	ICP[c] n	ICP[c] $\bar{x} \pm s$	ICP[c] RSD (%)	AAS[c] n	AAS[c] $\bar{x} \pm s$	AAS[c] RSD (%)	RPD[d]
1	1	1	4	0.226 ± 0.018	8.0	6	0.232 ± 0.037	16	-2.6
	2	1	4	0.930 ± 0.039	4.2	6	0.865 ± 0.052	6.0	+7.3
	2	2	6	0.952 ± 0.075	7.9	6	0.948 ± 0.022	2.3	+0.42
2	1	1	4	0.239 ± 0.025	10	6	0.237 ± 0.036	15	+0.84
	2	1	4	1.039 ± 0.091	8.8	6	1.097 ± 0.061	5.6	-5.4
	2	2	6	1.028 ± 0.068	6.6	6	1.003 ± 0.027	2.7	+2.5
3	1	1	4	1.520 ± 0.079	5.2	6	1.53 ± 0.130	8.5	-0.66
	2	1	4	2.29 ± 0.270	12	6	2.36 ± 0.040	1.7	-3.0
	2	2	6	2.40 ± 0.140	5.8	6	2.335 ± 0.047	2.0	+2.7
4	1	1	4	0.174 ± 0.024	14	6	0.160 ± 0.033	21	+8.4
	2	1	4	0.934 ± 0.065	7.0	6	0.948 ± 0.035	3.7	-1.5
	2	2	6	0.928 ± 0.063	6.8	6	0.893 ± 0.031	3.5	+3.8
5	1	1	4	0.277 ± 0.018	6.5	6	0.064 ± 0.011	17	+143
	2	1	6	1.028 ± 0.079	7.7	6	0.793 ± 0.030	3.8	+26
	2	2	6	0.980 ± 0.096	9.8	6	0.782 ± 0.047	6.0	+22
6	1	1	6	0.208 ± 0.024	12	6	0.230 ± 0.012	5.2	-10
	2	1	6	0.975 ± 0.060	6.2	6	0.983 ± 0.028	2.8	-0.82
	2	2	6	0.910 ± 0.097	11	6	0.933 ± 0.040	4.3	-2.5

[a] Spike 1 = 20% of the EP toxicity concentration.
Spike 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] Results are expressed in mg/L.

[d] $$\text{RPD} = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

TABLE 11. COMPARISON OF ICP AND AAS RESULTS FOR Ba

Sample	Spike Level[a]	Digest[b]	ICP[c] n	ICP[c] $\bar{x} \pm s$	ICP[c] RSD (%)	AAS[c] n	AAS[c] $\bar{x} \pm s$	AAS[c] RSD (%)	RPD[d]
1	1	1	4	21.9 ± 1.7	7.8	6	24.8 ± 1.3	5.2	-12
	2	1	4	88.7 ± 7.0	7.9	6	91.8 ± 1.9	2.1	-3.4
	2	2	6	90.6 ± 7.2	8.0	6	86.4 ± 1.7	2.0	+4.8
2	1	1	4	15.1 ± 2.1	14	6	16.5 ± 0.77	4.7	-8.8
	2	1	6	95.7 ± 12	12	6	100.0 ± 1.9	1.9	-4.4
	2	2	6	6.43 ± 0.28	4.4	6	4.12 ± 1.0	27	+44
3	1	1	4	17.58 ± 0.54	3.1	6	17.62 ± 1.3	7.4	-0.23
	2	1	5	91.1 ± 12	13	6	93.1 ± 1.8	1.9	-2.2
	2	2	6	2.65 ± 0.37	14	6	1.23 ± 0.75	61	+73
4	1	1	4	10.7 ± 1.3	12	6	8.00 ± 0.77	9.6	+30
	2	1	6	8.22 ± 2.4	29	6	6.30 ± 0.43	6.8	+26
	2	2	6	0.73 ± 0.11	15	6	<2		-
5[e]	1	1	6	<0.4		6	<2		-
	2	1	6	<0.4		6	<2		-
	2	2	6	<0.4		6	<2		-
6	1	1	6	20.9 ± 1.4	6.7	6	19.4 ± 1.6	8.2	+7.4
	2	1	6	52.4 ± 2.0	3.8	6	52.6 ± 1.1	2.1	-0.38
	2	2	6	26.3 ± 1.2	4.5	6	11.8 ± 0.95	8.0	+76

[a] Spike 1 = 20% of the EP toxicity concentration.
Spike 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] Results are expressed in mg/L.

[d] $$\text{RPD} = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

[e] Added Ba lost as Ba SO_4 precipitate from this sulfuric acid matrix.

TABLE 12. COMPARISON OF ICP AND AAS RESULTS FOR Pb

Sample	Spike Level[a]	Digest[b]	ICP[c] n	ICP[c] $\bar{x} \pm s$	ICP[c] RSD (%)	AAS[c] n	AAS[c] $\bar{x} \pm s$	AAS[c] RSD (%)	RPD[d]
1	1	1	4	1.42 ± 0.54	38	6	1.61 ± 0.39	24	-12
	2	1	3	4.78 ± 2.08	44	6	5.33 ± 1.13	21	-11
	2	2	4	7.69 ± 1.5	21	5	5.06 ± 0.97	19	+30
2	1	1	7	64.5 ± 14.2	22	6	62.77 ± 0.85	1,4	+2.7
	2	1	8	86.4 ± 16.2	19	6	78.8 ± 1.5	1.9	+9.1
	2	2	6	19.7 ± 5,6	28	6	21.7 ± 0.77	3.5	-9.7
3	1	1	4	34.6 ± 3.6	10	6	38.83 ± 1.3	3.3	-11
	2	1	6	46.5 ± 6.3	14	6	43.3 ± 1.5	3.5	+7.1
	2	2	5	4.52 ± 2.2	49	6	4.28 ± 1.6	37	+5.5
4	1	1	4	3.49 ± 2.0	58	6	1.45 ± 0.21	14	+90
	2	1	2	3.60 ± 0.07	2.0	6	4.85 ± 1.1	23	-28
	2	2	1	1.66		6	1.65 ± 1.1	23	+0.6
5	1	1				6	6.10 ± 0.75	12	
	2	1	1	2.04		6	2.42 ± 0.48	20	-16
	2	2	1	1.13		6	2.62 ± 1.06	40	-61
6	1	1	2	1.75 ± 0.64	36	6	1.64 ± 0.32	20	+6.6
	2	1	2	4.78 ± 0.078	1.6	6	5.31 ± 1.1	21	-10
	2	2				4	1.06 ± 1.1	104	

[a] Spike 1 = 20% of the EP toxicity concentration.
Spike 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] Results are expressed in mg/L.

[d] $$RPD = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

TABLE 13. COMPARISON OF ICP AND AAS RESULTS FOR Ag

Sample	Spike Level[a]	Digest[b]	ICP[c] n	ICP[c] $\bar{x} \pm s$	ICP[c] RSD (%)	AAS[c] n	AAS[c] $\bar{x} \pm s$	AAS[c] RSD (%)	RPD[d]
1	1	1	4	0.926 ± 0.24	26	6	0.877 ± 0.12	14	+5.5
	2	1	3	1.79 ± 0.83	46	6	1.36 ± 0.15	11	+29
	2	2	5	0.634 ± 0.16	25	6	3.49 ± 0.65	19	-130
2	1	1	4	0.749 ± 0.16	21	6	0.667 ± 0.13	20	+10
	2	1	3	2.04 ± 0.34	17	6	1.97 ± 0.27	14	+3.5
	2	2	6	0.854 ± 0.20	23	6	2.76 ± 0.43	16	-105
3	1	1	4	0.735 ± 0.088	12	6	0.713 ± 0.068	9.5	+3.0
	2	1	3	1.90 ± 0.20	11	6	1.63 ± 0.17	10	+16
	2	2	6	1.65 ± 0.22	13	6	2.64 ± 0.23	8.7	-46
4	1	1	4	0.962 ± 0.24	25	6	1.005 ± 0.070	7.0	-4.4
	2	1	2	3.90 ± 1.1	28	6	4.38 ± 0.21	4.8	-11
	2	2	6	3.90 ± 0.30	7.7	6	4.45 ± 0.16	3.6	-13
5	1	1	3	0.18 ± 0.15	83	5	<0.5	-	-
	2	1	4	0.30 ± 0.25	83	6	0.086 ± 0.042	49	+125
	2	2	6	1.81 ± 0.48	26	6	4.47 ± 0.37	8.3	-85
6	1	1	6	0.816 ± 0.15	18	6	0.782 ± 0.085	11	+4.3
	2	1	6	1.36 ± 0.40	29	6	1.26 ± 0.17	14	+7.6
	2	2	6	1.53 ± 0.33	22	6	2.14 ± 0.21	9.8	-33

[a] Spike 1 = 20% of the EP toxicity concentration.
Spike 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] Results are expressed in mg/L.

[d] $$RPD = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

TABLE 14. COMPARISON OF DIGESTED AND UNDIGESTED ALIQUOTS BY ICP

Sample	Element	Digested Aliquot n	Digested Aliquot x ± s	Undigested Aliquot n	Undigested Aliquot x ± s	RPD (%)
1 (plating waste sludge)	Ag	4	1.79 ± 0.83	5	0.63 ± 0.16	+101
	Ba	4	88.7 ± 7.0	6	90.6 ± 7.2	-2.1
	Cd	4	0.930 ± 0.039	6	0.952 ± 0.079	-2.3
	Cr	4	4.55 ± 0.09	6	4.57 ± 0.19	-0.44
	Pb	3	4.8 ± 2.1	1	6.8 ± 1.5	-34
2 (drying bed solids)	Ag	3	2.04 ± 0.34	6	0.85 ± 0.20	+96
	Ba	6	96 ± 12	6	6.43 ± 0.28	+175
	Cd	4	1.039 ± 0.091	6	1.028 ± 0.068	+1.1
	Cr	6	4.87 ± 0.72	6	3.97 ± 0.06	+20
	Pb	8	86 ± 16	6	19.7 ± 5.6	+115
3 (NBS sludge)	Ag	3	1.90 ± 0.20	6	1.65 ± 0.22	+14
	Ba	5	91 ± 12	6	2.64 ± 0.37	+206
	Cd	4	2.29 ± 0.27	6	2.40 ± 0.14	-4.7
	Cr	6	4.85 ± 0.45	6	4.55 ± 0.25	+6.4
	Pb	6	46.5 ± 6.3	5	4.5 ± 2.4	+153
4 (Hg storage tank wastewater)	Ag	2	3.9 ± 1.1	6	3.90 ± 0.30	0
	Ba	6	8.2 ± 2.4	6	0.73 ± 0.11	+167
	Cd	4	0.934 ± 0.065	6	0.92 ± 0.052	+0.64
	Cr	6	4.77 ± 0.38	6	3.71 ± 0.22	+25
	Pb	2	3.60 ± 0.07	1	1.66	+66
5 (sulfuric acid scrubber waste solution)	Ag	4	0.30 ± 0.25	6	1.81 ± 0.48	-125
	Ba[a]	6	<0.4	6	<0.4	
	Cd	6	1.028 ± 0.079	6	0.980 ± 0.22	+4.8
	Cr	6	384.5 ± 3.4	6	365 ± 4.1	+5.2
	Pb	1	2.04	1	1.13	+57
6 (Hg settling basin sludge)	Ag	6	1.36 ± 0.40	6	1.53 ± 0.33	-12
	Ba	6	52.4 ± 2.0	6	26.3 ± 1.2	+66
	Cd	6	0.975 ± 0.060	6	0.910 ± 0.097	+6.9
	Cr	6	30.0 ± 1.4	6	28.6 ± 2.0	+4.8
	Pb	6	8.8 ± 5.3	5	8.4 ± 4.7	+4.6

[a] Added Ba lost as $BaSO_4$ precipitate from this sulfuric acid matrix.

TABLE 15. COMPARISON OF DIGESTED AND UNDIGESTED ALIQUOTS BY AAS

Sample	Element	Digested Aliquot n	Digested Aliquot x ± s	Undigested Aliquot n	Undigested Aliquot x ± s	RPD (%)
1 (plating waste sludge)	Ag	6	1.36 ± 0.15	6	3.49 ± 0.65	-88
	Ba	6	91.8 ± 1.9	6	86.4 ± 1.7	+6.1
	Cd	6	0.865 ± 0.052	6	0.948 ± 0.022	-9.2
	Cr	6	4.27 ± 0.20	6	4.47 ± 0.34	-4.6
	Pb	6	5.3 ± 1.1	5	5.06 ± 0.097	+4.6
2 (drying bed solids)	Ag	6	1.97 ± 0.27	6	2.76 ± 0.43	-33
	Ba	6	100.0 ± 1.9	6	4.1 ± 1.0	+184
	Cd	6	1.097 ± 0.061	6	1.003 ± 0.027	+9.0
	Cr	6	5.00 ± 0.37	6	3.93 ± 0.38	+24
	Pb	6	78.8 ± 1.5	6	21.7 ± 0.8	+114
3 (NBS sludge)	Ag	6	1.63 ± 0.17	6	2.64 ± 0.23	-47
	Ba	6	93.1 ± 1.8	6	1.23 ± 0.75	+195
	Cd	6	2.360 ± 0.040	6	2.335 ± 0.047	+1.1
	Cr	6	4.65 ± 0.22	6	4.59 ± 0.31	+1.3
	Pb	6	43.3 ± 1.5	6	4.28 ± 1.6	+164
4 (Hg storage tank wastewater)	Ag	6	4.38 ± 0.21	6	4.45 ± 0.16	-1.6
	Ba	6	6.30 ± 0.43	6	<2	
	Cd	6	0.948 ± 0.035	6	0.893 ± 0.031	+6.0
	Cr	6	4.87 ± 0.36	6	3.43 ± 0.23	+35
	Pb	6	4.8 ± 1.1	6	1.6 ± 1.1	+100
5 (sulfuric acid scrubber waste solution)	Ag	6	0.086 ± 0.042	6	4.47 ± 0.37	-192
	Ba[a]	6	<2	6	<2	
	Cd	6	0.793 ± 0.030	6	0.782 ± 0.047	+1.4
	Cr	5	422 ± 12	6	381 ± 18	+10
	Pb	6	2.42 0.48	6	2.4 ± 1.1	+0.83
6 (Hg settling basin sludge)	Ag	6	1.26 ± 0.17	6	2.14 ± 0.21	-52
	Ba	6	52.6 ± 1.1	6	11.8 ± 0.9	+127
	Cd	6	0.983 ± 0.028	6	0.933 ± 0.040	+5.2
	Cr	6	31.1 ± 1.4	6	28.8 ± 1.6	+7.7
	Pb	6	5.3 ± 1.1	4	1.1 ± 1.1	+131

[a] Added Ba lost as $BaSO_4$ precipitate from this sulfuric acid matrix.

TABLE 16. COMPARISON OF STANDARD-ADDITIONS AND DIRECT-CALIBRATION RESULTS FOR Ba BY ICP

Sample	Spike Level[a]	Digest[b]	SA[c] n	SA[c] $\bar{x} \pm s$	SA[c] RSD (%)	C[c] n	C[c] $\bar{x} \pm s$	C[c] RSD (%)	RPD[d]
1	1	1	4	21.9 ± 1.7	7.8	4	23.10 ± 0.65	2.8	-5.3
	2	1	4	88.7 ± 7.0	7.9	4	87.5 ± 1.6	1.8	+1.4
	2	2	6	90.6 ± 7.2	7.9	6	89.3 ± 4.6	5.2	+1.4
2	1	1	4	15.1 ± 2.1	14	4	15.8 ± 1.1	7.0	-4.5
	2	1	6	95.7 ±12	12	6	99.6 ± 8.5	8.5	-4.0
	2	2	6	6.43 ± 0.28	4.4	6	6.44 ± 0.22	3.4	-0.16
3	1	1	4	17.58 ± 0.54	3.1	4	17.58 ± 0.40	2.3	0
	2	1	5	91.1 ±12	13	6	92.9 ± 8.9	9.6	-2.0
	2	2	6	2.64 ± 0.37	14	6	2.57 ± 0.10	3.9	+2.7
4	1	1	4	10.7 ± 1.3	12	4	9.19 ± 0.51	5.5	+15
	2	1	6	8.22 ± 2.4	29	6	7.24 ± 0.78	11	+13
	2	2	6	0.73 ± 0.11	15	6	0.621± 0.058	9.3	+16
5	1	1		<0.4			<0.4		
	2	1		<0.4			<0.4		
	2	2		<0.4			<0.4		
6	1	1	6	20.9 ± 1.4	6.9	6	20.68 ± 0.98	4.7	+1.1
	2	1	6	52.4 ± 2.0	3.8	6	54.4 ± 3.6	6.6	-3.8
	2	2	6	26.3 ± 1.2	4.6	6	28.2 ± 1.1	3.9	-7.0

[a] Spike Level 1 = 20% of the EP toxicity concentration.
Spike Level 2 = 100% of the EP toxicity concentration.

[b] Digest 1 = digested sample.
Digest 2 = undigested sample.

[c] SA = results from standard additions.
C = results from direct calibration. Results are expressed in mg/L.

[d] $$\text{RPD} = \frac{\bar{x}_{ICP} - \bar{x}_{AAS}}{\frac{n_{ICP}\,\bar{x}_{ICP} + n_{AAS}\,\bar{x}_{AAS}}{n_{ICP} + n_{AAS}}} \times 100\%$$

EVALUATION OF SW-846 METHODS FOR METAL EXTRACTION/DISOLUTION FROM AQUEOUS, OIL, AND SOLID WASTE MATRICES

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ABSTRACT

The objective of this study was to evaluate two selected digestion methods (Methods 3010 and 3020) for aqueous wastes, two selected digestion methods (Methods 3030 and 3040) for oil wastes, and two selected digestion methods (Methods 3050-FLAA and 3050-GFAA) for solubilizing metals in solid wastes. This effort was designed to provide information on several aspects of metal determination, including accuracy, precision, recovery, matrix effects, and other methodological parameters. Analyses of the digestates were performed by flame atomic absorption and graphite furnace atomic absorption utilizing the method of standard additions for quantitation.

The work was performed in two categories. During category 1 experiments, a variety of waste samples were digested using all methods. Spiked and unspiked waste samples were analyzed in duplicate. During category 2 experiments, seven separate aliquots of one aqueous waste sample, one oil waste sample, and one solid waste sample were digested using the appropriate methods. Each sample was prepared unspiked, spiked at level 1, and spiked at level 2. In addition, procedural blanks and controls were prepared from standard solutions. They were subjected to the digestion procedure and analyzed exactly as the waste samples.

The results were analyzed statistically. The usefulness of each method for solubilizing the metals in a variety of matrices was evaluated from the results obtained for the category 1 experiments. Accuracy, as reflected by the recovery of spikes and control samples, and precision, as reflected by the coefficient of variation, were determined from the category 2 experiments.

Method 3010 is recommended for the majority of metals tested (except Ba and Mn). Limited information was obtained for Methods 3020 and 3050-GFAA; they were labor intensive and are recommended only when the limit of detection of flame atomic absorption is not sufficient for the particular application.

It is recommended that inductively coupled argon plasma spectroscopy be considered for evaluation as an alternative analytical technique to graphite furnace atomic absorption.

Method 3030 is recommended for only a few of the metals tested: Cu, Ag, Be, Cr, and Hg. Method 3040 was found applicable and is recommended only for Cu, Cd, Cr, Fe, and Mn. The conclusions obtained for Methods 3030 and 3040 indicate applicability only to oil-soluble

organometallic compounds. No extrapolations to other inorganic forms of metals (e.g., emulsions or suspended solids) should be made.

Method 3050-FLAA is recommended for the majority of metals tested. Exceptions are Ag, V, and Zn.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The second edition of "Test Methods for Evaluating Solid Waste" [1] contains the procedures that may be used by the regulated community or others to determine whether a waste is hazardous as defined by the Resource Conservation and Recovery Act (RCRA). This document describes methodology for collecting representative samples of the waste and for determining the ignitability, corrosivity, reactivity, extraction procedure (EP) toxicity, and composition of the waste.

The manual includes methods approved by the U.S. Environmental Protection Agency (EPA) and used by the regulated community to support waste evaluations. The methods are used for listing and delisting petitions, and for describing the methods that will be used by EPA in conducting investigations. The manual serves as a compilation of state-of-the-art methodology for conducting such tests. However, many of the methods presented in the manual have not been fully evaluated by EPA using materials characteristic of the wastes regulated under RCRA.

The objective of this study was to evaluate the metal solubilization procedures (Methods 3010, 3020, 3030, 3040, and 3050) as described in the EPA Office of Solid Waste (OSW-EPA) manual. The Research Triangle Institute (RTI) evaluated these solubilization methods for liquid and solid hazardous waste materials. The methods were evaluated by analyzing the resulting solution and comparing precision and accuracy estimates and other methodological parameters. A variety of aqueous, oil, and solid wastes were used in the evaluation. This study was divided into two categories as described below.

In category 1 the purpose was to evaluate the usefulness of the digestion procedures for a variety of actual wastes and to investigate possible chemical matrix effects on spike recovery. The focus of the work in the category 2 was to establish for each element and method, an estimate of the precision and accuracy for a typical sample matrix at three concentration levels. In category 1, each sample was subjected to the digestion procedure in duplicate according to the methods appropriate to that type of sample (e.g., aqueous samples, Methods 3010 and 3020; oil and grease samples, Methods 3030 and 3040). The first experiments performed consisted of the digestion of all the unspiked wastes using the appropriate methods. A procedural blank and control were also subjected to the digestion procedure and treated as the samples. These digestates were then analyzed and, from these

results, the spiking levels were determined (approximately 10 times the original concentration). The second step was to digest all the spiked wastes using the appropriate method following both the category 1 and category 2 design. Again, a procedural blank and control were subjected to the digestion procedure. Finally, all digestates were analyzed and the data were treated using statistical methodology.

For each element in the SW-846 manual, the sample preparation method is either specifically referenced or described. In this work only the referenced elements in each preparation method were evaluated. Two of the methods, 3010 and 3020, are written specifically for flame (FLAA) and graphite furnace (GFAA) atomic absorption spectroscopy, respectively, and Method 3050 provides direction for the use of both techniques. In category 1, all sample preparation and analyses by FLAA of Methods 3030 and 3040 digestates were completed before GFAA analyses were attempted. If the concentration of an element in the sample was within the analytical range of the FLAA calibration curve and more than 10 times the limit of detection, GFAA analysis of that sample was not performed. All graphite furnace analyses were quantitated by the method of standard additions, unless a single-addition spiking procedure verified that the method of standard additions was not required. For the method of standard additions, the digestate was spiked at two different concentrations. The large spike doubled the apparent original concentration or added an amount equal to the midpoint of the calibration curve, whichever was the larger. The second spike was one-half the first. The spiking solution was a discrete solution for each element because the spiking levels differed. The sample solution was diluted if the measured concentration exceeded the linear portion of the analytical calibration curve.

After the work in category 1 was completed, the data were reviewed to select a hazardous waste material appropriate for estimating method precision and accuracy. For this work, one sample was selected for each method and seven replicates analyzed at three fortified concentration levels for each element. The criteria used for the selection of the waste for category 2 experiments were based on (1) the presence of the metals under study in the original waste, (2) the availability of the waste, and (3) the origin of the waste.

The three levels spanned the range of the calibration curve. In many cases, the lowest concentration was near the estimated instrumental detection limit and the highest concentration was near the upper limit of the calibration curve. The middle level was a concentration between the lowest and highest concentrations. If the elemental concentration in the sample was above 500 ug/mL or 500 ug/g, spiking was not performed. If the concentration in the sample was appreciably above the analytical linear range, provisions were made for diluting the sample before analysis. Since the elemental concentration in the various samples was different, no one sample material sufficed for all elements.

In all cases, the analytical technique used after sample preparation was either FLAA or GFAA spectroscopy. Fourteen different liquid and

solid waste samples were employed. These samples were selected from the following types of matrices: four aqueous waste samples, four oil- or grease-containing waste samples, and six solid waste samples.

Statistical analyses were performed and the final data were summarized as recovery of spikes and controls as well as precision as expressed by the coefficient of variation.

MATERIALS AND EXPERIMENTAL PKROCEDURES

Materials

All of the chemicals used in this study were reagent grade obtained from commercial sources. The water used was deionized laboratory grade (ultrapure, resistivity at 25 C, 18 megohm-cm). Aqueous Certified Atomic Absorption Standards were used for preparation of controls, spiking solutions, and calibration solutions for the AA instrument. Oil-based standards were obtained from Conostan, Inc. and were used for preparation of controls, spiking solutions, and calibration solutions; xylene was obtained from Fisher Scientific. A few highly concentrated standard solutions were prepared at approximately 10,000 ug/mL in this laboratory from the salts. After drying, these salts contained an undetermined amount of H20; therefore, the concentrations were not calculated from gravimetric measurements. Concentrations were determined by inductively coupled argon plasma (ICP) spectroscopy analysis. The ICP instrument was calibrated with the Aqueous Certified AA Standards.

Waste Samples

A variety of liquid and solid wastes were used in this evaluation. For aqueous samples were used for the evaluation of Method 3010 and 3020. Four samples containing oil or grease were used for the evaluation of Methods 3030 and 3040, and six solid waste samples were used for the evaluation of Method 3050. Included in the evaluation was a used lubricating oil and an oil/water emulsion from a cold-rolling facility. Of the six solid samples collected, one was a mixed wastewater treatment sludge, one a solid waste sample from an electroplating operation, and one a soil contaminated by metal-containing solid waste. The remaining three solid samples were sludges selected from other industrial sources.

When possible, samples used in the evaluation were collected from hazardous waste sources that were regulated for the greatest number of elements. The hazardous waste classification code [2] was consulted to determine and select the industrial waste sources. This approach allowed the methods to be evaluated with realistic sample matrices.

A solid sample was supplied by the QA Branch of the EPA Environmental monitoring Systems Laboratory (Cincinnati, OH). This sample was a municipal sludge previously analyzed and used as a standard for Method 3050. The remainder of the samples were obtained from local industries. The description and origin of all samples are listed in Table I.

In addition, Triangle Resources, Inc., Reidsville, NC, supplied three types of oil samples. Also, a waste motor oil sample was obtained from a local service station. This latter sample was composed primarily of used lubricating oil from car engines operated with leaded gasoline. The EPA Office of Solid Waste (OSW) supplied soils contaminated with metals.

METHODS

Method 3010: Acid Digestion Procedure for Flame Atomic Absorption Spectroscopy

The acid digestion procedure for flame atomic absorption (FLAA) analysis was used to determine the total amount of metal in the sample. This digestion procedure is prescribed by the OSW for preparing aqueous samples, EP and mobility procedure extracts, and certain nonaqueous wastes for analysis by FLAA spectroscopy. The FLAA analytical procedure has been described in the EPA 7000 series.

The metals tested in this study are Sb, Ba, Cd, Cr, Pb, Ni, Be, Cu, Fe, Mn, Na, V, and Zn.

In the acid digestion procedure, the sample is digested with nitric acid (HNO_3) to near dryness in a Griffin beaker. This step is repeated with additional portions of HNO_3 until the digestate is light in color or until its color has stabilized. After the digestate is brought to near dryness, it is cooled and taken up in dilute hydrochloric acid (HCl). The sample is then ready for FLAA analysis.

Method 3020: Acid Digestion Procedure for Furnace Atomic Absorption Spectroscopy

The acid digestion procedure is prescribed for preparing aqueous samples, mobility procedure extracts, and certain nonaqueous wastes for analysis by furnace atomic absorption (GFAA) spectroscopy. It was used for the following metals in this study: Ba, Be, Cd, Cu, Cr, Fe, Pb, Mn, Ni, Tl, Ag, V, and Zn.

In the digestion procedure, the sample is digested with HNO_3 to near dryness in a Griffin beaker. This step is repeated with additional portions of HNO_3 until the digestate is light in color or until its color had stabilized. After the digestate is brought to near dryness, it is cooled and taken up in dilute HNO_3 to a final dilution of 0.5 percent (v/v) HNO_3. The samples are then analyzed by GFAA.

Method 3030: Acid Digestion of Oils, Greases, or Waxes

The acid digestion procedure for oils, greases, and waxes is prescribed for preparing samples that contain substantial amounts of oil, grease, or wax. In this study, the samples were analyzed for the total concentration of the following metals: Sb, Ba, Cd, Cr, Pb, Ni, Ag, As, Se, Hg, Be, Cu, Fe, Mn, Tl, V, Zn, and Na.

To describe the method briefly, a representative sample is placed in a Kjeldahl or similar flask and digested with sulfuric acid (H_2SO_4), HNO_3, and hydrogen peroxide (H_2O_2). The digestate is then analyzed for metal content by either FLAA or GFAA.

Method 3040: Dissolution Procedure for Oils, Greases, or Waxes

Method 3040 is prescribed for preparing samples containing oil, grease, or wax for the following elements: Sb, Ba, Ca, Cr, Pb, Ni, Ag, As, Se, Be, Cu, Fe, Mn, Tl, V, Zn, and Na. This method may also be applicable to the analysis of other metals in these matrices.

The method is briefly described as follows. A representative sample is dissolved in an appropriate solvent (e.g., xylene or methyl isobutyl ketone). Organometallic standards are prepared using the same solvent, and the samples and standards are analyzed by either FLAA or GFAA.

Method 3050: Acid Digestion of Sludges

Method 3050 is an acid digestion procedure used to prepare sludge and soil samples for analysis by FLAA and GFAA or by ICP spectroscopy. Samples prepared by Method 3050 were analyzed by atomic absorption spectroscopy for the following metals: Sb, Ba, Cd, Cr, Pb, Ni, Ag, Se, Be, Cu, Fe, Mn, Tl, V, Zn, and Na.

To summarize the method, a dried and pulverized sample is digested in HNO_3 and H_2O_2. the digestate is refluxed with either HNO_3 or HCl. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Ag and Sb or the flame analysis of Ag, Sb, Be, Cd, Cr, Tl, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn.

DIGESTION PROCEDURES

All the unspiked wastes were digested in duplicate according to the appropriate method (i.e., aqueous wastes by methods 3010 and 3020, oil wastes by methods 3030 and 3040, solid wastes by method 3050). The digestates were analyzed by atomic absorption (AA) spectroscopy and the results were used to estimate the spiking levels for category 1 and category 2 experiments (samples were spiked at approximately 5 and 10 times the original concentration or 5 and 10 times the LOD). For those samples in which the original concentration of an element was very high (>500 ug/mL), additional element was not added.

After the wastes were spiked, they were digested according to the design for both category 1 (all wastes in duplicate) and category 2 (one waste in seven replicates) experiments. One procedural blank and one control were digested together with the unspiked samples and another procedural blank and control were subjected to the digestion procedure with the spiked samples (categories 1 and 2).

Method 3010

The procedural blank consisted of deionized water, and the control consisted of a standard mixture of approximately 10 ug/mL for each of the required metals prepared in deionized water. The 10 ug/mL concentration value was chosen because most regulated metals have a hazardous limit in the 5 to 10 ppm range.

The wastes were homogenized and a representative 100.0 mL aliquot of each waste was used per digestion. The aliquots were transferred by a 100.0 mL volumetric pipet into 400 mL Griffin beakers, which had previously been acid-washed in 5 percent HNO3. For those samples that required spiking, the appropriate volume of spiking solution was added. Three milliliters of concentrated HNO3 were added to each beaker, the beakers covered with a watch glass and placed on the hot plate. Samples were evaporated to approximately 25 to 50 mL. The samples were cooled (except for 2258-9-A-3A), and another 3 mL of HNO3 added. This process was continued several times until the digestion was completed. Since sample 2258-9-A-3A solidified when cooled, acid was added while the sample was still warm.

Due to the nature of some of the samples being digested, reduction to near dryness as specified was impossible. The samples were initially saturated solutions and concentration caused substantial precipitation and finally solidification upon cooling. For this reason, samples were removed from the hot plate before solidification occurred.

For category 1, digested samples 2258-9-A-3C and 2258-9-A-4A readily dissolved in dilute HCl when they were diluted to a 100.0 mL final volume. Digested samples 2258-9-A-3A and 2258-9-A-3B, however, did not dissolve in 100.0 mL and were subsequently diluted to 500.0 mL. Sample 2258-9-A-3A readily dissolved in the 500.0 mL, but sample 2258-9-A-3B did not. The liquid portion of the latter was decanted and analyzed.

Sample 2258-9-A-3C was chosen for Method 3010 category 2 digestions because it contained measurable amounts of most of the elements of interest.

Method 3020

The wastes were homogenized and a representative 100.0 mL aliquot of each waste was used per digestion. The aliquots were transferred by 100.0 mL volumetric pipet into 400 mL Griffin beakers, which were acid-washed in 5 percent HNO3. Three milliliters of concentrated HNO3 were added to each beaker, the beakers covered with a watch glass and placed on the hot plate. Samples were evaporated to approximately 25 to 50 mL.

The samples were cooled (except for 2258-9-A-3A), and another 3 mL HNO3 added. This process was continued several times until the digestion was completed. Since sample 2258-9-A-3A solidified when cooled, acid was added while the sample was still warm. Final dilution of samples was with dilute HNO3.

The procedural blank was prepared with 100.0 mL deionized water and was treated the same as the samples. The control was prepared using 100.0 mL distilled, deionized water spiked with metals at approximately 0.25 ug/mL.

After digestion, sample 2258-9-A-3A solidified to green crystals. The digestate was diluted to a final volume of 500 mL (rather than 250 mL used for other samples) to dissolve it completely. A clear emerald green solution resulted.

Sample 2258-9-A-3B formed a gelatinous material after digestion. In fact, the first attempt to digest this waste resulted in serious "bumping" and contaminated the other samples. All these samples were discarded and digestion was repeated with fresh materials. Sample 2258-9-A-3B (second attempt) dissolved incompletely in 500 mL.

Samples 2258-9-A-4A and 2258-9-A-3C formed dark brown sludge-like crystals after digestion. All solids readily dissolved in 250 mL water. All the above described digestates were then prepared for graphite furnace atomic absorption (GFAA).

Sample 2258-9-A-3C was used for the Method 3020 category 2 digestions since it was also used for the Method 3010 category 2 digestions.

Method 3030

The oil waste samples were homogenized by stirring, aliquoted, and digested by the procedure described in Method 3030. A minor change was made in the procedure to allow for a final dilution to 100 mL instead of 25 mL. This change was necessary to ensure a sufficient volume of digestate for all of the required elemental analyses. For each digestion, a sample weight of approximately 8.0 g was used for the unspiked samples. A procedural blank was prepared using Conostan base oil, and a control was prepared using the Conostan metal standards. The final concentrations of the controls were in the 50 to 100 ug/g range.

The exact sample amount was determined by placing an excess of the sample into a small container and weighing it with a Pasteur pipet and bulb. The weight was noted and portions were transferred, using the pipet, to a 300 mL acid-washed Kjeldahl flask. The weight of the container, sample, and pipet was again noted after the removal of some sample. The weight difference was the weight of the sample added to the flask (weight by difference). In cases where an aqueous and an organic phase were present, the phases were separated prior to weighing and only the organic phase was digested.

An acid-washed glass bead (6 mm) plus 40 mL concentrated H_2SO_4 were added to each weighed sample. The flask and the contents were swirled to ensure complete mixing.

The necks of the Kjeldahl flasks were cooled during the digestion by directing a stream of ambient air from a heat gun around the middle

portion. The flasks were heated gently until white acid fumes appeared. At this point, 1 mL concentrated HNO_3 was added dropwise to the hot mixture using a Selectapette pipet. After the HNO_3 had boiled off and the white fumes reappeared, another addition of HNO_3 was made. If the fumes did not appear in a reasonable amount of time (5-10 min), the heat was increased slightly. This process was continued until the sample was no darker than a straw or amber color. A minimum of 7 mL concentrated HNO_3 (the volume added to the blank and control) was added to the samples, blanks, and controls.

After the initial additions of HNO_3, when the sample was partially oxidized to a straw color, 0.5 mL additions of 30 percent H_2O_2 were made dropwise using another Selectapette pipet. These H_2O_2 additions were immediately followed by a 1 mL addition of HNO_3. Once the white fumes reappeared, an additional 0.5 mL volume of H_2O_2 and a 1.0 mL volume of HNO_3 were added. These additions continued until the sample was nearly colorless and clear or until 33 additions had been made. The temperature was gradually increased over the duration of the digestion.

After digestion was complete, the flasks were cooled and the contents quantitatively transferred to 100 mL volumetric flasks. When the digestion had to be interrupted (e.g., overnight), the flasks were cooled to room temperature and Parafilm placed over the top until the digestion could be resumed.

All of the samples were pale yellow and clear at the end of the digestion. As they cooled they became colorless and, with the exception of sample 2258-9-0-2B, they remained clear. Sample 2258-9-0-2B was slightly cloudy. Several of the samples produced a fine white precipitate upon dilution with water. The amount of time required for the sample digestions was 7 to 10 hours; however, the blank and control required 27 hours. The blank and control were digested first and at a lower, more gentle heat, thus they required a longer time to digest. Since these digestions took an excessive amount of time, the temperature was increased for the samples. The samples were generally started on a low setting and the setting was gradually increased over the duration of the initial digestion with HNO_3. The samples were then kept on a high setting throughout the H_2O_2 treatment.

The oil waste samples were spiked with Conostan organometallic standards and digested according to the procedure outlined in Method 3030. Approximately 4.0 g of sample were used for digestion. The amount of spike added was determined by the concentration of the Conostan standards available and by the need to keep the total oil spiking volume to 5 g or less. Sample 2258-9-0-1A was used for the 3030 category 2 digestions.

Method 3040

The unspiked oil samples were prepared for analysis according to Method 3040. A representative aliquot of approximately 10 g was weighed directly into a dry 100 mL acid-cleaned volumetric flask.

Weighing was performed on a top loading digital balance. The samples were then diluted to volume using xylene. In the case of sample 2258-9-0-2B, for which several phases were present, only the phases that would dissolve in xylene were used. Sample phases were separated with a separatory funnel prior to weighing.

The procedural blank was prepared by weighing Conostan 75 base oil into a volumetric flask and diluting with xylene. The controls were prepared at approximately 100 and 170 ug/g by weighing amounts of the Conostan standards into a volumetric flask and then diluting to volume with xylene.

All samples dissolved readily in xylene. Samples 2258-9-0-1A, 2258-9-0-2A, and 2258-9-0-2B each left a small amount of light-colored precipitate after settling.

Oil waste samples were spiked with Conostan organometallic standards and dissolved in xylene as described in Method 3040. The samples were weighed directly into dry 100 mL volumetric flasks. A balance capable of weighing to 0.001 g was used to weigh approximately 5.000 g of each sample.

Spiking levels were based on the concentration of the Conostan standards available and also on the need to keep the total ratio of oil (sample plus standards) to xylene at 1:10. This restriction limited the total mass of the standards to approximately 5.0 g.

Sample 2258-9-0-1A was chosen for Method 3040 category 2 dissolutions based on the elements present in the unspiked sample and on the availability of this particular waste. For the level 1 spiked samples, approximately 5.0 g of sample were used with 2.5 g of base oil and approximately 3 g of standards (total standards combined). The level 2 spike consisted of approximately 5.0 g of sample, no base oil, and approximately 5.5 g of standards (total standards combined). The unspiked samples consisted of approximately 5.0 g of sample and approximately 5.0 g of base oil. All samples were diluted to 100.0 mL with xylene.

Method 3050

The unspiked solid samples were prepared for FLAA analysis according to Method 3050. Wastes were homogenized by careful mixing and then aliquoted.

Sludge samples were first dried in an oven set at 60 C. The oven was placed inside a fume hood and the drying time varied for each sample. When the wastes were dry they were pulverized with a mortar and pestle. The dried wastes were then transferred to glass bottles with Teflon-lined screw caps.

One gram of each sample was weighed to the nearest 0.1 mg and quantitatively transferred to a 250 mL acid-washed Phillips beaker. Ten milliliters of 1:1 HNO_3 were added per beaker and each beaker covered with a watch glass. The samples were heated at approximately

95 C (temperature estimated by comparison to 30 mL water at this setting). The samples were refluxed at this temperature for approximately 10 minutes. After cooling, 5.0 mL of concentrated HNO3 were added, the watch glass replaced, and the samples again refluxed for 30 minutes.

After this second reflux, the samples were cooled to room temperature. Deionized water (2 mL) and 30 percent H2O2 (3 mL) were added to each beaker. The beakers were covered, returned to the hot plate, and gently warmed. The samples effervesced. Once effervescence had subsided, the beakers were again cooled and additional 1 mL aliquots of 30 percent H2O2 were added. This sequence was repeated a total of seven times (total volume of 10 mL H2O2 added).

For FLAA analysis, 10.0 mL deionized water and 5.0 mL 1:1 HCl were added and the samples refluxed for 10 minutes. After cooling, the samples were filtered using Whatman No. 42 filter paper that had been washed with 0.5 percent HNO3. Samples were filtered directly into 100 mL volumetric flasks and diluted to 100.0 mL final volume.

The control was prepared by adding a spike of 1.00 mL of each aqueous atomic absorption standard (1,000 ug/mL standard) into a Phillips beaker and drying at 60 C. This treatment of the control is consistent with the handling of sludge samples since the evaporation of the aqueous portion of samples at 60 C is necessary for them as well. The element concentrations in the control were approximately 1,000 ug/g.

All samples were digested without difficulty. The filtration step, however, was rather slow (approximately 2 hours) due to occlusion of the filter by the fine particles left after digestion.

Unspiked solid samples were prepared for GFAA analysis according to Method 3050. The element concentrations in the controls were approximately 25 and 1,000 ug/g.

Sample preparation was basically the same as the FLAA method. After the addition of H2O2, the samples were left on the hot plate, the cover glass was removed, and the volume was reduced to approximately 2 mL. The samples were cooled, 10 mL deionized water were added, and the mixture was rewarmed. The samples were then cooled and filtered.

The procedural blank was prepared in the same manner as the samples. The control was prepared by adding 25 uL of 1,000 ug/mL aqueous standards to the 250 mL Phillips beaker, drying at 60 C, and then digesting. All samples digested with no problems. The filtration step was somewhat faster (approximately 1 hour) than for flame preparation due to a smaller final volume.

Solid waste samples were spiked with aqueous standards, dried, and digested according to the procedure outlined in Method 3050. One set of samples was digested for flame analysis and another set for furnace analysis. One gram of each sample weighed to the nearest 0.1 mg was used for each digestion.

Sample 2258-9-S-5B was used for the Method 3050 category 2 digestions.

ATOMIC ABSORPTION ANALYSIS

Flame Atomic Absorption

An Instrumentation Laboratories, Inc. (IL) Model 357 single-beam atomic absorption spectrometer equipped with a deuterium arc background corrector was used for all FLAA analyses. The method of standard additions was used for the calculation of metal content. The appropriate 7000 series protocols and the instrumental manual [4] were consulted for analytical wavelength and other experimental conditions.

The standard that typically corresponded to the top of the linear portion of the calibration curve was prepared for the element of interest and run at the start of each analytical day. For this measurement, the instrument was auto-zeroed with an analytical blank, which consisted of the acid mixture characteristic of the method under evaluation. Then, the samples for analysis were diluted so that their absorbance was equal to or less than one-third the absorbance of the standard described above.

Based on this treatment, an approximate analyte concentration was estimated for each sample. The higher standard additions spike added to the sample digest was designed to double the element concentration in the sample. The lower standard additions spike was typically one-half of the higher one.

FLAA analysis was performed on Methods 3010, 3030, and 3050 digestates. Dilutions were made with deionized water or 0.5 percent HNO_3 (if high dilution factors were needed) for Methods 3010 and 3030 digestions, and with 2.5 percent HCl for 3050-FLAA digestions.

Samples from metal extraction method 3040 were also analyzed by FLAA. The equipment used and general procedure were the same as described for FLAA analysis of Method 3010 digestates. After the xylene-diluted spiked samples were prepared, each set was run as a standard addition analysis. The Method 3040 digestates were not analyzed for Tl (there is no commercial source for a Tl-in-oil standard). Analysis for Ba by FLAA in Method 3040 digestates was impossible; analytical Method 7080 is specific for samples prepared by Method 3040 (dissolution in xylene) yet it requires the use of potassium chloride (KCl) in water as an ionization suppressant. This is not compatible with the xylene solvent. Attempts to analyze without the KCl were not successful. Besides the ionization problem noted in Method 7080, there is also a significant emission problem. Occasional negative absorbances (noted on the energy meter) lead to overflow conditions and "flex curve" error messages. Method 7080 is not consistent on the question of background correction. Section 2.0 requires its use while Sections 3.0 and 7.0, Interferences and Procedure, do not mention it. Background correction was not used for Ba since the deuterium arc system could not balance with the source lamp at this high a

wavelength (553.6 nm). Comments here concerning background correction for Ba also apply to Method 7770 for Na. Phenomena such as light scattering are a function of wavelength, and background correction, documented in several reports, is not usually considered a requirement past Cu at 324.7 nm. However, an exhaustive literature search was outside the scope of this project.

Graphite Furnace Atomic Absorption

The IL instrument described above was used for most of the GFAA analyses. A second instrument used for a portion of the GFAA work was a Perkin-Elmer Model 603 AA with the model 2100 graphite furnace, an AS-1 autosampler, a PRS-10 printer, and a deuterium arc background correction system. The instrument was used with the following switch settings: concentration, peak height, background correction, and expansion. Charring and atomization temperatures were taken from the manufacturer's handbook. An injection of 20 uL was used. Peaks were recorded on a strip-chart recorder with peak height response printed on the PRS-10. The samples analyzed with the Perkin-Elmer instrument are noted on the results tables. Care was taken to use the same calibration standards with both instruments to verify their equivalency.

GFAA analyses were performed on unspiked samples from extraction Method 3020 and 3050, and on those elements from Methods 3030 and 3040 that were below the LOD of FLAA.

Analysis was performed by the method of standard additions, in a manner similar to that for FLAA. The appropriate 7000 series method was consulted for the required wavelength, background correction requirements, and matrix modifiers. An aqueous standard was prepared at a level expected to be at the top of the linear working curve. This standard was used to confirm satisfactory response under these experimental conditions. The appropriate dilution factors and spiking levels were determined by surveying diluted digestates versus this aqueous standard. Diluted and spiked digestates were then prepared and analyzed by the method of standard additions. Dilutions were made with 0.5 percent HNO3 for Methods 3020 and 3050-GFAA digestions; deionized water or 0.5 percent HNO3 was used for Method 3030 digestions and xylene was used for Method 3040 digestions.

A number of difficulties were encountered that required certain modifications to the procedures.

For As and Se analysis, a solution of 1,000 ug/mL Ni is required as a matrix modifier by the 7000 methods. Information obtained from application chemists with IL indicated that this level of Ni leads to suppression in their furnace and that 200 ug/mL Ni is more appropriate. This trend was confirmed experimentally at RTI. Two hundred micrograms per milliliter Ni was, therefore, used for the GFAA analysis of 3030 and 3050 digestates for As and Se. An additional modification was made in that the atomization temperature was set at 2,500 C rather than the manufacturer's recommended 1,800 C.

Analyses of As and Se in samples prepared by Method 3040 were attempted unsuccessfully on both the IL and Perkin-Elmer instruments. Both analytical procedures call for the addition of nickel nitrate as an aqueous solution. This addition is not possible for preparation Method 3040 in which the samples are diluted with xylene. Charring temperatures greater than 1,500 C were necessary to reduce the background to a correctable level. This temperature resulted in a loss of As and Se. Char temperatures below 400 C for times greater than 5 minutes did not combust the matrix.

For Ba and V, the manufacturer's recommended conditions are pyrolytic graphite tubes with an atomization temperature of 2,500 C. Even at 2,700 C, no more than a rise in baseline was observed when standard solutions were used. These two elements are difficult to analyze on any graphite furnace because of the formation of highly refractory carbides.

Analysis of Ba was attempted unsuccessfully on both instruments. Application chemists with IL and Perkin-Elmer were consulted. They described the analysis as possible but extremely difficult. Carbide that forms in the furnace is extremely refractory, which makes high atomization temperatures necessary. In addition, the presence of strong Ba emission lines close to the absorbance line leads to a high noise level. Perkin-Elmer stated that the alignment of the furnace about the light path is critical to this analysis. Two chemists attempted this alignment. An atomization temperature of 2,800 C (the highest marking on the furnace power supply) was used without success on the Perkin-Elmer instrument. IL lists an atomization temperature of 2,500 C. We attempted 2,700 C in the IL instrument without success. Higher temperatures were not tried for fear of burning out the temperature sensor. IL indicates that a fast heating rate modification of the power supply is beneficial to this analysis. This modification was not available to this project.

Cold Vapor Atomic Absorption

Mercury was analyzed in oil samples prepared by Method 3030 by the cold vapor technique. Stannous chloride (0.5M) and the open system alternatives from Method 7470 were used. The response was recorded on a strip-chart recorder and peak height was measured electronically. The method of standard additions was used for calibration, as it had been throughout the entire study. A desiccant tube was not used. Past experience in this laboratory has shown that the problems associated with clogging of the tube cause more trouble than the water vapor. The reading lamp heater alternative was used instead. Deuterium arc background correction was used to correct for nonspecific absorption resulting from the water vapor reaching the cell. No problems were experienced with the analytical procedure.

Statistical Analysis Procedures

Upon completion of the chemical analysis, the data obtained were keyed into online computer data sets. Category 1 data were collected to provide recovery information, as a measure of usefulness. The formulas used in calculating recoveries are:

$$\text{Percent matrix recovery} = \frac{\text{(Spiked sample measured-procedural blank)} - \text{(Unspiked sample measured-procedural blank)}}{\text{Spiking concentration}} \times 100$$

$$\text{Percent control recovery} = \frac{\text{(Control measured-procedural blank)}}{\text{(Control concentration)}} \times 100$$

Note that for statistical analysis purposes all values reported as the LOD were divided by 2 prior to being used; all data reported as below the analytical blank were considered 0. While the matrix recovery incorporates both spiked and unspiked data, the control recovery is developed separately for spiked data and for unspiked data. There is a matrix recovery for each method, waste sample, element, and replicate combination. There is a control recovery for each method, element, and spiking combination.

The waste-specific matrix recovery means were developed from the two replicate recoveries for each method and element. The overall matrix recovery means are based on eight recoveries for Methods 3010, 3020, 3030, and 3040. Since Methods 3050-FLAA and 3050-GFAA involved 6 waste samples each, the overall means are based on 12 recoveries.

Methods 3030 and 3040 are special cases: the unspiked sample data for these methods are a mixture of FLAA and GFAA data. For each, the GFAA data, when available, were first incorporated into the data set. The FLAA data were added to complete the data set. When a FLAA waste sample measurement was used in a calculation, so were the corresponding blank and control measurements. Calculations involving a GFAA waste sample measurement used its corresponding procedural blank and control measurements.

Category 2 data were collected to provide single-laboratory accuracy and precision information. For each method, there are seven replicates for one waste at each of three spiking levels. All seven replicates were excluded from the statistical analysis when four or more measurements were at the LOD.

Percent matrix recoveries were calculated as a measure of accuracy. There is a matrix recovery for each method, element, and spiking levels 1 and 2.

The procedural blanks used in calculating category 2 recoveries were the same blanks used for category 1. Since all spiked samples (both category 1 and category 2) were digested at the same time, only one procedural blank and control were needed. As noted above for Methods 3030 and 3040, the GFAA data, when available, were first incorporated into the data set and then FLAA data were added to complete it. The blanks available from the data set for Methods 3030 and 3040 recoveries calculation were usually GFAA data.

To evaluate precision, the coefficient of variation (CV) was calculated for each method, element, and spiking level combination.

RESULTS AND DISCUSSION

The waste matrices were digested according to the procedures described in Methods 3010 and 3020 for aqueous matrices, Methods 3030 and 3040 for oil matrices, and Method 3050 for solid matrices. A total of 262 digestions were performed, and appropriate blanks and controls were included. Digestates were analyzed by flame atomic absorption (FLAA) and/or graphite furnace atomic absorption (GFAA) according to the requirements of the methods. A total of 5,050 analyses was performed using the method of standard additions.

The results of category 1 experiments provided information to evaluate the usefulness of each method for solubilizing the metals in various matrices. The performance criteria used for this evaluation were as follows: recovery $\pm$ 15 percent of the expected value (100 percent) was good; recovery between $\pm$ 15 percent and 30 percent of the expected value was fair; and recovery greater than $\pm$ 30 percent of 100 percent is poor. Although the criteria do not constitute a rugged statistical test, they represent reasonable performance levels in complex matrices.

The results of category 2 experiments provided single-laboratory accuracy (as shown by the recovery of spikes) and precision at three different levels. The precision of the method was estimated from the category 2 experiments by calculating the coefficient of variation (CV): a CV of less than 10 was considered good; a CV of more than 30, poor; and fair was in between these two limits. A summary of results for both categories is listed in Table II.

The limit of detection (LOD) for this study was defined as the concentration that would yield an absorbance equal to three times the standard deviation (SD) of a series of procedural blank measurements, or the concentration that would give, after a series of measurements, a percent relative standard deviation (% RSD) of 33.3 percent [5].

Sample analytes exhibiting an instrument response greater than 10 times the flame LOD were always measured by the preferred FLAA technique. Moreover, the concentration equivalent to 10 times the FLAA LOD was defined as the maximum sample concentration appropriate for GFAA analysis.

Although all matrices were digested and analyzed for all the required elements, data reported here for Methods 3020 and 3050-GFAA include only those results within the range of applicability of GFAA.

Because of this limited applicability of GFAA analysis and because most metals are regulated and considered hazardous by the Resource Conservation and Recovery Act (RCRA) at a much higher concentration level (in the 1 to 10 ug/mL range) [6,7], the usefulness of Methods

3020 and 3050-GFAA for waste samples is limited. In the event the analysis of ordinary samples at levels of environmental interest is easily satisfied by FLAA, analysis by GFAA is neither necessary nor recommended. An alternative analytical technique like ICP should be explored for metals of interest. GFAA is less cost effective and more time consuming and labor intensive than FLAA or ICP; therefore, it should be used only when FLAA or ICP are not applicable.

In all tables showing analytical results, elements that were found at concentrations below the LOD are reported as less than the LOD (<). When the absorbance observed was less than the analytical blank, B is reported in the tables. The LOD is matrix dependent and was calculated as three times the average noise level determined before each analytical run.

Because the samples used in this study were of actual wastes, many of the elements were present in very high concentrations. Therefore many of the data reported here are above the linear range of FLAA. The actual measurements, however, were all made within these linear ranges. Digestates were diluted prior to analysis to bring the elemental concentrations within range.

CATEGORY 1 RESULTS

Category 1 experiments consisted of unspiked and spiked duplicate digestions of four wastes by Methods 3010, 3020, 3030, and 3040 and the same treatment of six wastes by Methods 3050-FLAA and 3050-GFAA. The digestates were analyzed by FLAA and/or GFAA to determine concentrations of the required elements.

Method 3010

The analytical results obtained for duplicate unspiked and spiked aqueous waste digestates using Method 3010 are shown in Table III. Due to the originally high concentration of several elements, they were not added as spikes.

To evaluate the applicability and usefulness of Method 3010, the recovery of spikes and controls was calculated. This information was not obtained for elements that were not spiked because of their originally high concentrations (e.g., Na).

The performance criteria defined earlier were used to classify the usefulness of Method 3010. Be, Cd, Cr, Cu, Pb, and Zn exhibited good recovery from both the samples and control, whereas Ba and Mn exhibited poor recovery from the samples but good recovery from the control. Matrix composition obviously affected the recovery of these two elements. This conclusion can also be extended to Fe, Ni, and V although the effect was less pronounced for them. Sb was the only element for which control recovery was significantly higher than the recovery from the sample matrix and was above the expected value. The 217.6 mm line used for Sb analysis by FLAA had an interference with Pb

(which is present in all spiked samples and controls), which resulted in a false high absorbance value for Sb. All calculated recoveries were higher than the actual value.

Method 3020

Analytical results for duplicate unspiked and spiked aqueous digestates obtained by Method 3020 are listed in Table IV. Measurements were all performed at the linear range of GFAA; to do so, the digestates were in some cases diluted more than would be recommended to maintain good performance of the overall procedure. Therefore, only those elements determined within the range of applicability of GFAA are reported here. Because of the originally high concentrations of some elements, they were not added as spikes. The determination of Be, V, and Tl by GFAA presented difficulties. Alternative analytical techniques like ICP should be evaluated for these metals.

Tl analyzed using the IL instrument presented difficulties in unspiked Method 3020 digestates of sample 2258-9-A-3A. Complete suppression of Tl response occurred. Further dilution did not improve the assay. No response was observed from the sample or from Tl spikes added to the sample. This analysis was attempted twice at different dilution factors on the IL instrument. It was later analyzed on the Perkin-Elmer instrument.

The analysis of V by GFAA was not consistent throughout this project. While analysis of Method 3050 samples proceeded reasonably well, the attempt to analyze Method 3020 samples failed. Poor peak shape and inconsistent response characterized the entire run, and eventually there was no differentiation of response. This lack of success is not considered related to the samples or the preparation method. Such random behavior has been observed before in the variations in graphite tubes. This behavior may be explained by surface area, number of active sites, and oxygen content of the purge gas as previously described [8]. Deterioration of the graphite tube prevented the determination of Be in spiked sample 2258-9-A-4A digested by Method 3020.

Quantitative data for the calculation of recoveries from controls were obtained for only a few elements. The others were either above the range of applicability of GFAA or were not successfully determined. Recovery from control samples was obtained for Cr, Cu, Ni, Pb, Mn, Tl, and V. Good recovery was found for Mn and V, acceptable recovery was obtained for Cu and Tl, and poor recovery was obtained for Cr and Pb.

Method 3030

All samples were analyzed first by FLAA and, for those elements below the FLAA LOD, GFAA was performed. The analytical results obtained for duplicate unspiked and spiked oil waste samples digested by Method 3030 are shown in Table V.

The determination of Ba, As, Se, and Tl presented difficulties that adversely affected many analyses. Tl analysis of Method 3030 unspiked digestates required extra dilution to minimize background levels.

Ba was impossible to analyze in Method 3030 digestates because it is insoluble in sulfuric acid (H_2SO_4). To confirm this insolubility, equal levels of Ba standards were prepared in 15 percent H_2SO_4 (the matrix of 3030 samples) and in 0.5 percent nitric acid (HNO_3). The absorbance of the standard in H_2SO_4 was initially low relative to the standard in HNO_3 and decreased to near zero over a period of hours.

As was analyzed twice in digestates from Method 3030. The analysis was first done in a used pyrolitic graphite tube; this method yielded poor results. The sample was later reanalyzed in a tantalum-coated tube, and an improvement in the response resulted.

Since there was no commercially available oil-soluble Tl standard, no measurement of this element was performed.

The determination of Se by GFAA in oil samples prepared by Method 3030 was unsuccessful. Se response was almost totally suppressed in these samples. A spike of 40 mg Se/mL added to the Method 3050 control gave a response greater than 50 percent of full scale. The same spike added to the Method 3030 control yielded only 1 to 2 percent of full scale. In the case of Method 3030, the sulfate matrix is suspected as the cause. Separation techniques may well be appropriate in this case.

The measurement of Pb in oil-matrix samples prepared by Method 3030 was not straightforward. Pb in such samples occurs in a number of organic and inorganic forms. Organolead compounds may be lost by volatilization at the H_2SO_4 reflux temperature. In addition, losses could occur due to the insolubility of lead sulfate ($PbSO_4$). If the difficulty with determination of Pb after sample preparation by Method 3030 arises from the insolubility of $PbSO_4$, a slight modification to the method could solve the problem. Working up sulfate samples for Pb determination in geological samples is given in Reference [9]. The referenced procedure involves dissolution of $PbSO_4$ with ammonium acetate to form the soluble lead acetate. Barium acetate is also quite soluble in water. The revised digest method incorporating this change follows: (1) digesting as described in 3030; (2) transferring the digestate and one wash to the volumetric flask; (3) boiling a small amount of 50 percent HCl in the flask; (4) adding some ammonium acetate solution and bringing to a second boil; (5) transferring the mixture to the volumetric flask; and (6) bringing up to volume with several washes.

Since $BaSO_4$ does not come out of solution until the acid is diluted, solid precipitation occurs after transfer to the volumetric flask. Perhaps the first dilution could be made in the Kjeldahl flask with the first transfer delayed until the $BaSO_4$ has settled out of solution. Whereas HCl is the preferred matrix for FLAA, it is not recommended for GFAA. The substitution of dilute HNO_3 should be

investigated.

An alternative analytical technique like ICP should also be explored for these metals. GFAA is less cost effective and more labor intensive than FLAA and therefore should be used only when FLAA or ICP are not suitable.

The cold vapor technique for the determination of Hg yielded good results. However, a shortened version of the analytical procedure might benefit samples prepared by Method 3030.

The recovery of elements from spiked and control samples was calculated to determine the usefulness of the digestion method. A few elements (Be, Cr, Hg, and Cu) exhibited relatively good recovery for both samples and control. Several elements showed poor recovery for both samples and control (As, Na, Pb, Mn, and Zn). Others showed suppression of the recovery due to matrix effects (Cd, Fe, Se, and V). As in the case of Method 3010, Sb had very poor (high) recovery that can be attributed to Pb interference in the analysis. Ag exhibited good recovery for the spiked samples and poor recovery for the control; normally Ag has poor solubility in the presence of ions like SO4 (which is present in all digestates). If the wastes contained chelating agents that complex the Ag ions. However, this would result in good recovery for the samples and poor recovery for controls. High recovery of the Ni control could be attributed to laboratory error.

The EPA Office of Solid Waste provided RTI with a preliminary report by Mr. David Payne, Quality Assurance Coordinator, Region V, EPA, on the evaluation of Method 3030 using Conostan standard solutions. Payne's preliminary results indicated that recoveries for Ba, Pb, Hg, and Se were unacceptable, but that recoveries of Cd, Cr, and Ag were good in one case and fair in another. These results are in agreement with the ones reported here; Hg is the exception.

Method 3040

All samples were analyzed by FLAA and for those elements below the LOD, GFAA was performed. The analytical results obtained for unspiked and spiked oil waste extracts using Method 3040 are shown in Table VI. Ba, V, As, and Se could not always be determined by either FLAA or GFAA, which is consistent with previous results. The measurement of Pb in these oil matrices had problems. Pb is expected to be present in oil wastes in several chemical forms, including inorganic compounds that would be insoluble in xylene, the extracting solvent. This lack of solubility should result in at least a partial separation during aspiration.

The literature [10] suggests an alternative to extraction Method 3040 for the GFAA determination of As in petroleum products. J.H. Fabec presents a room temperature, closed-system workup procedure that could offer some advantages. Some of the data presented suggest equivalent response for different As species. A good correlation is presented between this procedure, neutron activation, and X-ray fluorescence. A

slight modification to the procedure allows spiking with aqueous-based As standards that would avoid any instability of the Conostan oil-based standard this laboratory has seen in the past. No information is presented in the manuscript on the fate of other metals.

There is also a total-metals-in-oils procedure described in R.E. Kauffman et al. [11]. Here, the oil sample is treated with a mixture of concentrated acids at room temperature. The sample is then emulsified with a product called Neodol 91-6 and MIBK or kerosene. Reasonable recoveries (>70%) for 13 metals are reported.

To determine the usefulness of extraction Method 3040, the recoveries of spikes and controls were calculated. Relatively good recoveries were obtained for samples and controls in the case of Be, Cd, Cr, Cu, Fe, Mn, Ni, and Sb. Na and Ag appeared to have experienced strong matrix effects as indicated by the low matrix recovery compared to the relatively good control recovery. Pb showed good control recovery but very high matrix recovery. V exhibited good recovery from samples and very high control recovery, which was attributed to experimental error. Zn showed higher sample and control recoveries than expected. This can be attributed in part to the fact that one of the wastes had very high Zn levels in the unspiked sample; the addition of a relatively small spike could have led to substantial errors. This was also true for Pb matrix recovery.

Method 3050-FLAA

The analytical results obtained for duplicate unspiked and spiked solid waste digestates are shown in Table VII. Due to their originally high concentrations, several elements were not spiked; these elements were Na, Fe, Zn and, in some cases, Cu, Ni, and Cr.

Sample 2258-9-S-5B, of known composition, was supplied by the EPA-Cincinnati Quality Assurance Office. A comparison of results with previous analyses of this sample show good agreement. A discussion is presented under the quality assurance/quality control section.

To determine the usefulness of digestion Method 3050-FLAA, the recovery of spikes from sample matrices and a control solution was calculated. Most elements (Ba, Be, Cd, Cr, Mn, Na, Ni, and Pb) exhibited relatively good recoveries from both the samples and the control. In addition, Fe, Sb, Tl, and Zn demonstrated good recoveries from the control. As expected, Ag showed a very low control recovery and only a fair recovery from the sample matrices due to the presence of chloride. The Ag spiking level of the wastes was significantly lower (100 ug/mL) than the Ag concentration in the control (1,000 ug/mL); therefore, it was expected that recoveries from the samples (72%) and control (12%) would be low. A lower Ag concentration had less of a chance of precipitating silver chloride (AgCl) out of solution. Cu showed acceptable recoveries from the sample matrices and control solution. Sb, Tl, and V consistently exhibited very low matrix recovery from almost all sample matrices.

Method 3050-GFAA

The analytical results obtained for unspiked and spiked solid digestates are shown in Table VIII. The determination of Ba and V encountered difficulties as explained previously and therefore no results are reported. Alternative techniques such as ICP should be evaluated for these metals.

Sample 2258-9-S-5B, of known composition, was supplied by the EPA-Cincinnati Quality Assurance Office. A comparison of results with previous analyses of this sample shows good agreement.

Useful quantitative data for the calculation of recoveries of spikes was obtained for only a few elements: As, Se, and Sb (one matrix only). Most of the elements that were determined were found to be above the range of applicability of GFAA, and therefore no recovery calculation is reported.

The overall recovery of Se from the spiked waste appeared to be very good. In addition, the recovery of Se from the control was within the acceptable range. The overall recovery of As from the spiked wastes was also within the acceptable range although recovery of the control was poor. Most of the Sb determinations are not reported because the levels of Sb found were above the limit of applicability of GFAA. One waste (No. 2258-9-S-5B), however, contained a relatively low level of Sb and recovery calculations could be made. In this case, the recovery of Sb was near zero.

CATEGORY 2 RESULTS

Category 2 experiments consisted of seven replicate digestions by all methods (Methods 3010, 3020, 3030, 3040, 3050-FLAA, and 3050-GFAA). The samples were digested unspiked, spiked at level 1, and spiked at level 2. The digestates were then analyzed by FLAA or GFAA to determine concentrations of the elements under evaluation.

The accuracy of the methods was estimated by calculating the percent recovery of the two spiking levels. The performance criteria for evaluating method accuracy were the same as those applied to category 1 experiments (recoveries within $\pm$15% of the expected value were good, between $\pm$15% and $\pm$30% were fair, and greater than $\pm$30% were poor).

Method 3010

The precision of Method 3010 was evaluated by examining the CV by element. Cd, Cr, Cu, Fe, Ni, Pb, Sb, and Zn had consistently low CVs (<10) at all spiking levels. Ba, Mn, and V had consistently higher CVs (>10) at all spiking levels. Be had a high CV in the unspiked sample and Na had a high CV in the spiked level 2 sample. Method 3010 demonstrated good precision (CV<10) for the majority of elements.

Because of the intrinsically high concentration of some elements in the waste, Cr, Cu, Fe, Na, Ni, and Sb were not added as spikes and no recovery data were obtained for these elements. In addition, the performance criteria described earlier were applied to the recovery as a measure of accuracy. Good accuracy was obtained for Cd and Zn and fair accuracy was obtained for Be, Pb, and V. Poor accuracy was obtained for Ba and Mn. These results indicate that the accuracy of Method 3010 is element dependent and that no generalizations can be made from results obtained by it.

Method 3020

All elements were determined by GFAA. Most of them, however, exceeded the limit of applicability of GFAA and therefore are not reported here. Ba, Tl, Be, and V determinations encountered the same difficulties described for category 1 experiments. Quantitative information was obtained for Ag and Tl only. The CVs calculated for these two elements were high, indicating poor precision at the reported levels.

Method 3030

Elements were determined by FLAA, except for As (determined by GFAA) and Hg (determined by the cold vapor technique). Tl was not spiked because no commercial oil standard was available for this element. The precision of Method 3030 (as shown by the CV) can be examined by element. Cu exhibited good precision (CV<10) at all spiking levels. Ag, Cd, Cr, and Na exhibited good precision for the two spiked samples. As, Be, Fe, Mn, Sb, and V exhibited significantly better precision for the two spiked samples than at the unspiked level. Hg and Pb had CVs between 10 and 20 for at least two of the spiking levels. Ni and Zn exhibited extremely poor precision at one of the spiking levels. For most elements, the precision of Method 3030 was better at the higher spiking levels.

In terms of accuracy, the recovery of spikes indicates that Method 3030 demonstrates good accuracy for Ag, Be, Cu, and Hg, and good or fair accuracy for at least one spiking level for Cr, Mn, and Na. Poor recovery was obtained at all spiking levels for As, Cd, Fe, Ni, Pb, Sb, V, and Zn. Thus the accuracy of Method 3030 is element dependent and the majority of elements tested exhibited poor recovery.

Method 3040

All elements were determined by FLAA. The precision of Method 3040 can be estimated by evaluating the CV of each element. Na, Pb, and Fe showed good precision at all spiking levels. Ag, Cd, Cr, Cu, Mn, and V exhibited good precision at the two higher spiking levels. Be and Sb showed poor precision at the unspiked level. Zn had fair precision at all levels and Ba had poor precision at all levels. For most

elements studied, the precision of Method 3040 was good at the higher spiking levels.

The accuracy of Method 3040 can be estimated from recovery data. Cd, Cu, and Mn exhibited good recovery at all spiking levels. Be, Cd, Fe, Na, and Sb showed better recovery at the higher spiking level. Ni, V, and Zn demonstrated poor recoveries. Ag and Pb behaved anomalously; they had considerably better recovery at the low spiking level than at the higher spiking level. The behavior of Pb may be attributed to the intrinsically high initial concentration of Pb in the waste compared to the added amount of spike (which was part of the Conostan S-21 standard mixture). However, both the Ag and Pb response was more likely due to experimental error, since the category 1 results for these two elements do not agree with these data.

Method 3050-FLAA

The precision of Method 3050-FLAA can be estimated from the CV data. For Ba, Cd, Cr, Cu, Fe, and Mn, the precision appeared to be good at all levels of spiking concentrations. Be, Ni, Pb, Sb, Tl, and V exhibited better precision at the higher levels of spiking. Ag and Zn had better precision at the lower concentration (unspiked sample). Na demonstrated relatively good precision independent of spiking level. Overall, Method 3050-FLAA had relatively good precision for most of the elements studied.

The accuracy of Method 3050-FLAA can be estimated from the recoveries. Cu, Fe, Na, and Zn were not spiked because of the intrinsically high concentrations of these elements in the waste. Therefore, no recovery data were obtained for these elements. Be, Cd, Mn, Ni, and Sb exhibited good recovery for both levels of spiking. Ba, Cr, Pb, Tl, and V showed at least fair recovery for one of the spiking levels. Ag recovery was poor at all levels of spiking; this is not unexpected since HCl is present in the matrix and AgCl would not be soluble at the experimental conditions.

Method 3050-GFAA

All specified elements were determined. However, most of them were found above the limit of applicability of GFAA and therefore are not reported here. The precision of Se determination by Method 3050-GFAA was relatively good especially at the higher spiking levels. As exhibited acceptable CVs at the higher spiking levels but a rather poor CV at the unspiked level. The recovery of As was good at all levels and the recovery of Se was fair at all levels.

CONCLUSIONS AND RECOMMENDATIONS

The overall evaluation of methods was performed based on the results of category 1 experiments, which yielded recovery information as a measure of the usefulness of the methods. In addition, category 2 experiments provided recovery information as an estimate of the accuracy and coefficient of variation as an estimate of precision.

Method 3010

Method 3010 is applicable for the preparation of aqueous wastes for flame atomic absorption (FLAA) analysis, and it yields good precision and accuracy for Cd, Pb, and Zn. In addition, Method 3010 can be recommended with caution for Be, Cr, Cu, Fe, Na, Ni, and V. It is not recommended for Ba and Mn. Data for Sb are inconclusive. It is also recommended that the written protocol he modified to give the analyst more guidance when encountering difficult samples.

Method 3020

Because of the limited data obtained on this method, no conclusions regarding its applicability could be made. However, Method 3020, which is specific to the preparation of aqueous wastes for graphite furnace atomic absorption (GFAA) analysis, is more labor intensive (by a factor of 2) and of limited application. Use of the method, when applicable, should be restricted only to those cases in which the limit of detection (LOD) of FLAA is too high to justify using flame techniques. Further research to evaluate inductively coupled argon plasma (ICP) spectroscopy as an alternative analytical technique to GFAA is recommended. As with Method 3010, Method 3020 should be revised to give the analyst more guidance and to accommodate samples that show difficult digestions.

Method 3030

Method 3030 is applicable for the preparation of oil wastes for FLAA or GFAA analyses, and it offers good precision and accuracy for Cu. Method 3030 can be recommended with caution for Ag, Be, Cr, and Hg. It is not recommended for As, Ba, Fe, Mn, Ni, Pb, Sb, Se, and Zn. The results for Cd and V are inconclusive.

The above conclusions and recommendations for Method 3030 apply only to oil-soluble organometallic compounds and should not be extrapolated to inorganic forms of metals present as emulsions or suspended solids in oil wastes. Further research is needed to develop and evaluate digestion methods for inorganic forms of metals suspended or emulsified in oil wastes.

Method 3040

Method 3040 is applicable for the extraction of Cu from oil wastes and has good precision and accuracy for that element. It can be

recommended with caution for Cd, Cr, Fe, and Mn. Method 3040 is not recommended for Ag, As, Ba, Ni, Se, V, and Zn. Results are inconclusive for Be, Na, Pb, and Sb.

The recommendations made for Method 3040 apply only to oil-soluble organometallic compounds and no conclusions or recommendations should be extrapolated to inorganic forms of metals present in oil wastes as emulsions or suspended solids. Further research is recommended to develop and evaluate extraction methods for inorganic forms of metals suspended or emulsified in oil wastes.

Method 3050-FLAA

Method 3050-FLAA has wide applicability and demonstrates good precision and accuracy for Ba, Be, Cd, Cr, Mn, and Pb. It is not recommended for Ag, V, and Zn. Method 3050-FLAA is recommended with caution for Na, Cu, Ni, and Tl. Results for Sb and Be are inconclusive.

Further research is recommended to evaluate other analytical techniques that do not require sample digestion that can modify the original sample. Possible alternatives are X-ray photoelectron spectroscopy for qualitative and quantitative analysis of solid wastes and the determination of valence states on solid samples, which may be crucial for the toxicity of some metals (e.g., Cr III vs. Cr VI).

Method 3050-GFAA

Limited data were obtained for Method 3050-GFAA. Based on available data, however, the method is not recommended for Sb and is recommended with caution for As and Se. As explained for Method 3020, use of Method 3050 followed by GFAA, when applicable, should be restricted to cases in which the LOD of FLAA is too high to justify using flame techniques. It is recommended that ICP be considered for evaluation as an alternative analytical technique. ICP is a fast multielement analytical technique, applicable to the determination of metals in environmental samples with reported limit of detection in ng/mL for some elements.

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TABLE I WASTE SAMPLES FOR METALS EXTRACTION

Type/origin	Hazardous waste No [a]	Description	pH	RTI assigned sample code [b]
Oil Samples				
	NA [c]	Used lubricant motor oil; black viscous liquid	NA	2258-9-0-1A
	NA	Used diesel oil from shipyard, brown liquid composite of two wastes	NA	2258-9-0-2B
	NA	Used diesel oil from shipyard, black, very viscous, semi-solid	NA	2258-9-0-2A
EMSL-EPA, Cincinnati	NA	Oil/water emulsion from cold rolling facility, representative of animal fat oils	NA	2258-9-0-5A
Aqueous Samples				
	F007	Spent nickel-plating solution from metal finishing operation, clear emerald green liquid with solids	~5	2258-9-A-3A
	F009	Spent stripping and cleaning bath solution from metal finishing operation, foamy/cloudy yellowish liquid	~13-14	2258-9-A-3B
	F007	Spent chrome plating solution from metal finishing operation, dark amber liquid with suspended solid	~0 5	2258-9-A-3C
	F007	Chromic acid waste solution with proprietary catalyst from electroplating operation, dark amber liquid with bright orange suspended solid	~1	2258-9-A-4A
Solid Samples				
	F006	Waste water treatment sludge from plating operation, black solids with moisture	~12	2258-9-S-3D
	F006	Precipitated metals waste sludge from electroplating operation, brown solids with moisture	~6	2258-9-S-4B
EMSL-EPA, Cincinnati QA Branch	NA	Municipal sludge standard sample; dry powder, grey	NA	2258-9-S-5B
EMSL-EPA, Cincinnati	F006	Sludge resulting from lime neutralization of wastewater from an electroplating facility, contains bound cyanide and sulfide	NA	2258-9-S-5C
OSW-EPA, Washington	NA	API separator sludge, black solids suspended in liquid, strong odor	NA	2258-9-S-6A
OSW-EPA, Washington	NA	Soil contaminated with metals	NA	2258-9-S-6B

[a] From reference (3)

[b] Designates Project No -Sample Type-Origin

[c] NA = Not available or not applicable

TABLE II. SUMMARY OF RESULTS

Method/ element	Percent recovery		CV[c]		
	Category 1[a]	Category 2[b]	Level 0	Level 1	Level 2
3010					
Ba	15	1/-2	10.1	12.6	43.6
Be	89	85/81	35.2	2.0	1.1
Cd	93	99/99	3.9	3.0	1.5
Cr	90	--[d]	6.4	1.0	1.3
Cu	91	--	3.5	1.1	4.6
Fe	84	--	3.7	3.1	3.6
Mn	69	27/54	27.9	27.5	15.6
Na	--	--	2.8	5.0	13.2
Ni	79	--	7.2	5.5	5.0
Pb	91	89/79	2.1	1.6	2.0
Sb	81	--	2.2	4.0	1.3
V	77	55/76	17.4	20.9	13.2
Zn	109	91/92	6.5	6.6	7.3
3020					
Ag	--	--	37.0	32.0	--
Tl	--	--	--	110.0	--
3030					
Ag	100	88/88	24.7	6.5	2.1
As	52	26/53	125.0	21.0	43.0
Ba	--	--	--	--	--
Be	86	100/94	55.8	12.1	19.0
Cd	84	26/60	61.0	4.1	5.1
Cr	92	75/79	13.3	3.8	4.4
Cu	95	101/99	8.1	4.2	3.6
Fe	44	567/215	35.7	13.5	9.4
Hg	90	99/94	--	18.8	16.6
Mn	117	43/79	44.0	14.6	9.8
Na	11	77/85	19.0	2.9	5.1
Ni	88	27/39	35.4	137.0	22.2
Pb	48	-4/-4	18.2	13.5	39.5
Sb	193	167/180	40.5	13.5	14.2
Se	--	--	--	--	--
V	81	58/52	81.9	30.1	20.1
Zn	182	-671/931	17.6	23.6	98.4
3040					
Ag	120	95/56	44.5	3.5	11.7
As	--	--	--	--	--
Ba	96	--	59.2	67.3	52.1
Be	74	69/82	79.4	7.5	14.4
Cd	123	68/84	13.2	8.5	4.1

(continued)

TABLE II. (continued)

Method/ element	Percent recovery		CV[c]		
	Category 1[a]	Category 2[b]	Level 0	Level 1	Level 2
3040 (con.)					
Cr	102	110/90	43.6	4.3	1.2
Cu	74	94/89	11.3	5.5	4.1
Fe	111	52/74	2.8	2.6	10.1
Mn	130	99/99	35.1	12.9	7.3
Na	111	12/72	7.8	7.5	8.8
Ni	120	19/48	47.4	55.5	5.9
Pb	98	93/-25	9.0	9.1	7.8
Sb	79	68/80	46.6	14.2	6.7
Se	--	--	--	--	--
V	164	885/312	29.6	5.9	8.7
Zn	130	-471/47	8.6	10.9	14.6
3050-FLAA					
Ag	72	36/18	3.8	5.9	24.0
Ba	99	72/88	3.9	2.6	2.0
Be	93	90/91	93.8	2.7	4.8
Cd	109	104/99	2.9	1.8	1.3
Cr	106	72/83	5.0	1.5	2.1
Cu	126	93/98	1.7	2.7	3.7
Fe	--	--	4.3	5.4	3.7
Mn	102	--	5.3	2.5	3.5
Na	95	--	1.3	10.2	2.8
Ni	89	86/101	98.9	19.0	5.1
Pb	97	64/92	11.3	4.2	1.7
Sb	50	91/91	--	11.8	4.3
Tl	70	70/75	31.5	8.9	5.8
V	47	69/81	91.4	11.9	1.6
Zn	326	--	8.6	19.6	18.8
3050-GFAA					
As	75	102/94	59	13	11
Sb	0	--	--	--	--
Se	99	79/79	19	8.2	6.4

[a]Recovery data from category 1 results represent the mean over all matrices.

[b]Recovery data from category 2 results are reported at two levels of spikes.

[c]Coefficient of variation at three concentration levels.

[d]Data not available; see Discussion.

TABLE III RESULTS OF FLAA ANALYSIS OF AQUEOUS WASTE SAMPLES BY METHOD 3010, CATEGORY 1

Sample No	Element (µg/mL)[a] Ba	Be	Cd	Cr	Cu	Fe	Mn	Na	Ni	Pb	Sb	V	Zn
Unspiked													
2258-9-A-3A	<2 60	<0 160	<0 720	<1 60	<0 360	147	52 0	16,000	70,000	<1 11	<4 80	<6 00	0 405
	<0 960	<0 130	<0 130	<2 00	<0 430	153	65 0	23,800	88,500	<0 99	<8 40	<12 0	0 447
2258-9-A-3B	1 08	0 332	<0 0600	<1 10	<0 230	<0 470	<0 190	13,700	<0 510	<1 35	<5 70	<5 10	1 18
	<0 600	0 312	<0 051	2 20	<0 550	1 30	<0 270	21,000	<0 440	<0 960	<1 80	<2 50	1 07
2258-9-A-3C	12 3	0 214	0 713	125,000	832	798	6 10	1,650	1,320	60 3	926	4 62	27.3
	21 1	0 0236	0 710	158,000	1,010	878	9 91	1,480	1,370	48 5	918	3.54	27 8
2258-9-A-4A	5.38	0 0500	0 463	114,000	398	2,480	33 4	10,200	89 3	36 1	114	10 2	47 6
	5 09	0 0282	0.480	174,000	363	2,670	30 8	11,700	90 2	40 8	142	7 76	51 0
Blank	<0 110	<0 0100	<0 00600	<0 200	<0 0300	0 460	<0 0300	0 465	0.0500	0 0600	<0.450	<0 690	<0 0120
Control[b]	10 9	8.47	10.2	7 64	10 2	8 88	9 01	14 6	10 0	9 70	10 3	8.08	9 43
Spiked													
2258-9-A-3A	2 00	1 80	1 46	19 2	3 88	226	124	14,500	70,000	11 7	92.5	99 0	5 49
	3 00	1 65	1 47	18 0	4 29	219	152	13,700	88,000	12 0	95 0	87 0	5 31
2258-9-A-3B	10.0	4 41	1 04	24 2	5 68	13 9	3.68	9,870	7 35	14 6	<5 5	48 2	16 7
	9.50	4 28	1 05	23 9	6 14	12 6	<4 2	10,100	6 60	14 9	7.00	45 6	14.9
2258-9-A-3C	10 4	0 837	8 59	109,000	840	1,320	62 2	1,390	1,850	139	871	48 1	154
	12 1	0 825	8 50	116,000	885	1,320	62 7	1,110	1,850	138	871	44 6	143
2258-9-A-4A	7.35	0 950	5 89	102,000	578	2,690	152	1,570	119	126	304	94 2	144
	9 15	0 932	6 07	101,000	587	2,830	156	1,330	108	129	290	98 7	146
Blank	<0 18	<0 009	<0 005	0 240	<0 09	0 350	<0 3	0 24	<0 09	<0 16	<1 1	1 10	0 02
Control[b]	11 1	11 6	11 4	10 6	9 38	9 60	12 3	9 88	10 7	11 3	27 2	11 9	11 0

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] Control prepared at approximately 10 µg/mL of each element

TABLE IV RESULTS OF GFAA ANALYSIS OF AQUEOUS WASTE SAMPLES BY METHOD 3020, CATEGORY 1

Sample No	Element (µg/mL)[a]												
	Ag	Ba	Be	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Tl	V	Zn
Unspiked													
2258-9-A-3A	<0 0038	--[d]	†[e]	<0 0021	<0 11	0 14	†	†	†	0 0095	--[d]	--[d]	†
	<0 0038	--	†	<0 0045	<0 23	<0 032	†	†	†	0 072	--	--	†
2258-9-A-3B	<0 0038	--	<0 0026	<0 0018	1 5	0 19	0 23	0 0036	<0 19	0 20	<0 0032	--	†
	<0 0038	--	<0 0026	<0 0018	0 85	0 13	0 16	<0 0035	<0 19	0 14	<0 0032	--	†
2258-9-A-3C	0 043	--	†	†	†	†	†	†	†	†	0 0053	--	†
	0 075	--	†	†	†	†	†	†	†	†	<0 0016	--	†
2258-9-A-4A	0 84	--	†	†	†	†	†	†	†	†	<0 0016	--	†
	0 95	--	†	†	†	†	†	†	†	†	<0 0016	--	†
Blank	0 00019	--	<0.017	B[c]	0 0056	0 0021	B	0 00035	B	0 0030	0 00032	--	0 0014
Control[f]	0 14	--	†	†	0 19	0 24	†	0.25	0.14	0 16	0 13	--	†
Spiked													
2258-9-A-3A	B[c]	--[b]	†[b]	†	†	†	†	†	†[b]	†	<0 26[b]	†[b]	†
	B	--	†	†	†	†	†	†	†	†	<0 26	†	†
2258-9-A-3B	B	--	†	†	†	†	†	†	†	†	<0 13[b]	†	†
	B	--	†	†	†	†	†	†	†	†	<0 13	†	†
2258-9-A-3C	0.18[b]	--	†	†	†	†	†	†	†	†	B[b]	†	†
	0 17	--	†	†	†	†	†	†	†	†	B	†	†
2258-9-A-4A	<0 65[b]	--	--	†	†	†	†	†	†	†	<0.06[b]	†	†
	0 94	--	--	†	†	†	†	†	†	†	<0 06	†	†
Blank	0 0080[b]	--	B	<0 00029	0 11	0 0019	<0 0048	B	0 0038[b]	0.008	B[b]	<0 125[b]	0 043
Control[f]	6 20[b]	--	†	†	0 22	0 12	†	0 21	†[b]	0 11	0 27[b]	<0 62[b]	†

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] Analyzed on Perkin-Elmer Instrument

[c] B = Below the analytical blank

[d] Unsuccessful analyses

[e] These elements were determined above the level of GFAA applicability

[f] Control was prepared at approximately 0 25 µg/mL

TABLE V RESULTS OF FLAA ANALYSIS OF OIL WASTE SAMPLES BY METHOD 3030, CATEGORY 1

Sample No	Element (µg/g)[a]															
	Ag	As[b]	Ba	Be	Cd	Cr	Cu	Fe	Hg[c]	Mn	Na	Ni	Pb	Sb	Tl	V	Zn
Unspiked																	
2258-9-0-1A	B[e]	<0 26	--[d]	<0 07	1 07	6 71	19 2	386	B	10 6	189	<2 60	27 0	<21 0	B	<24 0	1,420
	B	<0 26	--	<0 08	0 89	4 09	19 4	294	<0 024	11 5	174	<4 70	18 1	<22 0	B	<25 0	468
2258-9-0-2A	0 674	<0 26	--	<0 1	1 15	<4 10	10 6	113	B	<0 9	13 6	4 77	23 0	67 9	B	<34 0	.30 3
	B	<0 26	--	<0 1	1 04	<2 80	9 4	95 8	<0 024	<0 82	19 5	<1 70	21 1	65 4	B	<16.0	26 1
2258-9-0-2B	B	<0 26	--	<0 05	0 42	<3 40	6 80	149	B	<0 82	9 60	<2 00	31 1	70 1	B	<13 0	26 5
	B	<0 26	--	<0 05	0 42	<2 00	6 90	175	B	<1 30	10 5	<1 80	38 6	108	B	<18 0	18 7
2258-9-0-5A	B	<0 26	--	<0 11	<0 38	<3 30	2 60	172	<0 024	12 1	9 90	<3 60	2 75	44 4	B	16 2	5 00
	B	<0 26	--	<0 1	0 37	3 49	2 40	147	<0 024	11 2	10 0	5 84	0 75	27 7	B	<7 50	3 30
Blank	<3 00	B	--	0 11	<0 018	<2 60	2 00	1 91	B	<0 036	10 7	8 68	8 46	<0 93	B	15 8	<0 0021
Control	62.7	22	--	88 6	69 6	59 7	63 8	56 3	6 7	64 9	80.4	110	19 8	156	B	61.1	79 4
Spiked																	
2258-9-0-1A	122	18	--[d]	181	94 8	112	142	710	24 5	119	140	55 0	38 8	308	--[d]	61 0	1,580
	115	18	--	117	93 6	105	135	706	17 0	97 3	139	54 3	46 9	279	--	65 2	1,320
2258-9-0-2A	125	8 6	--	94.4	139	119	119	121	25 8	145	31 8	127	82.7	319	--	103	131
	130	14	--	105	148	126	130	94 8	46 7	164	37 4	142	64 9	287	--	95 3	142
2258-9-0-2B	122	8 9	--	140	132	123	119	110	22 5	171	42 4	121	219	300	--	141	149
	124	6 9	--	115	129	126	112	110	23 1	181	45 2	142	50 0	327	--	114	153
2258-9-0-5A	125	9 0	--	135	128	134	119	<7 00	11 0	167	40 0	144	<45 0	362	--	133	153
	126	27	--	118	127	127	120	120	13 0	183	40 0	145	38 5	378	--	131	171
Blank	<0 2	B	--	0 3	20 2	3 40	<0 4	1 68	B	4.20	6 80	<8 64	<3 60	19 0	--	<22 0	0 26
Control	89 6	12	--	111	104	110	87 7	94 8	22 1	323	42 9	109	9 30	244	--	158	125 3

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] Analyzed by GFAA

[c] Hg was analyzed using cold vapor procedure

[d] No analysis attempted, see text for explanation

[e] B = Below the analytical blank

TABLE VI RESULTS OF FLAA ANALYSIS OF OIL WASTE SAMPLES BY METHOD 3040, CATEGORY 1

Sample No	Element (µg/g)[a]														
	Ag	Ba[b]	Be	Cd	Cr	Cu	Fe	Mn	Na	Ni	Pb	Sb	Tl[b]	V	Zn
Unspiked															
2258-9-0-1A	<2 00	--	<0 03	B[d]	<4 50	14 2	88 5	3 48	63 6	2 54	346	12 7	--	<24.0	1,030
	<2.20	--	<0 04	B	<6 90	19 3	378	3 66	99 4	<3.40	662	<4 27	--	<21 9	1,030
2258-9-0-2A	<1.40	--	<0 08	B	<5 60	2 14	46 1	<5 30	<1 40	1 76	449	14 8	--	<25 0	18 9
	<1.40	--	<0.07	B	<1 30	<3 60	48 0	<3 70	<0 24	<0 8	438	9.50	--	<31.0	19 1
2258-9-0-2B	<1.60	--	<0 06	B	<5 00	7 60	71 6	<4 60	<0 78	<1 00	397	7 60	--	<21 9	15 9
	<1.40	--	<0.03	B	<2 30	2 46	96 6	<4.40	<0 54	<1.40	457	8 80	--	<61.9	15 1
2258-9-0-5A	<0.96	--	<0.05	B	7 18	6 72	131	<6 00	<1 60	<1 30	<9 60	<9.80	--	<19 0	1 94
	<0.3	--	<0 11	B	5 75	4 25	131	<3.60	<1 10	<2.70	<11 0	<3.40	--	<9 00	1 50
Blank	<0 74	--	<0 05	<0 3	<2 00	<0 95	<0 74	<3 00	<0 54	<1.50	<10 4	2.37	--	<14 9	<0 36
Control	110	--	101	157	118	96 6	106	183	90 3	94 3	102	66 8	--	196	142
Spiked															
2258-9-0-1A	174	<54 0	151	169	204	205	494	141	145	104	870	166	--	<260	1,460
	174	<80 0	136	172	210	196	530	148	151	96.0	929	180	--	440	1,430
2258-9-0-2A	38 4	<920	219	201	175	184	240	202	120	148	680	184	--	256	224
	45 1	<750	178	211	180	198	260	148	123	<95.0	579	240	--	307	178
2258-9-0-2B	174	<96.0	249	209	189	202	291	251	77 0	153	878	249	--	75 8	277
	176	<140	237	204	189	189	276	222	82.8	172	870	200	--	182	248
2258-9-0-5A	139	<230	230	218	256	188	286	325	163	288	183	204	--	91 9	258
	152	106	249	226	260	192	290	368	164	242	199	214	--	110	268
Blank	<0 78	<13 0	<0 36	<0 18	<1 2	<0 6	1 22	B[c]	B	<3 6	<6.0	<3 6	--	<24.0	B
Control	194	172	203	254	148	168	201	200	229	139	175	171	--	253	206

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] -- = No analysis attempted, see text

[c] B = Below the analytical blank

TABLE VII RESULTS OF FLAA ANALYSIS OF SOLID WASTE SAMPLES BY METHOD 3050, CATEGORY 1

Sample No	Element (µg/g)[a]														
	Ag	Ba	Be	Cd	Cr	Cu	Fe	Mn	Na	Ni	Pb	Sb	Tl	V	Zn
Unspiked															
2258-9-S-3D	23 4	<180	<1 90	<1 20	10,200	11,900	19,000	133	118,000	87,400	260	<260	<30 0	<760	537
	24 4	<120	<0 600	<2 40	29,700	10,000	22,400	126	134,000	82,100	148	<130	<30 0	<650	541
2258-9-S-4B	7 00	396	<1 30	<1 80	77,900	2,280	298,000	1,240	8,750	91 2	288	<470	<24 0	<550	785
	6.00	320	<1 20	<1 80	91,700	2,150	329,000	1,080	8,850	111	774	<500	<42 0	<1,070	800
2258-9-S-5B	86 8	428	<1.60	17 4	140	1,650	17,300	175	730	192	676	<190	<18 0	348	12,300
	72 6	276	<1.90	18 8	187	1,050	24,900	267	474	182	456	<250	<12 0	<780	17,800
2258-9-S-5C	50 2	<72 0	<1 90	<3 60	17,100	98 8	94,000	1,830	649	243	101	<240	48 0	<310	43,200
	<11 0	<48 0	<2.20	<2 40	14,900	96 5	92,100	1,820	1,370	300	124	<250	<24 0	<800	20,600
2258-9-S-5D	<6 60	<84 0	<1 40	4 60	453	47 4	22,800	106	142	32 2	62 0	<90 0	<24 0	<600	195
	<9 00	<110	<2 00	5 60	<210	50 8	16,000	94 4	60	27 0	<42 0	<160	<18 0	<980	205
2258-9-S-6A	<6 00	<160	<1 60	<1 80	<270	262	31,700	216	4,500	86 7	456	<360	<54 0	1,890	1,980
	<5 40	<110	<1 10	<1 20	<430	242	27,100	212	4,500	109	342	<190	<48 0	<470	1,250
Blank	<3 3	B[b]	B	<0 9	<64 0	<9 6	9 50	B	41.0	B	B	<140	B	<39 0	B
Control[c]	125	1,810	1,070	809	829	1,530	916	1,040	1,020	1,090	1,050	880	940	724	909
Spiked															
2258-9-S-3D	77 6	930	88 8	103	16,600	9,640	17,500	1,210	111,000	8,950	1,120	1,020	86 0	814	6,380
	77 6	1,080	88 3	105	16,500	9,330	18,600	1,220	112,000	8,990	1,090	980	104	810	5,750
2258-9-S-4B	122	1,360	98 9	113	96,700	2,320	287,000	1,230	20,000	488	1,550	820	96 0	1,000	4,060
	116	1,480	100	116	102,000	2,380	305,000	1,250	21,300	914	1,580	740	100	986	3,720
2258-9-S-5B	92 4	1,190	88 7	124	1,290	1,040	14,900	1,140	539	955	1,480	860	106	824	4,630
	93 4	1,220	87 9	125	1,290	1,080	15,200	1,150	544	1,080	1,400	840	100	918	3,430
2258-9-S-5C	99 4	1,090	98 6	109	10,900	1,030	78,300	1,970	472	999	1,160	520	100	904	23,700
	104	1,070	99 7	107	11,400	1,020	82,300	2,040	486	928	1,050	640	110	932	23,400
2258-9-S-5D	94 4	1,040	92 6	120	1,240	1,040	14,600	1,060	1,020	1,440	1,090	280	96 0	812	1,320
	93 8	1,020	91 3	129	1,250	1,050	15,300	1,100	1,050	1,520	1,240	320	98 0	1,000	1,390
2258-9-S-6A	89 7	1,100	95 4	107	1,950	1,090	20,800	1,240	3,690	980	1,230	420	100	1,490	1,770
	96 6	1,220	103	115	2,090	1,130	23,300	1,380	3,510	995	1,350	560	98	1,500	1,610
Blank	<4 8	8 00	0 950	1 80	282	<5 4	8 20	<2 4	27 2	5 60	B[b]	110	12 0	67 0	1 01
Control[c]	115	930	1,020	1,290	1,100	1,040	1,060	1,100	1,050	1,080	845	1,180	1,140	990	994

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] B = absorbance was less than the analytical blank

[c] The control was prepared at approximately 1,000 µg/g

TABLE VIII RESULTS OF GFAA ANALYSIS OF SOLID WASTE SAMPLES BY METHOD 3050, CATEGORY 1

Sample No	Element (µg/g)[a] Ag	As	Ba	Be	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	Tl	V	Zn
Unspiked																
2258-9-S-3D	†[d]	1 5	--[c]	†	†	†	†	†	†	†	†	†	<0.074	<0 033	--	†
	†	1 7	--	<0 075	†	†	†	†	†	†	†	†	<0 074	0 84	--	†
2258-9-S-4B	†	7 3	--	<0 075	†	†	†	†	†	<32	†	†	<0 074	<0 033	--	†
	†	8 7	--	†	†	†	†	†	†	<32	†	†	0 53	<0 033	--	†
2258-9-S-5B	†	<0 54	--	†	†	†	†	†	†	<64	†	4.1	1 0	0.089	--	†
	†	0 71	--	<0 075	†	†	†	†	†	†	†	11	2 1	0.16	--	†
2258-9-S-5C	†	<0 54	--	†	†	†	†	†	†	†	†	<4 0	<0 15	<0 66	--	†
	†	<0 54	--	†	†	†	†	†	†	†	†	<4 0	0 51	0 31	--	†
2258-9-S-5D	†	2 0	--	†	†	†	†	†	†	<32	†	<4 0	<0 074	0 057	--	†
	†	6.6	--	†	†	†	†	†	†	<32	†	<4.0	0 32	<0.033	--	†
2258-9-S-6A	0 29	0 63	--	†	†	†	†	†	†	†	†	<4 0	27	<0.033	--	†
	†	<0.54	--	†	†	†	†	†	†	†	†	<4 0	20	<0 033	--	†
Blank	0.0066	0 54	--	<0.0015	0 0090	0 48	0 061	B[c]	0 035	B	0 047	B	<0.74	0 0090	--	†
Control[g]	†	13	--	†	†	†	†	†	†	†	†	†	13	†	--	†
Spiked																
2258-9-A-3D	†[d]	83[b]	--[b,c]	†[c]	†	†	†[b]	†[b]	†	†	†	†	130[b]	†	<1,600[b]	†
	†	110	--	†	†	†	†	†	†	†	†	†	130	†	<1,600	†
2258-9-S-4B	†	140	--	†	†	†	†	†	†	†	†	†	100	†	<1,600	†
	†	96	--	†	†	†	†	†	†	†	†	†	110	†	<1,600	†
2258-9-S-5B	†	87	--	†	†	†	†	†	†	†	†	†	79	†	†	†
	†	76	--	†	†	†	†	†	†	†	†	†	85	†	†	†
2258-9-S-5C	†	<19	--	†	†	†	†	†	†	†	†	<2 5	34	†	<1,600	†
	†	<19	--	†	†	†	†	†	†	†	†	3 2	26	†	<1,600	†
2258-9-S-5D	†	73	--	†	†	†	†	†	†	†	†	†	140	†	†	†
	†	98	--	†	†	†	†	†	†	†	†	†	130	†	†	†
2258-9-S-6A	†	70	--	†	†	†	†	†	†	†	†	†	160	†	†	†
	†	71	--	†	†	†	†	†	†	†	†	†	150	†	†	†
Blank	†	0 43	--	†	B[e]	0 67	†	†	B	B	B	<0 25	2 9	<0 78	<1,600	†
Control[f]	†	970	--	†	†	†	†	†	†	†	†	†	1,000	†	<1,600	†

[a] LODs are reported as less than (<) The LOD is calculated as three × average noise level determined before each analytical run

[b] Analysis performed with the Perkin-Elmer AAS instrument

[c] Unsuccessful analysis, see text for explanation

[d] Determined to be above the level of GFAA applicability

INTERFERENCE REDUCTION STUDIES INVOLVING HYDRIDE GENERATION ARSENIC AND SELENIUM DETERMINATIONS UTILIZING ATOMIC ABSORPTION AND PLASMA EMISSION SPECTROMETRY

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HEALTH AND REGULATORY ASPECTS

Regulatory and environmental concerns have made the determination of trace amounts of arsenic and selenium extremely important. Selenium is an essential trace nutrient while arsenic is a cumulative poison. Unlike synthetic organic chemicals, these "heavy metals," of course, are not man-made. Environmental pollution problems associated with these elements, therefore, are the result of redistribution of the naturally occurring elements by agricultural and industrial processes.

Arsenic, which accounts for approximately 5 x 10-4 percent of the earth's crust, is produced as a by-product of the mining and refining of other minerals and is used commercially, primarily in pesticide formulations and agricultural applications. Organic arsenicals, hundreds of which have been synthesized, are widely used as livestock feed additives and as therapeutic drugs. Inorganic and aliphatic organic arsenicals are poisonous to all lower animals. The toxicity varies greatly with formulation and valence state, with the most dangerous preparations being the trivalent arsenites.

Selenium accounts for 10-5 percent of the earth's crust with selenides often being found in sulfide ores. Selenium is obtained from flue dusts produced in the roasting of sulfide ores and as a by-product of sulfuric acid manufacture. The largest current use of selenium is as a food supplement to animal feeds.

Specific Environmental Protection Agency (EPA) regulations now apply to arsenic and selenium in drinking water (1) and in Extraction Procedure Toxicity Leachates (2) of sludges and solid wastes. Arsenic (as As2O3) is regulated in food (3) while Occupational Safety and Health Administration (OSHA) limits in air have been set to protect workers' health (4). These regulations are summarized in Table I. Finally, many states regulate the levels of arsenic and selenium in solid waste.

The object of our research was to develop improved hydride generation methods for the analysis for these and other hydride-forming elements in difficult matrices. Although hydride generation methods are widely used, it has been known since the middle 1970's (5) that these methods are subject to interelement interferences. Although we studied six hydride-forming elements to some extent, we will focus here on the improvements made for arsenic and selenium.

arsenic (7061) and selenium (7741) in solid and liquid samples. The

samples are prepared by a nitric/sulfuric acid digestion before being converted to a volatile hydride. The hydride gas is swept into an argon-hydrogen flame located in the optical path of an Atomic Absorption Spectrophotometer (AAS).

However, the currently published methods are approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt and molybdenium. "High level" is undefined. Cautions are also issued in that certain arsenic and selenium compounds are volatile and therefore may be lost during the digestion. The use of spiked samples and relevant reference materials is necessary to determine the applicability of the methods to a given waste.

Although many real world samples can be accurately analyzed using the SW-846 methods, many others contain high levels of interfering elements. We have recently investigated interelement interference reduction techniques in hydride generation AAS and Inductively Coupled Plasma Emission Spectrometry (ICP). These included manipulation of acid strength and sodium borohydride concentration and the comparison of multiple hydride generation systems. Extensive studies were also performed using both Chelex 100 and AG 50W resins as a means of reducing the interferent to analyte ration in real world samples.

EXPERIMENTAL ASPECTS

Apparatus and Operating Procedures

The I.L. Model 951 dual channel Atomic Absorption Spectrophotometer fitted with the conventional, single slot burner head was used for these studies. All analyses were performed using an argon hydrogen entrained air flame and the peak area integration modes.

The I.L. Model 100 Sequential Plasma Emission Spectrometer was utilized for the ICP hydride determination.

Three commercially available hydride generation devices were used in this study. The I.L. manual device was designed to produce a transient AAS signal following the $NaBH_4$/sample mixing. The P.T. Analytical (Wilmington, Mass.) device was designed to produce a steady state signal and was designed to be used with either AAS or ICP systems. The I.L. plasma hydride device (Figure 1) was designed to produce a steady state signal for ICP determinations. All samples were acidified to form Se (IV) or reduced with KI to form AS (III).

PRELIMINARY INTERFERENCE STUDY

The interelement interference effects of 50 elements were examined during the hydride generation AAS and ICP determinations of arsenic and selenium. The 35 elements in Table II resulted in interelement interferences of less than 10% when present at levels of 1,000 fold greater than the analyte. The 15 elements in Table III exhibited

interferences of greater than 10% for either As or Se, or both, at interferent levels of 5 to 1,000 fold in excess of the analyte. Representative recoveries are presented in Table III.

Figures 2 and 3 show typical interelement interference curves. The analyte concentration was held constant at 0.100 ug/ml while the interferent concentration was varied. These interferent levels were selected to span the range from no interference to nearly complete signal suppression. Hydride interelement interference was first identified during the middle 1970's, but even today only very inadequate techniques for dealing with these interferences are available.

INTERFERENCE REDUCTION TECHNIQUES

Effect of Acid Strength

Constant levels of interferents were prepared in 1.2, 2.4, 4.8 and 7.2 M HCl. These solutions also contained 0.100 ug/ml analyte. Thus, in contrast to the interference study previously discussed, this work varied the acid level while the interferent concentration remained constant.

Variation in acid strength caused only small changes in the standard readings but resulted in very large changes if significant levels of certain interferents were present.

Higher acid concentrations greatly improved the signal for both arsenic and selenium when the following interferents were present: cobalt, copper, lead, molybdenum, nickel, palladium and rhodium. The signals from standard solutions containing no interferents, while changing slightly, were not affected to nearly the same extent. The interference of gold and iridium on selenium was reduced, as was that of tungsten.

Figures 4 and 5 present typical examples of this improvement. Slight improvement was noted for the gold interference on arsenic and selenium and for mercury interference on selenium. No reduction was noted for the iridium and platinum interferences on arsenic. Higher acid levels yielded no reduction for the germanium, platinum and tellurium interferences on selenium.

It is interesting to note that a few interferences were less severe at moderate acid strength than at either extreme. These include platinum and tellurium (on selenium).

Only one interferent resulted in much poorer analyte recovery at high acid strength. Arsenic produced poor selenium recovery at arsenic levels of 100 ug/ml.

In summary, with the exception of arsenic and germanium, the effect of all interferents remained essentially constant or was significantly reduced at high acid concentration for either or both arsenic and

selenium. Thus, the final acid level in real world samples becomes critical if a hydride determination is to be performed.

Cation Exchange Separation

Several resins were evaluated to provide a means of separating the interfering elements from the hydride-forming elements. The goal was to develop a clean-up procedure that was rapid, inexpensive, relatively independent of pH and applicable to a wide variety of real world samples.

The following table compares the results obtained following a minicolumn resin separation.

The elements that had previously been found to interfere most severely with hydride generation were subjected to the mini-column tretment at pH 2 on both AG 50W-X16 and Chelex 100. The percent removal is shown in Table IV.

As can be seen, levels of six of the elements (cobalt, copper, lead, mercury, nickel and silver) were reduced by at least 96%. Gold and palladium were removed by greater than 98% on the Chelex resin.

Platinum and rhodium were not removed to a significant extent on either resin. Bismuth removal was greater than 98% on Chelex 100 while tellurium removal was greater than 75% on both resins.

Arsenic and selenium were not removed to a significant extent. That is, they both passed through the resin without being retained.

APPLICATIONS

Reference Materials

These clean-up techniques were applied to various standard reference materials and to real world samples. Table V provides results obtained on EPA WP 1178/481 concentrates 1 and 2. Tables 6 and 7 provide data on NBS materials following nitric/perchloric/sulfuric acid digestions. The pH of the digest was adjusted with dilute ammonium hydroxide before being subjected to resin treatment. Each slide provides examples of at least one sample that required the use of either high acid concentrations or resin treatment in order to obtain acceptable results.

Leachates

Tables 8 and 9 provide examples of arsenic and selenium recovery data in leachates from solid waste samples.

Sludge Samples

Municipal sludge samples were obtained from various cities in Pennsylvania. Following acid digestions, arsenic and selenium were determined by hydride generation (Tables 10 & 11).

SUMMARY

The hydride generation AAS methods found in SW 846 are applicable to many environmental samples. However, these methods will not provide acceptable results on samples that are highly contaminated with interfering elements. Interference reduction techniques such as the adjustment of acid strength and ion exchange clean-up are necessary when dealing with difficult sample matrices.

References

1. Code of Federal Regulations, Title 40, 141.11.

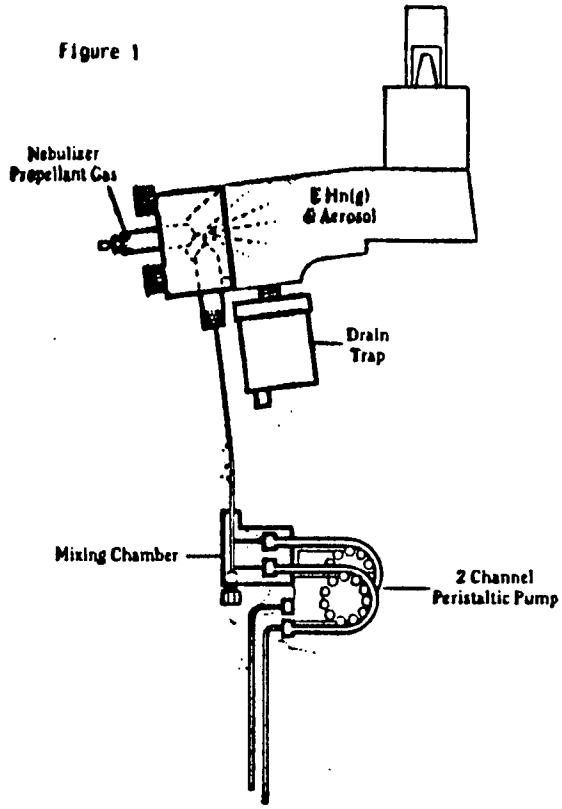
2. Federal Register, May 19, 1980, 33127.

3. Code of Federal Regulations, Title 40, 180, 192-196.

4. NIOSH Publication 81-123, Jan. 1981, U.S. Government Printing Office, Washington, D.C., 20402.

5. A.E. Smith, Analyst, 100, 300 (1975).

Figure 1



Schematic of I.L. Plasma Hydride Generator

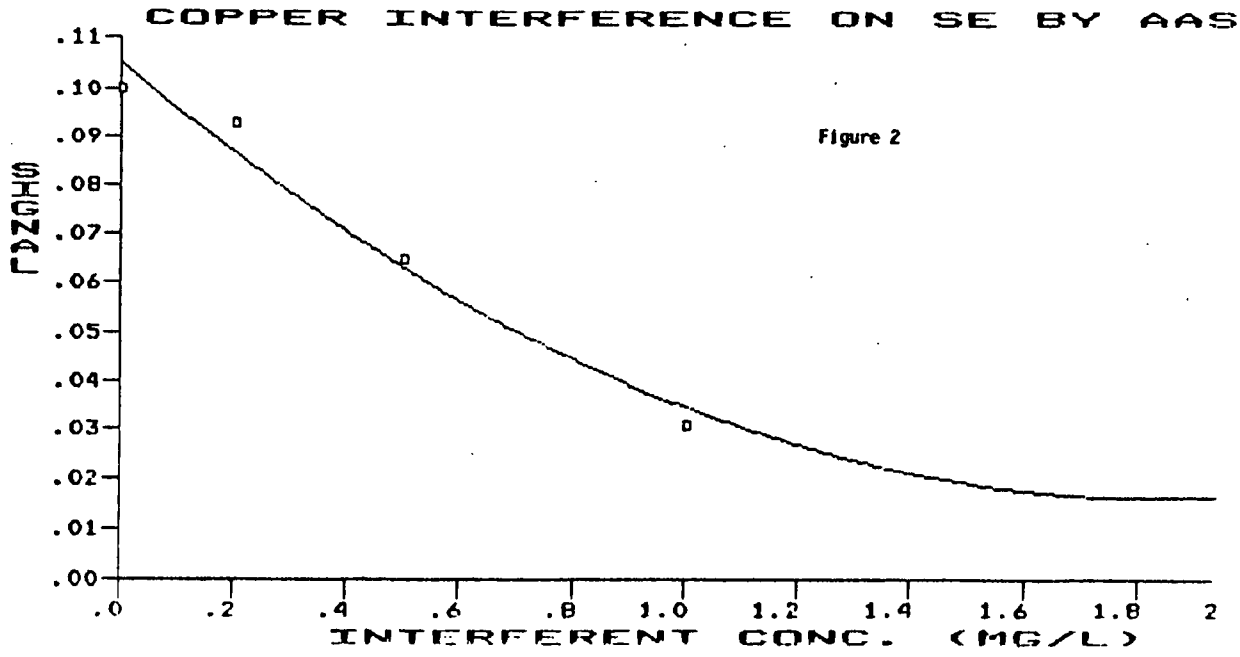


Figure 2

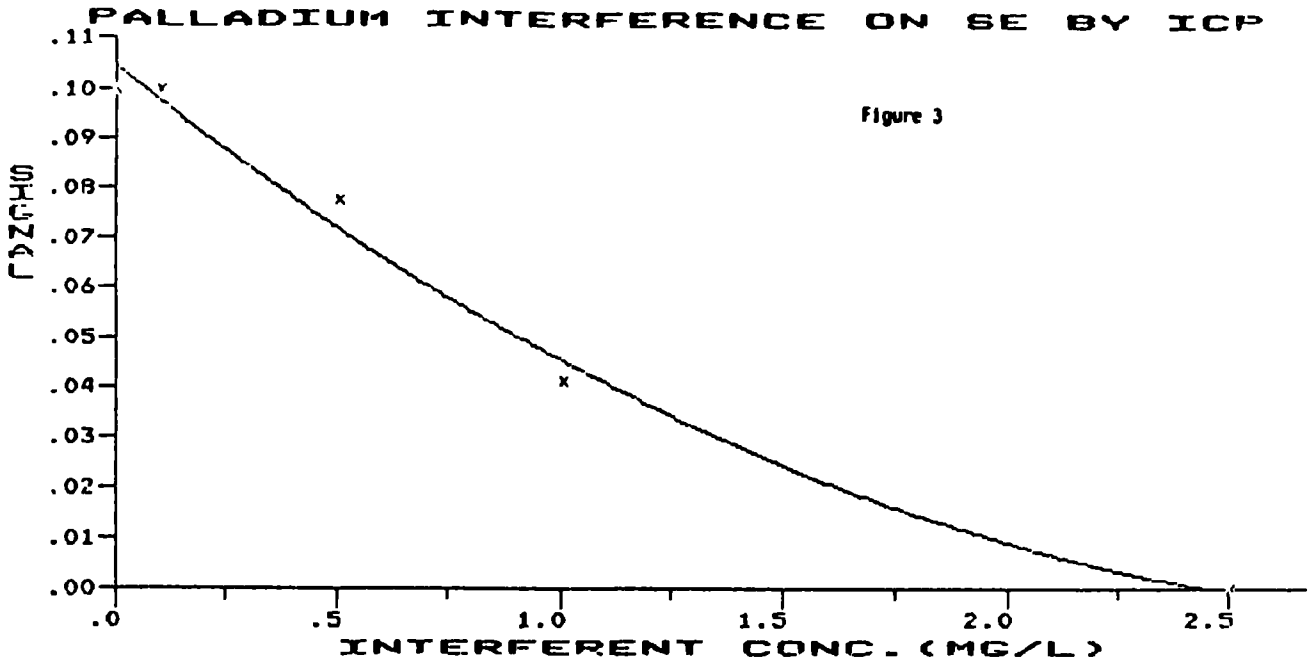


Figure 3

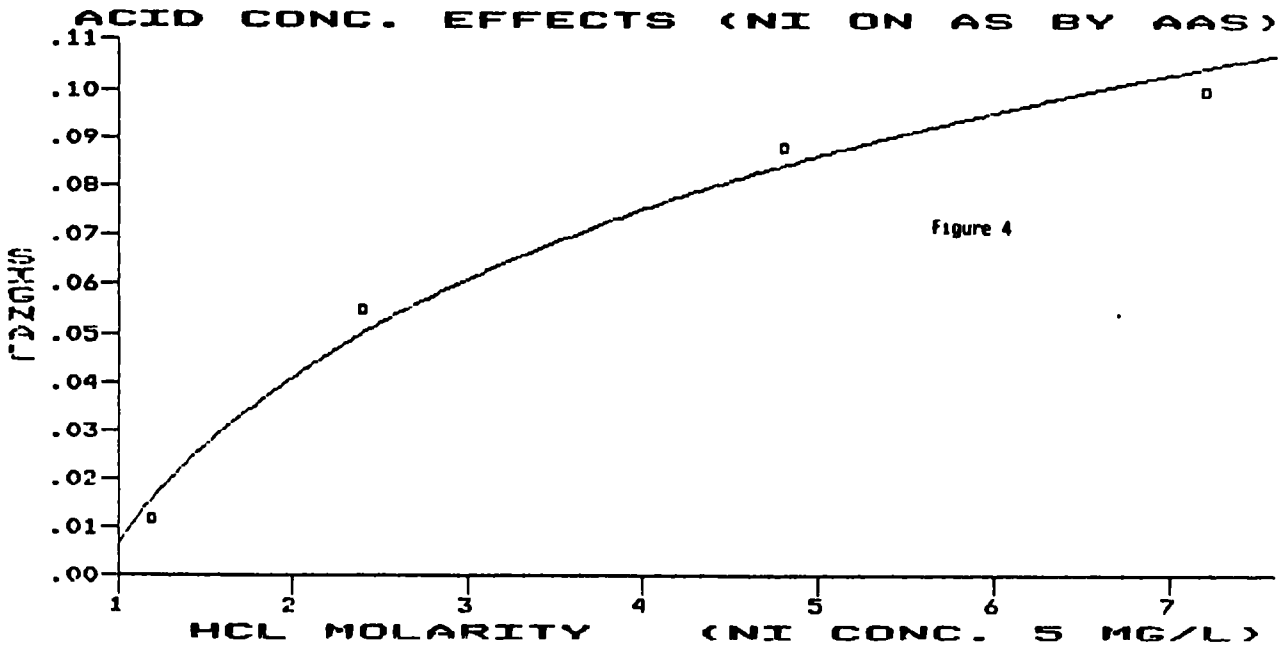


Figure 4

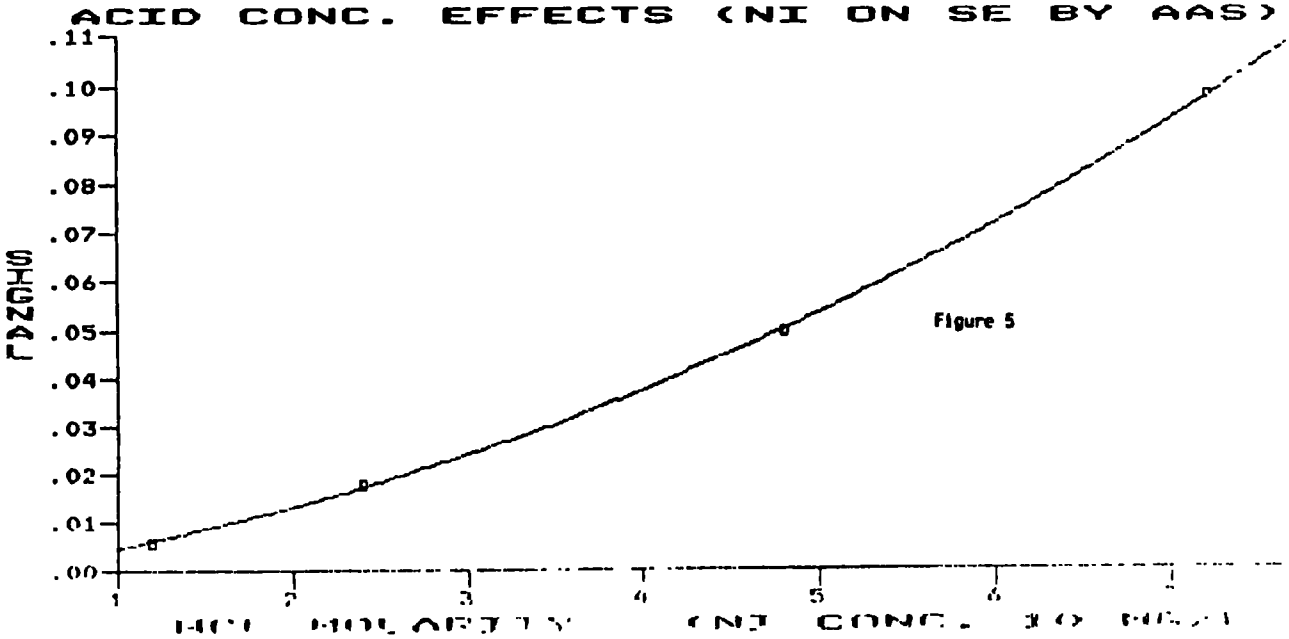


Figure 5

TABLE I

MAXIMUM ALLOWABLE LEVEL

Agency	Matrix	Arsenic	Selenium
EPA	Drinking Water	0.05 mg/l	0.01 mg/l
EPA	EP Toxicity Extract	5.0 mg/l	1.0 mg/l
OSHA	Workplace Air (1)	10. ug/m^3	0.2 mg/m^3
World Health Organization	Drinking Water	0.05 mg/l	0.01 mg/l
EPA	Food (2)	3.5 ppm	

(1) Eight hour time weighted average
(2) As As_2O_3

TABLE II

NON-INTERFERING ELEMENTS

Aluminum	Phosphorus
Barium	Potassium
Beryllium	Scandium
Boron	Selenium
Cadmium	Silicon
Calcium	Sodium
Cerium	Strontium
Cesium	Tantalum
Chromium	Thallium
Gallium	Thorium
Iridium	Tin
Iron	Titanium
Lanthanum	Tungsten
Lithium	Vanadium
Magnesium	Yittrium
Manganese	Zinc
Mercury	Zirconium
Niobium	

Elements not interfering with the I.L. Manual Hydride-AAS determination of Arsenic, Antimony, Bismuth and Selenium. Interferent concentrations were 100 ug/ml or greater while analyte concentrations were 0.100 ug/ml.

TABLE III

INTERELEMENT INTERFERENCES BY AAS

Interferent	Conc. (µg/ml)	Percent Recovery	
		Selenium	Arsenic
Antimony	100	89	159 (1)
Arsenic	100	34	--
Bismuth	100	75	92
Cobalt	100	28	33
Copper	100	2	101
Germanium	100	20	88
Gold	50	57	88
Lead	100	84	96
Molybdenum	100	74	97
Nickel	10.0	42	45
Palladium	0.5	104	47
Platinum	0.5	97	79
Rhodium	0.5	71	95
Silver	5.0	12	97
Tellurium	100	124 (1)	67

(1) Apparent contamination in standard.
Analyte concentration 0.100 µg/ml

TABLE IV

% REMOVAL DURING
MINI-COLUMN PROCESS AT pH 2

Element	AG 50W-X16	Chelex 100
Antimony	6.2	34.2
Arsenic	0	5.8
Bismuth	12.2	>98
Cobalt	>99.9	99.5
Copper	>99.9	>99.9
Germanium	0	6.0
Gold	69.4	98.6
Lead	>99.9	99.7
Mercury	>98	93
Nickel	>99.9	99.5
Palladium	42.2	>99.8
Platinum	0	12.2
Rhodium	11.8	18.8
Selenium	0	2.4
Silver	>99.9	>99.9
Tellurium	78.4	72.0

12.5 ml of pH adjusted 100 mg/l standard were subjected to the minicolumn process.

TABLE V

EPA WP1178/481 CONCENTRATES 1 AND 2

	Experimental					EPA Values				
Sample No.	Results				X	True	X	C.I.	Mini-Column Resin Treatment	Element
1	26.5,	26,	26.5,	26	26.3	27	26.3	19.8 - 34.2	No	Arsenic
2	257,	253,	261	247	255	235	234	182 - 286	No	Arsenic
1	10.5,	11.0,	11.5,	10.5	10.9	11	10.3	6.5 - 14.1	No	Selenium
2	27.0,	28.0,	28.0,	26.5	27.4	50	46.7	31.3 - 62.1	No	Selenium
2	44.0,	48.0,	48.0,	54.0	48.5	50	46.7	31.3 - 62.1	Yes	Selenium

All values are given in micrograms per liter.

X = Average

C.I. = 95% Confidence Interval

TABLE VI

ARSENIC RESULTS ON
NBS STANDARD REFERENCE MATERIALS

SRM	Experimental	Certified Value
1566	13.6	13.4 ± 1.9
1568	0.40	0.41 ± 0.05
1572	3.3	3.1 ± 0.3
1575	0.23	0.21 ± 0.04
1633a	133*	145 ± 15

* In 6 M HCl

All values are given in micrograms per gram. No resin treatment was necessary.

TABLE VII

SELENIUM RESULTS ON NBS STANDARD REFERENCE MATERIALS

SRM	Before Resin Treatment	After Resin Treatment	Certified Value
1566	1.5	2.1	2.1 ± 0.5
1567	0.90	0.99	1.1 ± 0.2
1568	0.19	0.49	0.4 ± 0.1
1577	0.37	1.1	1.1 ± 0.1
1577a	0.11	0.73*	0.71 ± 0.07
1633a	7.7	10.0*	10.3 ± 0.7

* In 6 M HCl

The AG 50W-X16 mini-column resin process was utilized. All values are given in micrograms per gram.

TABLE VIII

ARSENIC RECOVERY FOLLOWING MINI-COLUMN RESIN PROCESS

		% Spike Recovery	
Sample No.	Initial pH	AG 50W-X16	Chelex 100
284286	1	104	--
284286	4	97	91
284286	7	101	88
278030	1	99	--
278030*	4	101	89
278030*	7	104	55

SELENIUM RECOVERY FOLLOWING MINI-COLUMN RESIN PROCESS

		% Spike Recovery	
Sample No.	Initial pH	AG 50W-X16	Chelex 100
284286	1	104	--
284286	4	102	84
284286	7	99	73
278030	1	105	--
278030*	4	48	28
278030*	7	44	23
285553	1	90	--
285553*	4	91	4
285553*	7	89	<4

*Significant precipitate present after pH adjustment to 4 and 7.

TABLE IX

SELENIUM RECOVERY IN E.P. TOXICITY LEACHATE EXTRACTS

Sample No.	Original Sample Following Resin Treatment	Sample Spiked, No Resin Treatment	Sample Spiked, Then Passsed Through Resin
333342	0.004	0.020	0.101
333343	<0.004	0.017	0.102
337567	<0.004	0.007	0.104
337918	<0.004	0.018	0.097
337919	<0.004	0.006	0.106
339540	0.004	0.028	0.102
343009	<0.004	0.091	0.103
344313	0.005	0.034	0.107
344880	<0.004	0.015	0.101
344881	<0.004	0.017	0.103
344882	<0.004	0.015	0.103
344883	<0.004	0.018	0.102
344884	<0.004	0.016	0.102
344885	0.004	0.014	0.103
345348	<0.004	0.059	0.103
345984	<0.004	0.088	0.099
346269	<0.004	0.058	0.101

The resin used was AG 50W-X16. The spike concentration was 0.100 mg/l.

All values in mg/l.

TABLE X

ARSENIC RECOVERY IN MUNICIPAL SLUDGE DIGESTS

City Number	Arsenic	% Recovery
1	2.8	96
2	2.5	95
3	2.1	94
4	2.0	96
5	2.6	100
6	1.2	96
7	1.1	92
8	<1	92
9	<1	105
10	<1	99
11	<1	108
12	2.4	102
13	<1	104
14	<1	102
15	1.3	104
16	1.4	101

The arsenic values are given in micrograms per gram on an as received (wet) basis. Digests were spiked at the 0.100 mg/l level.

TABLE XI

PERCENT SELENIUM RECOVERY IN MUNICIPAL SLUDGE DIGESTS

City Number	No Resin Treatment		Minicolumn Resin Treatment	
	1.2 N HCl+ 1.8 N H_2SO_4	6.6 N HCl+ 0.9 N H_2SO_4	1.2 N HCl+ 1.8 N H_2SO_4	6.6 N HCl+ 0.9 N H_2SO_4
1	31	80	30	86
2	39	77	58	101
3	38	92	40	93
4	32	83	42	101
5	51	64	53	78
6	45	102	52	102
7	27	88	27	89
8	51	95	56	97
9	100	105	102	95
10	95	110	99	100
11	67	102	69	97
12	101	109	100	104
13	51	98	54	96
14	98	109	96	104
15	102	91	102	97
16	56	111	59	104

The values tabulated above are given in percents. The selenium results in the sample, obtained after resin treatment and the higher level acidification, were all below 4 micrograms per gram on an as received (wet) basis.

EMPLOYMENT OF ALKALINE DIGESTION PROCEDURES FOR DETERMINATION OF METALS IN INDUSTRIAL WASTES

JOSEPH H. LOWRY AND D. S. KENDALL, NATIONAL ENFORMCEMENT INVESTIGATIONS CENTER, U. S. ENVIRONMENTAL PROTECTION AGENCY, DENVER, COLORADO

ABSTRACT

For the past five years, NEIC has been involved in the analysis of samples collected from hazardous waste sites. The waste samples have included mostly drum samples, but samples of piles, logoons, tankers, and spills also have been analyzed at NEIC. The diversity and complexity of the waste compositions encountered demanded widely applicable methods for the analysis of these samples for trace and major elemental constituents. Often samples were mixed phases containing any combination of an aqueous liquid, organic solvent, solids, pastes, gels, greases and tars. A number of analytical strategies have been studied and decomposition of the sample matrix with a molten fusion followed by Inductively Coupled Argon Plasma Optical Emission Spectroscopic analysis has been found satisfactory for most sample types and study objectives. This approach has been employed successfully in the analysis of the matrices found in drum samples and has also worked well in the analysis of soils.

Data for the analysis of a wide variety of reference materials demonstrates that highly precise and accurate analyses can be obtained with this methodology. Comparison of this method's results to that of X-Ray Fluorescene Spectroscopy in the analysis of contaminated soils further verifies the quality of data that can be achieved. Precision and accuracy data gathered during the use of this method over the past few years will be present.

The selection and applicability of a method of analysis is based largely on what is a significant level for a particular study. One important factor in defining a significant concentration is the distribution of an element in the sample population. Abundant data for most environmental media is available. Such data, however, is scarce for drum samples. To aid in filling this data base void, the frequency and level of occurence for thirty-two elements from 1,000 samples collected from forty-five sites in thirty-one states will be presented. These elemental distributions will be used to evaluate the applicability of a selected method to different study objectives.

SECOND SESSION

METHODS FOR IDENTIFYING HAZARDOUS WASTE CHARACTERISTICS

1:30 pm - 5:00 pm

Wednesday, July 24, 1985

Chairperson: Todd A. Kimmell
Methods Program
Office of Solid Waste
U. S. Environmental
Protection Agency
Washington, D. C.

PERFORMANCE OF AN IGNITABLE SOLIDS METHOD IN CHARACTERIZING HAZARDOUS WASTES: A COLLABORATIVE STUDY

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

The United States Environmental Protection Agency (EPA) has specified in the Federal Register that a solid waste exhibits the characteristic of ignitability if "it is capable of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard." At the present time, there are no suitable, validated procedures for determining the ignitability characteristic of solid (non liquid) wastes.

Since current ignitability wastes are designed for liquids, an evaluation of potential testing methods for solids was performed at the Research Triangle Institute (RTI). Techniques for ignitability measurements were developed and tested on a wide variety of waste materials. Results of this work were presented at the ASTM D-34 Hazardous Waste Symposium in May, 1984.

The following test procedures were developed: Radiant Heat Test, Flame Propagation Test, and Water Extinguishability Test. All tests were performed in a chamber constructed for this study (Figure A). In addition to reference materials, actual waste samples were utilized in the evaluation of these test procedures.

The following wastes were tested:

- Wood wool excelsior
- Textile lint
- Paint manufacturing waste (3) - putty, fibrous and sandy texture
- Paint wastes (4)
  - amorphous, paste (2), and flake consistency
- Coconut/tolunce
- Styrene polymore/vermiculite
- Still bottoms
- Petroleum waste/vermiculite
- Coal/Xylene
- Red oak sawdust/kerosene
- Paint filter
- Oil pad
- Fuel oil pad
- Sludge bargewaste
- Waste oils
- Lighter fluid
- Sterile cotton
- Pipe tobacco
- Polymethane foam
- Polystyrene

An interlaboratory study was conducted to evaluate the three ignitability test methods. The study consisted of two phases. The first phase involved the replicate measurements of two well-characterized test materials (coal/xylene and red oak sawdust/kerosene) and a reference material by nine laboratories.

Interlaboratory test materials included the folloiwing:

- Sterile cotton
- Polyurethane foam
- Paint waste
- Used motor oil
- 60% used oil/blend 40% sand
- Waste solvent
- 80% sawdust/20% kerosene

Wood wool excelsior was chosen as a reference material in this study because of its use by Underwriter's Laboratories as a standard for class A fire extinguisher and its low measurement variability noted during the single laboratory study. The second phase included similar replicate measurements of seven varied test materials by a final roster of only five laboratories.

The study results showed that not all sample types are amenable to measurement by each test. Although all of the procedures showed some deficiency, the Radiant Heat and Flame Propagation test results indicated that, with some minor changes in chamber design, they would be potentially useful routine methods. The Water Extinguishability test is in need of more major improvements.

RTI has been charged with responding to these needs and is proceeding to incorporate the recommendations into the existing protocols. We anticipate having a draft final report ready in early 1986 for review by the various EPA program offices and the Regions.

Another collaborative study will be conducted; consequently, participants will be needed. We hope most of the collaborators will come from this group.

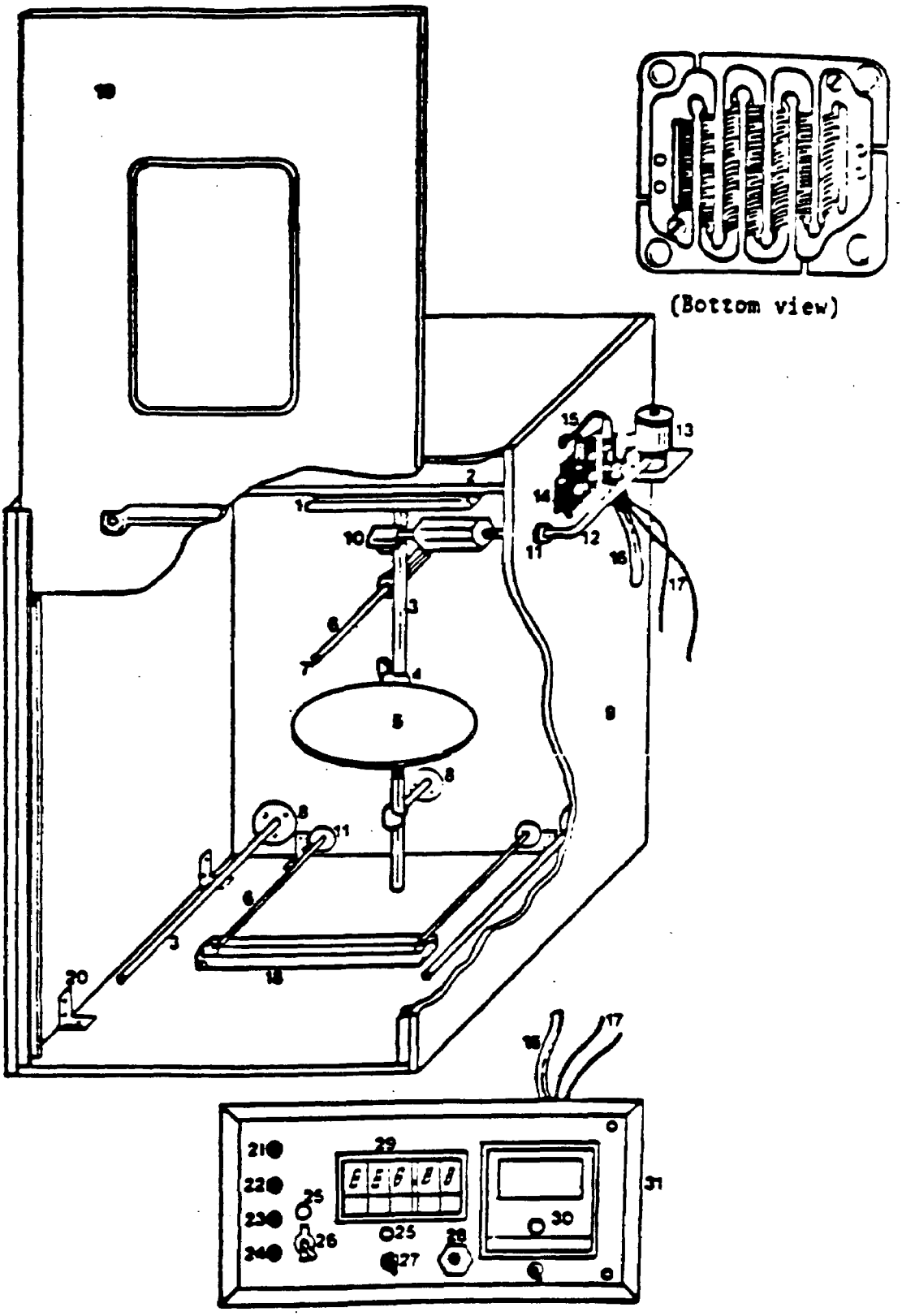


Figure A Ignitability Test Chamber and Controller/Sensor.

REACTIVE SULFIDES AND CYANIDES: TEST METHODS AND REGULATORY THRESHOLD SETTING MODELS

Dr. PAUL H. FRIEDMAN, STUDIES AND METHODS BARNCH, OFFICE OF SOLID WASTE, U. S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, D. C.

ABSTRACT

Reactivity, with respect to sulfide- and cyanide-bearing wastes refers to the volatility and the rate of evolution of hydrogen sulfide and hydrocyanic acid from wastes when these wastes are exposed to an acidic environment. Determining a hazardous waste as reactive requires an empirical test and a mathematical model. The test determines the rate of release of the reactive component from the waste. The model relates the results of the test to short-term and short-range exposure of the gas to a receptor.

Both the test and the model are approximations of reality. Both are described and discussed in terms of their strengths and weaknesses in pre-dicting evolution rates and down wind concentrations of the toxic gas. Alternative procedures for determining evolution rates are discussed and contrasted. Alternative models also are surveyed.

Work in progress is described.

MOBILITY OF TOXIC COMPOUNDS FROM HAZARDOUS WASTES: COMPARISON OF THREE TEST METHODS TO A LYSIMETER MODEL

MICHAEL MASKARINEC AND CHESTER W. FRANCIS, CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE

ABSTRACT

In order to assess the environmental impact of the disposal of solid wastes, it is necessary to develop test methods capable of predicting this impact. This work has the objective of providing a data base from which assessments of the mobility of toxic compounds from solid wastes can be made. The scenario was codisposal of industrial wastes in a municipal waste landfill at a level of 5%. The experimental design included the use of large lysimeters to generate municipal waste leachate, which was then used to leach contaminants from industrial wastes.

Four lysimeters (lined concrete cylinders 1.8 meters in diameter and 3.6 meters high) were filled with 1.5 Mg of municipal refuse collected from the Oak Ridge, Tennessee area. Two were used for the initial phase of this work (Phase I) and two were used for validation studies (Phase II). Distilled de-ionized water was applied to the tops of the lysimeters and the leachate generated was used to leach industrial wastes. The leachates were collected and analyzed over time in order to construct leaching curves for each contaminant. From these curves, a target concentration was developed for laboratory ex-tractions to simulate.

A total of 34 different laboratory extractions were tested for their ability to match the target concentrations. Factors including medium, liquid to solid ratio, and extraction techniques were varied. Based on the Phase I data, two procedures were chosen for further evaluation, acetate buffer (0.1N pH 5), and distilled de-ionized water saturated with carbon dioxide, both in a rotary extraction device at a liquid to solid ratio of 20. The EPA Extraction Procedure was also tested. A number of statistical procedures were used to rank the various extraction procedures. Where statistically significant differences were found, the acetate system was found to best simulate the leaching data obtained from the field lysimeters.

APPLICATION OF THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) TO INDUSTRIAL WASTES: A SINGLE LABORATORY EVALUATION

Dr. L. R. WILLIAMS, U. S. ENVIRONMENTAL PROTECTION AGENCY-EMSL, LAS VEGAS, NEVADA

ABSTRACT

A vital step in the process of validating, testing, and measuring methods for Agency use is the "single-laboratory study." Such studies are intended to identify and test critical variables in method protocols and provide bases for revising the written protocols for emphasis, clarity, and ease of use. In addition, these studies develop data on the accuracy, precision, and limits of reliable measurement for the test method with representative sample materials in one or more capable laboratories. These studies represent the vital, and frequently missing, link between the written method and multi-laboratory collaborative study. The role of the single-laboratory study in overall strategy of method validatiion was highlighted using the current evaluation of the Toxicity Characteristic Leaching Procedure (TCLP) as the primary example. Study design and preliminary results of the single-laboratory testing of the TCLP were presented and discussed. Aspects of this method evaluation were conducted at two different laboratories in a parallel effort.

THIRD SESSION

ANALYZING FOR ORGANICS

8:00 am - Noon

Thursday, July 25, 1985

Chairperson: Dr. Paul H. Friedman
Methods Program
Office of Solid Waste
U. S. Environmental
Protection Agency
Washington, D. C.

APPLICATION OF SW-846 METHODS TO GROUNDWATER MONITORING PROGRAMS: EXPERIENCES OF TWO CONTRACT LABORATORIES

Dr. DENIS C. K. LIN, DAVID SPEIS, KAREN KOTZ-GEBEL, AND DIANE FOSTER, ENVIRONMENTAL TESTING AND CERTIFICTION CORPORATION, EDISON, NEW JERSEY

INTRODUCTION

On July 26, 1982, the U.S. Environmental Protection Agency (EPA) published interim final regulations under the Resource Conservation and Recovery Act (RCRA), which set permit procedures and operating standards for hazardous waste land disposal facilities. These regulations also established groundwater monitoring requirements for such facilities. Under certain circumstances the regulations required facility owners to conduct chemical analyses for the compounds listed in Appendix VIII, Part 261. On September 21, 1982, a notice published in the Federal Register (Vol. 47, No. 183, at pages 41562 through 41563) amended two sections of the regulations (specifically, in title 40, Code of Federal Regulations, Section 122.20 of the consolidated permit regulations and Section 260.11 of the hazardous waste regulations) to incorporate by reference the Second Edition of the EPA Manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846. More recently EPA proposed on October 1, 1984 to make SW-846 methods mandatory for all testing and monitoring activities defined under Subtitle C, as specified in 40 CFR parts 260-271. Thus, SW-846 has become a key document in the analysis of groundwater for the 375 Appendix VIII parameters (Table 1).

The Environmental Testing and Certification Corporation (ETC) has been involved in the analysis of Appendix VIII parameters in groundwater since the fall of 1982. In May, 1983, ETC reported to Chemical Manufacturers Association (CMA) the results of a project whose objective was to evaluate the effectiveness of SW-846 to serve as a methods manual for the sampling and analysis of groundwater on leachate for the Appendix VIII parameters. In the summer of 1984, ETC participated in an "Inter- and Intra-Laboratory Assessment of SW-846 Methods Manual for Analysis of Appendix VIII Compounds in Groundwater" sponsored by CMA. (1) In the fall of 1984, ETC performed a study for EPA to serve as a preliminary investigation in using presently available methodology to analyze as many Appendix VIII parameters as possible. Furthermore, over the past two and one-half years ETC has been developing an analytical scheme to meet the demand for Appendix VIII analysis. In this article we will report the present status of Appendix VIII analytical procedures based on our experience.

THE APPENDIX VIII PARAMETERS

To design an analytical scheme for the 375 Appendix VIII parameters in the Grand Table (Table 1), it is essential to examine the physical and chemical characteristics of the individual compounds. In the October 1, 1984 Federal Register (Vol. 49, Page 38786) EPA identified several

categories of parameters. It proposed to categorize 13 parameters as unstable in water; and 10 parameters as "exotic" in nature and for which no satisfactory analytical methods are available. Furthermore, for those parameters that have metals in their compositions it is sufficient to analyze for the metal components only. Fifty-one parameters were assigned to this category. Using the same rationale EPA proposed 14 parameters can be testd as cyanides. Since one exotic, two unstable, and seven cyanide compounds are also classified as metals, EPA categorization effectively addressed 78 parameters leaving 297 that need to be addressed in an analytical scheme.

The analytical scheme designed at ETC for the Appendix VIII parameters follows the rationale suggested by SW-846. Various parameters are categorized according to their chemical and physical characteristics and they are grouped together under analytical methods by which they can be quantified at optimal method detection limits. We agree with EPA's approach to the unstable, exotic and metallic compounds. We focus our attention on the remaining 297 parameters.

There are 11 additional parameters among the 297 that ETC believes should be classified as "unstable in water" (Table 2). EPA, while acknowledging that there are other unstable compounds, suggests that there is some likelihood they can be found in water. Since EPA has not yet reclassified any of these compounds as unstable, we have decided to incorporate them into our analytical scheme. However, we do not set data acceptance criteria for them.

There are another 33 parameters (Table 3) that ETC believes should be classified as exotic compounds because they require special methods for their analysis. Ten of these exotic compounds are antineoplastic agents or other drugs. Five are uncommon compounds where pertinent information is unavailable. Three are alkaloid poisons or mycotoxins. Two are water soluble dyes. One is a very volatile compound that can explode easily. These compounds and the remaining 12 compounds possess unusual chemical and physical characteristics, which in turn dictate that their analysis at meaningful detection limits would require individual tailor-made analytical methodology. In most of these cases, EPA recommends including them in analytical methods in SW-846. Little, if any, data is available to support such recommendations. Although ETC includes these parameters in its current Appendix VIII analytical scheme, we believe the recommended methodologies are unproven and most likely ineffective. We strongly urge EPA to re-examine its position. Perhaps only under certain circumstances should analysis be required for the selected exotic parameters in Table 3.

Among the 297 parameters there are 28 that are listed as "N.O.S." (not otherwise specified). These 28 parameters, along with aflatoxins, coal tars, cresote, cresols, phthalic acid esters, tetrachloroethane, and toluenediamine, constitute 35 complex mixtures or classes of compounds (Table 4). Since some of mixtures and classes include thousands of individual compounds it is necessary to select representatives for analysis. As much as possible, we have chosen "priority pollutants" and commonly available reference standard

compounds to represent the 35 parameters (see Table 4).

In the next section we will detail the present status of the Appendix VIII analytical scheme in our laboratory.

THE ETC ANALYTICAL SCHEME FOR APPENDIX VIII PARAMETERS

The ETC Analytical Scheme consists of analyses based on the methodology described in SW-846 and the parameters are divided into the following categories:

1. Water Soluble Compounds by Direct Aqueous Injection GC/MS. (DAI)

2. Volatile Compounds by Purge and Trap GC/MS. (P & T)

3. Extractable Acid/Base/Neutral/Pesticides Compounds by GC/MS. (A/B/N)

4. Pesticides by GC/EC. (PEST/HERB)

5. Pesticides by GC/FPD. (PEST/HERB)

6. Herbicides by GC/EC. (PEST/HERB)

7. Polar and Thermally Unstable Compounds by HPLC/UV). (HPLC)

8. Metallic and Organometallic Compounds by ICAP, AA, and Cold Vapor AA. (METALS)

9. Conventionals. (CONV)

Within the nine categories of compounds that can be specifically analyzed, not all the reference stardards are readily available. In Table 5 we list the number of such parameters in each appropriate category and the number for which reference standards are missing. In the GC/MS analyses we are able to search for the specific compounds that do not have corresponding reference standards by using standard spectra from the literature. In other cases, such as GC and HPLC, where retention time characteristics are the only means to identify the compounds, we are unable to draw any conclusions about those compounds for which corresponding reference standards are not available.

In each category we achieve rigorous compliance with the instrumental requirements and performance criteria of established EPA methods, such as those in methods 624 and 625, before any sample analysis is initiated. For GC/MS analysis where standards are available, identification is performed using relative retention times, the relative abundance of three characteristic ions and the abundance ratios. The entire mass spectrum is reviewed to confirm each

identification. Quantitative analysis is performed using an internal standard with a single characteristic ion. When compounds without corresponding reference standards are identified, they are quantified assuming the same response factor as the internal standard.

VOLATILE COMPOUNDS BY PURGE AND TRAP GC/MS

For the analysis of volatile compounds by Purge and Trap, Methods 8240 and 5030 are used. The analysis can be summarized as follows: Helium is bubbled through a 5 ml water sample contained in a specially designed purging chamber at ambient temperature. The purgeable volatile organic compounds are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the organic compounds are trapped. After the purge cycle is complete, the sorbent column is heated and back flushed with helium to desorb the organic purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeable mixture. The separated purgeable components are then identified and quantitated using a computerized mass spectrometer.

WATER SOLUBLE COMPOUNDS BY DIRECT AQUEOUS INJECTION GC/MS

For the analysis of water soluble compounds, 5 ul of aqueous sample is injected directly into the GC/MS system. The chromatographic column employed in the procedure is the same column used for purge and trap analysis. MS scanning was begun prior to sample injection to capture mass intensity data for early eluting compounds. The GC oven temperature program used is that specified in procedure 8240.

EXTRACTABLE ACID/BASE/NEUTRAL AND PESTICIDE COMPOUNDS BY GC/MS

For the analysis of the Acid, Base/Neutral and Pesticide compounds in water, Methods 3510 and 8270 are used. The analysis can be summarized as follows: a measured volume of sample, approximately 1 liter, is extracted with an aliquot of methylene chloride without pH adjustment and then the sample is adjusted to a pH greater than 11 and extracted with another aliquot of methylene chloride. These two aliquots were combined. The pH of the sample is then adjusted to a value less than 2 and extracted with another aliquot of methylene chloride. A separatory funnel or continuous extractor is used to perform the extractions. The two extracts are dried and concentrated to a 1 ml final volume. The extracts are then combined just prior to injection into a GC/MS instrument.

HERBICIDES AND PESTICIDES BY GC

The methods employed in the analysis for herbicides and pesticides are established EPA methods taken from the "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples," June, 1980 and methods 8080, 8140 and 8150.

The herbicide method can be summarized as follows: A measured volume of sample, approximately 500-1000 ml, to which sodium sulfate has been added is acidified and extracted with methylene chloride. The methylene chloride extract is evaporated to dryness, and the residue is derivatized with diazomethane and injected into a gas chromatograph equipped with a 63Ni electron capture detector.

The pesticide method can be summarized as follows: A measured volume of sample, approximately 500ml, is extracted with methylene chloride. The extract is dried and concentrated to a final volume of 1ml and injected into a gas chromatograph equipped with a 63Ni electron capture detector and Flame Photometric detector in phosphorus mode.

METALS

The determination of metals in aqueous samples is performed according to the methods published by EPA in "Methods for Chemical Analysis of Water and Wastes." EPA-600/4-79-020, March, 1979, and the inorganic methods in SW 846. Arsenic, selenium and thallium are determined by furnace AA; silver, aluminum, barium, beryllium, boron, cadmium, calcium, chromium, copper, cobalt, iron, magnesium, manganese, molybdenum, nickel, lead, sodium, antimony, tin, titanium, vanadium, and zinc are determined by ICP emission. The determination of mercury is performed by cold vapor AA.

THERMALLY UNSTABLE AND POLAR COMPOUNDS BY HPLC

The analysis of thermally unstable and polar compounds are based on the HPLC methods 8320 and 8330. The compounds analyzed fall into two categories: direct aqueous injection and Base/Neutral extractables. Twenty ul of the sample or extract is injected into an HPLC equipped with a reverse phase column. Gradient elution and UV detector at 210 and 250 nm are used.

CONVENTIONAL PARAMETERS

Total cyanide analysis is performed using Method 8010. Sulfide analysis is performed using Method 9030.

DISCUSSION

Our initial study on SW 846 sponsored by CMA concluded that SW 846 was not an acceptable manual but could serve as a base upon which to build an effective methods manual. The CMA inter- and intra-laboratory assessment of SW-846 methods manual for analysis of Appendix VIII compounds in groundwater studied specifically Methods 8240, (P & T, GC/MS), 8270 (A/B/N, GC/MS) and 8330 (HPLC). Three prominent laboratories were asked to analyze a series of groundwater samples for 36 compounds. The study concluded that: "the list of Appendix VIII

compounds reportedly amenable to Methods 8240 and 8270 was found to be somewhat less than reported by EPA. Method 8330 was found to be completely inadequate for the detection and quantification of the three compounds included in the study." From our experience such conclusions are not surprising since SW-846 does not provide sufficient procedural details for all appropriate Appendix VIII compounds.

Based on our EPA study and our extensive experience using the ETC analytical scheme, SW-846 can be applied diligently with success for a substantial number of Appendix VIII compounds. In the first phase of our EPA study, attempts were made to define which Appendix VIII compounds could be analyzed under the analytical scheme. To achieve this, the reagent water was spiked with compounds of interest at reasonably high levels so that all indications of non-performance for a parameter would be definitive. The first phase of the study was suggested adjustments that should be made in the analytical scheme. With the revised scheme, groundwater sample was spiked at high, medium and low levels. The high and low levels were analyzed in seven replicates and the medium level was analyzed in triplicate. Based on the results, method detection limits were proposed for individual compounds in the Appendix VIII parameters. However, the study was limited by the availability of Appendix VIII standard reference compounds. The data obtained in the spiking experiments were submitted to EPA. Spike recovery results of selected nonpriority pollutant Appendix VIII compounds are shown in Table 6.

For the 55 parameters (Table 5) we have included in the purgeable volatile GC/MS (P & T) fraction, six are listed in Table 1 and 2 as potential candidates as unstable or exotic. We do not expect the analysis for these six compounds using Method 8240 methodology can be performed successfully. For the other P & T compounds in this fraction our investigation showed that the methodology performed satisfactorily. The ions we select to identify and quantify the compounds, as well as their relative retention times, have been submitted to EPA for review. Our investigation also showed crotonaldehyde (Table 7) could not be analyzed satisfactorily. At 50 ug/l crotonaldehyde could not be recovered using Method 8240 methodology.

Twenty-two parameters were selected to be analyzed by direct aqueous injection GC/MS methodology (DAI). All of these 22 compounds are highly soluble in water. We suspected Method 8240 would not work for these compounds. The CMA inter- and intralaboratory study indeed showed unsatisfactory results for isobutanol. (1) In our investigations using DAI/INJ, eight parameters still yield unsatisfactory results (Table 7). We intend to try other methods on these water soluble compounds.

Of the 18 compounds we listed in Table 7 as compounds that require further investigation, nine originated from the extractable acid/base/neutral/pesticide compounds by GC/MS fraction (A/B/N). We suspect these nine compounds can be analyzed at higher method detection limits. While the Method 8270 methodology works well for

the compounds investigated, the success rate may not be the same for the 30 parameters for which reference standards were unavailable.

We did not list any parameters in Table 7 for pesticide and herbicide fractions. The SW-846 GC methods 8080, 8140 and 8150 for pesticides and herbicides are sound. We investigated all but three of the 28 parameters in these categories and did not discover any problems. We have just acquired the three compounds as reference standards and we do not expect any major difficulties in their analyses.

Contrary to the GC methods in SW-846, the HPLC methods appear to be unsound. In the inter- and intra-laboratory study none of the Method 8330 analytes were successfully analyzed. (1) We have substantially modified the HPLC methods in order to accommodate the 37 parameters included in this fraction and thus far have successfully analyzed for 19 parameters. We do not have reference standards for seven parameters. We are investigating the remaining 11 parameters in the HPLC analyses.

To summarize, among the 297 organic Appendix VIII parameters that need to be included in the ETC analytical scheme, 43 reference standards are unavailable at present. We have 40 newly acquired reference compounds on hand. Naturally, we intend to add these to our on-going investigation.

CONCLUSION

Of the total 375 Appendix VIII parameters, we presently have no spiking experimental data on 83 parameters. Some of these compounds (14) can be qualitatively searched for since their mass spectra are documented. Of the remaining 292 parameters, we are not satisfied with the experimental results of the 198 parameters as shown in Table 7.

Of the SW-846 methods employed for the organic parameters in Appendix VIII, the GC methods 8080, 8140 and 8150 performed satisfactorily. The HPLC methods 8320 and 8330 require extensive modifications. The Methods 8240 and 8270 GC/MS methodologies were found to be suitable for most of the compounds investigated in those appropriate fractions.

REFERENCE

1. George H. Stanko and Peter E. Fortini, Hazardous Waste and Hazardous Materials, Vol. 2(1), pp. 67-97, 1985.

TABLE 1
GRAND TABLE

ETC REF NO	COMPOUND NAME
1	Acetonitrile
2	Acetophenone
3	Warfarin
4	2-Acetylaminofluorene
5	Acetyl chloride
6	1-Acetyl-2-thiourea
7	Acrolein
8	Acrylamide
9	Acrylonitrile
10	Aflatoxins
10A	Aflatoxins, Total
11	Aldrin
12	Allyl alcohol
13	Aluminum phosphide
13A	Aluminum
14	4-Aminobiphenyl
15	Mitomycin C
16	5-(Aminomethyl)-3-isoxazolol
17	Amitrole
18	Aniline
19	Antimony and Compounds, N O.S.
19A	Antimony
20	Aramite
21	Arsenic and Compounds, N O.S.
21A	Arsenic
22	Arsenic acid (Orthoarsenic acid)
23	Arsenic pentoxide (Arsenic (V) oxide)
24	Arsenic trioxide (Arsenic (III) oxide)
25	Auramine
26	Azaserine
27	Barium and Compounds, N O.S
27A	Barium
28	Barium cyanide
29	Benz[c]acridine
30	Benz[a]anthracene
31	Benzene
32	Benzenearsonic acid
33	Dichloromethylbenzene
34	Benzenethiol
35	Benzidine
36	Benzo[b]fluoranthene
37	Benzo[j]fluoranthene
38	Benzo[a]pyrene
39	p-Benzoquinone
40	Benzotrichloride
41	Benzyl chloride
42	Beryllium and Compounds, N.O S.
42A	Beryllium
43	bis(2-Chloroethoxy)methane
44	bis(2-Chloroethyl) ether
45	Chlornaphazine
46	bis(2-Chloroisopropyl)ether
47	bis(Chloromethyl)ether
48	bis(2-ethylhexyl)phthalate
49	Bromoacetone
50	Methyl bromide
51	4-Bromophenyl phenyl ether
52	Brucine
53	2-Butanone peroxide
54	Butyl benzyl phthalate
55	2-sec-Butyl-4,6-dinitrophenol

TABLE 1
GRAND TABLE

ETC REF NO.	COMPOUND NAME
56	Cadmium and Compounds, N O S.
56A	Cadmium
57	Calcium chromate(Chromic acid,calcium salt)
57A	Calcium
58	Calcium cyanide
59	Carbon disulfide
60	Carbon oxyfluoride
61	Chloral
62	Chlorambucil
63	Chlordane
64	Chlorinated Benzenes, N O S
64A	1,2,3-trichlorobenzene
64B	2,4,6-trichlorobenzene
64C	1,2,3,4-tetrachlorobenzene
64D	1,2,3,5-tetrachlorobenzene
65	Chlorinated Ethane, N O S.
65A	Chloroethane
66	Chlorinated Fluorocarbons, N O.S
66A	Freon TF
67	Chlorinated Naphthalene, N O.S.
67A	1-chloronaphthalene
68	Chlorinated Phenol, N O S
68A	2,3,5,6-tetrachlorophenol
68B	2,3,4,5-tetrachlorophenol
69	Chloroacetaldehyde
70	Chloroalkyl Ethers, N O.S.
71	p-Chloroaniline
72	Chlorobenzene
73	Chlorobenzilate
74	p-Chloro-m-cresol
75	1-Chloro-2,3-epoxypropane
76	2-Chloroethyl vinyl ether
77	Chloroform
78	Methyl chloride
79	Chloromethyl methyl ether
80	2-Chloronaphthalene
81	2-Chlorophenol
82	1-(o-Chlorophenyl)thiourea
83	3-Chloropropionitrile
84	Chromium and Compounds, N O.S
84A	Chromium
85	Chrysene
86	Citrus red No 2
87	Coal Tars
87A	Acenapthene
87B	Acenaphthalene
87C	Anthracene
87D	Benzo(ghi)perylene
87E	Benzo(k)fluoranthene
87F	Fluorene
87G	Phenathrene
87H	Pyrene
88	Copper cyanide
88A	Copper
89	Creosote
89A	2,Nitrophenol
90	Cresols
90A	o-Cresol
90B	m+p-Cresol
91	Crotonaldehyde
92	Cyanides (soluble salts and complexes)N O S
92A	Cyanide, Total

TABLE 1
GRAND TABLE

ETC REF NO	COMPOUND NAME
93	Cyanogen
94	Cyanogen bromide
95	Cyanogen chloride
96	Cycasin
97	2-Cyclohexyl-4,6-dinitrophenol
98	Cyclophosphamide
99	Daunomycin
100	4,4'-DDD
101	4,4'-DDE
102	4,4'-DDT
103	Diallate
104	Dibenz[a,h]acridine
105	Dibenz[a,j]acridine
106	Dibenz[a,h]anthracene
107	7H-Dibenzo[c,g]carbazole
108	Dibenzo[a,e]pyrene
109	Dibenzo[a,h]pyrene
110	Dibenzo[a,i]pyrene
111	1,2-dibromo-3-chloropropane
112	1,2-Dibromoethane
113	Dibromomethane
114	Di-n-butyl phthalate
115	1,2-Dichlorobenzene
116	1,3-Dichlorobenzene
117	1,4-Dichlorobenzene
118	Dichlorobenzene, N O.S.
119	3,3'-Dichlorobenzidine
120	1,4-Dichloro-2-butene
121	Dichlorodifluoromethane
122	1,1-Dichloroethane
123	1,2-Dichloroethane
124	1,2-Trans-dichloroethylene
125	Dichloroethylene, N O.S.
126	1,1-Dichloroethylene
127	Methylene chloride
128	2,4-Dichlorophenol
129	2,6-Dichlorophenol
130	2,4-D
131	Dichlorophenylarsine
132	Dichloropropane, N.O S.
132A	1,3-Dichloropropane
133	1,2-Dichloropropane
134	Dichloropropanol, N O S.
134A	Dichloropropanol
135	2,3-Dichloropropene
136A	cis-1,3-Dichloropropene
136B	trans-1,3-Dichloropropene
137	Dieldrin
138	1,2,3,4-Diepoxybutane
139	Diethylarsine
140	N,N,-Diethylhydrazine
141	Carbophenothion
142	0,0-Diethylphosphoric acid, 0-p-nitrophenyl ester
143	Diethyl phthalate
144	Thionazin
145	Diethylstilbesterol
146	Dihydrosafrole
147	3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
148	Diisopropylfluorophosphate
149	Dimethoate
150	3,3'-Dimethoxybenzidine
151	p-Dimethylaminoazobenzene

TABLE 1
GRAND TABLE

ETC REF NO.	COMPOUND NAME
152	7,12-Dimethylbenz[a]anthracene
153	3,3'-Dimethylbenzidine
154	Dimethyl carbamoylchloride
155	1,1-Dimethylhydrazine
156	1,2-Dimethylhydrazine
157	Thiofanox
158	alpha-alpha-Dimethylphenethylamine
159	2,4-Dimethylphenol
160	Dimethyl phthalate
161	Dimethyl sulfate
162	Dinitrobenzene, N O.S
162A	m-Dinitrobenzene
163	4,6-Dinitro-o-cresol
164	2,4-Dinitrophenol
165	2,4-Dinitrotoluene
166	2,6-Dinitrotoluene
167	Di-n-octyl phthalate
168	1,4-Dioxane
169	Diphenylamine
170	1,2-Diphenylhydrazine
171	N-Nitrosodi-n-propylamine
172	Disulfoton
173	2,4-Dithiobiuret
174A	Endosulfan I
174B	Endosulfan II
175	Endrin
176	Ethyl carbamate
177	Ethyl cyanide
178	Ethylenebisdithiocarbamic acid
179	Ethyleneimine
180	Ethylene oxide
181	Ethylenethiourea
182	Ethyl methacrylate
183	Ethyl methanesulfonate
184	Fluoranthene
185	Fluorine
186	2-Fluoroacetamide
187	Fluoroacetic acid
188	Formaldehyde
189	Formic acid
190	Glycidylaldehyde
191	Halomethane, N O.S.
191A	Chlorodibromomethane
191B	Dichlorobromomethane
192	Heptachlor
193	Heptachlor epoxide
194	Hexachlorobenzene
195	Hexachlorobutadiene
196A	Alpha-BHC
196B	Beta-BHC
196C	Gamma-BHC
196D	Delta-BHC
197	Hexachlorocyclopentadiene
198	Hexachloroethane
199	Hexachlorohexahydro-endo, endo-dimethanonaphthalene
200	Hexachlorophene
201	Hexachloropropene
202	Hexaethyltetraphosphate
203	Hydrazine
204	Hydrogen cyanide
205	Hydrofluoric acid
206	Hydrogen sulfide

TABLE 1
GRAND TABLE

ETC REF NO	COMPOUND NAME
207	Hydroxydimethylarsine oxide
208	Indeno(1,2,3-cd)pyrene
209	Iodomethane
210	Iron dextran
210A	Iron
211	Methyl isocyanate
212	Isobutyl alcohol
213	Isosafrole
214	Kepone
215	Lasiocarpine
216	Lead and Compounds, N O S
216A	Lead
217	Lead acetate (Acetic acid, lead salt)
218	Lead phosphate (Phosphoric acid, lead salt)
219	Lead subacetate
220	Maleic anhydride
221	Maleic hydrazide
222	Malononitrile
223	Melphalan
224	Mercury fulminate
225	Mercury and Compounds, N.O S.
225A	Mercury
226	Methacrylonitrile
227	Methanethiol
228	Methapyrilene
229	Methomyl
230	Methoxychlor
231	2-Methylaziridine
232	3-Methylcholanthrene
233	Methyl Chlorocarbonate
234	4,4'-Methylenebis(2-chloroaniline)
235	Methyl ethyl ketone
236	Methyl hydrazine
237	2-Methyllactonitrile
238	Methyl methacrylate
239	Methyl methanesulfonate
240	Aldicarb
241	N-Methyl-N'-nitrosoguanidine
242	Methyl parathion
243	Methylthiouracil
244	Mustard gas
245	Naphthalene
246	1,4-Naphthoquinone
247	1-Naphthylamine
248	2-Naphthylamine
249	1-Naphthyl-2-thiourea
250	Nickel and Compounds, N.O S.
250A	Nickel
251	Nickel carbonyl (Nickel tetracarbonyl)
252	Nickel cyanide (Nickel (II)cyanide)
253	Nicotinic acid
254	Nitric oxide
255	p-Nitroaniline
256	Nitrobenzene
257	Nitrogen dioxide
258	Nitrogen mustard and hydrochloride salt
259	Nitrogen mustard N-Oxide and hydrochloride salt
260	Nitroglycerin
261	4-Nitrophenol
262	4-Nitroquinoline-1-oxide
263	Nitrosamines, N O S
263A	N-Nitrosodiphenylamine

TABLE 1
GRAND TABLE

ETC REF. NO.	COMPOUND NAME
264	N-Nitrosodi-n-butylamine
265	N-Nitrosodiethanolamine
266	N-Nitrosodiethylamine
267	N-Nitrosodimethylamine
268	N-Nitroso-N-ethylurea
269	N-Nitrosomethylethylamine
270	N-Nitroso-N-methylurea
271	N-Nitroso-N-methylurethane
272	N-Nitrosomethylvinylamine
273	N-Nitrosomorpholine
274	N-Nitrosonornicotine
275	N-Nitrosopiperidine
276	N-Nitrosopyrrolidine
277	N-Nitrososarcosine
278	5-Nitro-o-toluidine
279	Octamethylpyrophosphoramide
280	Osmium tetroxide (Osmium (VIII) oxide)
280A	Osmium
281	Endothal
282	Paraldehyde
283	Parathion
284	Pentachlorobenzene
285	Pentachloroethane
286	Pentachloronitrobenzene
287	Pentachlorophenol
288	Phenacetin
289	Phenol
290A	m-phenylenediamine
290B	o-phenylenediamine
290C	p-phenylenediamine
291	Phenylmercury acetate
292	N-Phenylthiourea
293	Phosgene
294	Phosphine
295	Phorate
296	Famphur
297	Phthalic acid esters
298	Phthalic anhydride
299	2-Picoline
300	Polychlorinated Biphenyl, N.O.S.
300A	Aroclor 1242
300B	Aroclor 1254
300C	Aroclor 1260
300D	Aroclor 1248
300E	Aroclor 1232
300F	Aroclor 1221
300G	Aroclor 1016
301	Potassium cyanide
301A	Potassium
302	Potassium silver cyanide
303	Pronamide
304	1,3-Propane sultone
305	n-Propylamine
306	Propylthiouracil
307	2-Propyn-1-ol
308	Pyridine
309	Reserpine
310	Resorcinol
311	Saccharin and salts
312	Safrole
313	Selenious acid (Selenium dioxide)
314	Selenium and Compounds, N.O.S.

TABLE 1
GRAND TABLE

ETC REF NO	COMPOUND NAME
314A	Selenium
315	Selenium sulfide (Sulfur selenide)
316	Selenourea
317	Silver and Compounds, N O S.
317A	Silver
318	Silver cyanide
319	Sodium cyanide
319A	Sodium
320	Streptozotocin
321	Strontium sulfide
321A	Strontium
322	Strychnine and salts
323	1,2,4,5-Tetrachlorobenzene
324	2,3,7,8-TCDD
325	Tetrachloroethane
326	1,1,1,2-Tetrachloroethane
327	1,1,2,2-Tetrachloroethane
328	Tetrachloroethylene
329	Carbon tetrachloride
330	2,3,4,6-Tetrachlorophenol
331	Tetraethyldithiopyrophosphate
332	Tetraethyl lead
333	Tetraethylpyrophosphate
334	Tetranitromethane
335	Thallium and Compounds, N O.S.
335A	Thallium
336	Thallic oxide (Thallium (III) oxide)
337	Thallium (I) acetate (Acetic acid, thallium
338	Thallium (I) carbonate
339	Thallium (I) chloride
340	Thallium (I) nitrate
341	Thallium selenite
342	Thallium (I) sulfate
343	Thioacetamide
344	Thiosemicarbazide
345	Thiourea
346	Thiuram
347	Toluene
348	Toluenediamine
348A	Toluene-2,4-Diamine
349	O-Toluidine hydrochloride
350	Toluene diisocyanate
351	Toxaphene
352	Bromoform
353	1,2,4-Trichlorobenzene
354	1,1,1-Trichloroethane
355	1,1,2-Trichloroethane
356	Trichloroethylene
357	Trichloromethanethiol
358	Trichlorofluoromethane
359	2,4,5-Trichlorophenol
360	2,4,6-Trichlorophenol
361	2,4,5-T
362	2,4,5-TP (Silvex)
363	Trichloropropane, N O S
363A	1,1,2-trichloropropane
363B	1,2,2-trichloropropane
364	1,2,3-Trichloropropane
365	O,O,O-Triethyl phosphorothioate
366	sym-Trinitrobenzene
367	Tris (1-Azridinyl) phosphine sulfide

TABLE 1
GRAND TABLE

ETC REF NO.	COMPOUND NAME
368	Tris(2,3-dibromopropyl) phosphate
369	Trypan blue
370	Uracil mustard
371	Vanadic acid, ammonium salt
372	Vanadium pentoxide (Vandium (V) oxide)
372A	Vanadium
373	Vinyl chloride
374	Zinc cyanide
374A	Zinc
375	Zinc phosphide

TABLE 2

PARAMETERS EXPECTED TO BE UNSTABLE IN WATER

40 Benzotrichloride
53 2-Butanone peroxide
75 1-Chloro-2,3-epoxypropane
79 Chloromethyl methyl ether
138 1,2,3,4-Diepoxybutane
148 Diisopropylfluorophosphate
161 Dimethyl sulfate
220 Maleic anhydride
295 Phorate
298 Phthalic Anhydride
331 Tetraethyldithiopyrophosphate

TABLE 3

"EXOTIC" COMPOUNDS THAT REQUIRE SPECIAL METHODS

10 Aflatoxins
15 Mitomycin C
25 Auramine
26 Azaserine
52 Brucine
62 Chlorambucil
86 Citrus red No. 2
98 Cyclophosphamide
99 Daunomycin
103 Diallate
147 3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol
173 2,4-Dithiobiuret
188 Formaldehyde
189 Formic acid
202 Hexaethyl tetraphosphate
241 N-Methyl-N'-nitrosoguanidine
262 4-Nitroquinoline-1-oxide
277 N-Nitrososarcosine
279 Diphosphoramide, octamethyl
281 Endothall
282 Paraldehyde
304 1,3-Propane sultone
306 Propylthiouracil
311 Saccharin and salts
320 Streptozotocin
322 Strychnine and salts
324 2,3,7,8-TCDD
334 Tetranitromethane
343 Thioacetamide
344 Thiosemicarbazide
367 Tri(1-azridinyl)phosphine sulfide
369 Trypan blue
370 Uracil mustard

TABLE 4
COMPOUND CLASSES

CLASS	REPRESENTATIVE		TABLE*
19 Antimony and Compounds, N O S	19A	Antimony	QR29
21 Arsenic and Compounds, N O S	21A	Arsenic	QR29
27 Barium and Compounds, N O S	27A	Barium	QR29
42 Beryllium and Compounds, N O S	42A	Beryllium	QR29
56 Cadmium and Compounds, N O S	56A	Cadmium	QR29
84 Chromium and Compounds, N O S	84A	Chromium	QR29
216 Lead and Compounds, N O S	216A	Lead	QR29
225 Mercury and Compounds, N O S	225A	Mercury	QR29
250 Nickel and Compounds, N O S	250A	Nickel	QR29
314 Selenium and Compounds, N O S.	314A	Selenium	QR29
317 Silver and Compounds, N O S	317A	Silver	QR29
335 Thallium and Compounds, N O S	335A	Thallium	QR29
10 Aflatoxins	10A	Aflatoxins, Total	QR28
64 Chlorinated Benzenes, N O S	64A	1,2,3-trichlorobenzene	QR28
	64B	2,4,6-trichlorobenzene	QR28
	64C	1,2,3,4-tetrachlorobenzene	QR28
	64D	1,2,3,5 tetrachlorobenzene	QR28
	115	1,2-Dichlorobenzene	QR28
	116	1,3-Dichlorobenzene	QR28
	117	1,4-Dichlorobenzene	QR28
	353	1,2,4-Trichlorobenzene	QR28
65 Chlorinated Ethane, N O S	65A	Chloroethane	QR27
	354	1,1,1-Trichloroethane	QR27
	355	1,1,2-Trichloroethane	QR27
66 Chlorinated Fluorocarbons, N O S	66A	Freon TF	QR27
67 Chlorinated Naphthalene, N O S	67A	1-chloronaphthalene	QR28
68 Chlorinated Phenol, N O S	68A	2,3,5,6-tetrachlorophenol	QR28
	68B	2,3,4,5-tetrachlorophenol	QR28
	128	2,4-Dichlorophenol	QR28
	129	2,6-Dichlorophenol	QR28
	359	2,4,5-Trichlorophenol	QR28
	360	2,4,6-Trichlorophenol	QR28
70 Chloroalkyl Ethers, N O S	44	bis(2-chloroethyl) ether	QR28
	46	bis(2-chloroisopropyl)ether	QR28
	76	2-Chloroethyl vinyl ether	QR27
87 Coal Tars	31	Benzene	QR27
	87A	Acenapthene	QR28
	87B	Acenaphthalene	QR28
	87C	Anthracene	QR28
	87D	3,4-Benzofluoranthene	QR28
	87E	Benzo(ghi)perylene	QR28
	87F	Benzo(k)fluoranthene	QR28
	87G	Fluorene	QR28
	87H	Phenathrene	QR28
	87I	Pyrene	QR28
	90	Cresols	SEE BELOW
	245	Napthalene	QR28
	289	Phenol	QR28
	347	Toluene	QR27

*Results table number in ETC Appendix VIII technical report

TABLE 4 (cont'd)
COMPOUND CLASSES

CLASS	REPRESENTATIVE		TABLE*
89 Creosote	74	p-Chloro-m-cresol	QR28
	89A	2,Nitrophenol	QR28
	90A	o-Cresol	QR28
	90B	m+ resol	QR28
	163	4,6-Dinitro-o-cresol	QR28
	261	4-Nitrophenol	QR28
90 Cresols	90A	o-Cresol	QR28
	90B	m+p Cresol	QR28
92 Cyanides, N O S	92A	Cyanide, Total	QR29
118 Dichlorobenzene, N O S.	115	1,2-Dichlorobenzene	QR28
	116	1,3-Dichlorobenzene	QR28
	117	1,4 chlorobenzene	QR28
125 Dichloroethylene, N O S.	126	1,1 Dichloroethylene	QR27
132 Dichloropropane, N O.S	132A	1,3-Dichlor ane	QR27
	133	1,2-Dichloropropane	QR27
134 Dichloropropanol, N O.S.	134A	Dichloropropanol	QR26
162 Dinitrobenzene, N O S.	162A	m-Dinitrobenzene	QR28
191 Halomethane, N O S.	191A	Chlorodibromomethane	QR27
	191B	Dichlorobromoethane	QR27
263 Nitrosamines, N.O.S.	263A	N-Nitrosodiphenylamine	QR28
	264	N-Nitrosodi-n-butylamine	QR28
	265	N-Nitrosodiethanolamine	QR28
	266	N-Nitrosodiethylamine	QR28
	267	N-Nitrosodimethylamine	QR28
	268	N-Nitroso-N-ethylurea	QR25
	269	N-Nitrosomethylethylamine	QR28
	270	N-Nitroso-N-methylurea	QR25
	271	N-Nitroso-N-methylurethane	QR28
	272	N-Nitrosomethylvinylamine	QR28
	273	N-Nitrosomorpholine	QR28
	274	N-Nitrosonornicotine	QR28
	275	N-Nitrosopiperidine	QR28
	276	N-Nitrosopyrrolidine	QR28
	277	N-Nitrososarcosine	QR28
297 Phthalic acid esters	48	bis(2-ethylhexyl)phthalate	QR28
	54	Butyl benzyl phthalate	QR28
	114	Di-N-Butyl phthalate	QR28
	143	Diethyl phthalate	QR28
	160	Dimethyl phthalate	QR28
	167	Di-n-octyl phthalate	QR28
300 Polychlorinated Biphenyl, N O S	300A	Aroclor 1242	QR30
	300B	Aroclor 1254	QR30
	300C	Aroclor 1260	QR30
	300D	Aroclor 1248	QR30
	300E	Aroclor 1232	QR30
	300F	Aroclor 1221	QR30
	300G	Aroclor 1016	QR30
325 Tetrachloroethane	326	1,1,1,2-Tetrachloroethane	QR27
	327	1,1,2,2-Tetrachloroethane	QR27
348 Toluenediamine	348A	Toluene-2,4-Diamine	QR25
363 Trichloropropane, N.O S.	363A	1,1,2-trichloropropane	QR27
	363B	1,2,2-Trichloropropane	QR27
	364	1,2,3-Trichloropropane	QR27

*Results table number in ETC Appendix VIII technical report

TABLE 5

SUMMARY OF PARAMETERS UNDER THE ETC ANALYTICAL SCHEME

PARAMETER CLASSIFICATION	NUMBER OF PARAMETERS	NUMBER OF UNAVAILABLE STD	NUMBER OF STD AND MASS SPECTRUM UNAVAILABLE
UNSTABLE	13*	N/A	N/A
EXOTIC	10*	N/A	N/A
METALS	48	0	N/A
CONV (Cyanide & Sulfide)	8	0	N/A
P&T	55	5	4***
DAI	22	1	0
A/B/N	149	30	25***
HERB/PEST	28	0	N/A
HPLC	37	7	N/A
CLASS	5**	N/A	N/A
TOTAL	375	43	29***

* See discussion under Appendix VIII Parameter Section
** Compound Class represented by other parameters
*** This number is included in the no standard number

N/A - Not Applicable

TABLE 6

SPIKING DATA OF SOME APPENDIX VIII COMPOUNDS
(N = 7)

	Compound	Concentration Added ug/l	Mean Recovery %	Std Deviation %
(DAI/INJ)				
12	Allyl alcohol	62500	112	12
182	Ethyl methacrylate	62500	121	13
307	2-Propyn-1-ol	62500	117	15
(P&T)				
209	Iodomethane	10	109	6
364	1,2,3-Trichloropropane	10	118	11
(A/B/N)				
2	Acetophenone	50	91	6
14	4-Aminobiphenyl	50	104	6
67A	1-chloronapthalene	50	128	30
151	p-dimethylaminoazobenzene	50	106	13
183	Ethyl methanesulfonate	50	65	12
239	Methyl methanesulfonate	50	65	8
247	1-Naphthylamine	50	82	5
248	2-Naphthylamine	50	93	10
255	p-Nitroaniline	300	87	5
275	N-Nitrosopiperidine	50	78	7
284	Pentachlorobenzene	50	92	10
286	Pentachloronitrobenzene	300	60	3
288	Phenacetin	50	120	8
299	2-Picoline	50	57	15
303	Pronamide	50	92	6
(PEST/HERB)				
101	4,4-DDE	0 5	107	10
144	Thionazin	2 5	53	12
172	Disulfoton	12 5	69	8
230	Methoxychlor	50	76	8
242	Methyl parathion	2 5	119	14
283	Parathion	2 5	125	9
296	Famphur	25	131	11
333	Tetraethylpyrophospate	125	58	19
361	2,4,5-T	10	92	28
362	2,4,5-TP (Silvex)	10	96	17

TABLE 6 (Continued)

	Compound	Concentration Added ug/l	Mean Recovery %	Standard Deviation %
(HPLC)				
3	Warfarin	250	53	
150	3,3'-Dimethoxybenzidine	250	83	3
249	1-Napthyl-2-thiourea	250	78	18
290B	--phenylenediamine	250		9
292	N-Phenylthiourea	250	11[illegible]	13
348A	Toluene-2,4-Diamine	250	53	25
8	Acrylamide	5250	97	10
82	1-(o-Chlorophenyl)thiourea	5000	81	2
292	N-Phenylthiourea	5000	109	1

TABLE 7

COMPOUNDS THAT REQUIRE FURTHER INVESTIGATION

	Compounds	Fractions
69	Chloroacetaldehyde	DAI
83	3-Chloropropionitrile	DAI
155	1,1-Dimethylhydrazine	DAI
203	Hydrazine	DAI
227	Methanethiol	DAI
236	Methyl hydrazine	DAI
237	2-Methyllactonitrile	DAI
305	n-Propylamine	DAI
91	Crotonaldehyde	P&T
16	5-(Aminomethyl)-3-isoxazolol	A/B/N
157	Thiofanox	A/B/N
158	a-a-Dimethylphenethylamine	A/B/N
223	Melphalan	A/B/N
265	N-Nitrosodiethanolamine	A/B/N
269	N-Nitrosomethylethylamine	A/B/N
310	Resorcinol	A/B/N
346	Thiuram	A/B/N
368	Tris(2,3-dibromopropyl)phosphate	A/B/N

THE USE OF SW-846 CLEANUP AND MASS SPECTROSCOPY METHODS TO IDENTIFY AND QUANTIFY COMPOUNDS IN COMPLEX INDUSTRIAL WASTES: PETROLEUM INDUSTRY CASE INDUSTRIES

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ABSTRACT

SW-846 cleanup techniques are designed to address two concerns: the elimination of matrix interferences and the lowering of detection limits for constituents of concern. Traditional SW-846 methods for semivolatile constituents in oily samples utilize a series of methylene chloride extractions to isolate the components of interest. An acid/base extraction may be used to separate constituents based on their equilibrium acidity constants. Additional cleanup can now be accomplished by the use of a proposed method that separates base/neutral constituents by polarity on an alumina column. Many constituents of concern in petroleum wastes are aromatic in nature, and their identification and detection is greatly enhanced through isolation from the aliphatics commonly found in petroleum residuals. Mass spectral techniques are used to identify and quantity constituents of concern for all isolated fractions.

INTRODUCTION

This paper presents a proposed SW-846 method designed to eliminate matrix interferences and lower detection limits for target constituents in oily wastes. The method is applicable to any sample containing significant concentrations of aliphatic hydrocarbons or highly polar compounds which interfere with GC/MS identification and quantitation of aromatic constituents. To date, the method has been applied to solid wastes from the petroleum refining, wood preserving, coke by-products, and coal slurry pipeline industries. It is applicable to virtually any sample matrix including oily sludges, emulsions, soils, dry solids, oily liquids, and aqueous liquids.

The work presented here is being funded by EPA's Office of Solid Waste, Characterization and Assessment Division. The initial development effort for the column cleanup method was performed by the ERCO Division of ENSECO, of Cambridge, Massachusetts, and S-Cubed, Inc., of La Jolla, California under contract to EPA. Radian Corporation (Contract No. 68-01-6940) continued the methods development effort and analyzed numerous petroleum refining samples as part of EPA's hazardous waste characterization effort.

The method, Column Cleanup for Oily Wastes, has been designated SW-846 Method 3570. Although only a proposed method, it is now used routinely by the Office of Solid Waste's Characterization and Assessment Division for the analysis of oily wastes. The method is almost always used in sequence with other SW-846 extraction and cleanup methods (the 3500 series). Extracts obtained are analyzed by

Gas Chromatography/Mass Spectrometry (GC/MS). In summary, a base/neutral extract of the waste to be analyzed is applied to a neutral alumina column. The column is sequentially eluted with hexane, methylene chloride, and methanol to obtain the aliphatic, aromatic, and polar constituents of the sample, respectively. The aliphatic fraction contains most of the interfering compounds and is generally not analyzed. The aromatic fraction is analyzed by Method 8270, GC/MS analysis for semivolatile organics. Analysis of the polar fraction has not been performed by Radian.

ANALYSIS OF OILY SAMPLES

Conventional SW-846 methods are designed to extract methylene chloride soluble constituents from a waste matrix in preparation for analysis of these constituents by GC/MS. In the analysis of petroleum refining wastes, it was found that this methodology frequently resulted in the extraction and identification of primarily aliphatic hydrocarbons. Further, the abundance and high concentration of these aliphatic hydrocarbons in petroleum samples interfered with identification and quantification of the aromatic constituents of interest to EPA. Constituents of interest include those given in Part 261, Appendix VIII of RCRA and other compounds believed to present a substantial threat to human health and the environment if mismanaged. The rather lengthy list of chemicals given in Appendix VIII was evaluated for constituents likely to be encountered in petroleum refining wastes. A target list of chemicals was then developed from this study of the industry. Many of the target compounds identified are indigenous to crude oil or are produced from crude during refining processes. Other chemicals are used in refining operations as process chemicals and end up in the industry's wastes. The list of target chemicals is presented in Table 1 and includes many structurally similar compounds, principally polynuclear aromatics (PNAs) and substituted aromatics.

EXTRACTION OF SEMIVOLATILE ORGANICS

Solid wastes as defined by RCRA occur in a wide variety of sample matrices. In the case of petroleum residuals, these matrices include oily sludges, dry solids, semisolids, emulsions, organic, and aqueous liquids. SW-846 methods for the analysis of semivolatile constituents employ Gas Chromatography/Mass Spectrometry (GC/MS) to identify and quantify constituents. As preparation for GC/MS, sample extraction and cleanup are performed in order to isolate target constituents. There are two objectives of extraction and cleanup: (1) to eliminate matrix interferences, and (2) to obtain adequately low detection limits for the constituents of concern. In the analysis of petroleum residuals, a series of extraction/cleanup techniques may be required to meet these objectives. The analytical scheme for a sample is designed based upon the known composition of the waste, upon the target constituents to be identified, and the detection limit required for the target constituents.

The column cleanup (Method 3570), is not dependent upon sample matrix.

In virtually all cases, an aliquot of the waste extract is subjected to column cleanup. The method selected for obtaining this waste extract does depend, however, upon the matrix of the sample. Five extraction and cleanup methods (SW-846) are currently used for the preparation of solid wastes for analysis. Two are specifically designed for aqueous liquids, and two are designed to be used with solid, semisolid, or emulsion sample matrices. The fifth method is used on extracts resulting from the use of one of the four other methods.

Figure 1 presents a typical series of extraction and cleanup methods (including a column cleanup step) used on an oily waste slated for semivolatile analysis via GC/MS. Organic liquids or solids which are completely soluble in methylene chloride (or hexane) do not require extraction, although the column cleanup for these samples is frequently necessary. Other liquids, generally aqueous samples, are extracted by either Method 3510 or 3520, Separatory Funnel and Liquid/Liquid Extraction, respectively. These methods extract semivolatile and nonvolatile constituents with methylene chloride. Acid/base extraction (discussed below) may be employed during the methylene chloride extraction for both these methods. Methods 3540 and 3550, Soxhlet and Sonication Extraction, respectively, are used to extract solids, sludges, semisolids, slurries, and emulsions.

Acid/base extraction may be used to isolate sample constituents as a function of their acidic, basic, or neutral properties. For petroleum samples, typical acid compounds include phenolics and thiols, although other compounds may also be included. Obtaining the acid fraction allows for the identification of phenolics and cresolics without necessitating the analysis of the polar fraction. Identification of phenolics in petroleum samples could be hindered by the presence of base/neutral compounds. Base/neutrals tend to interfere in the analysis of acid constituents in three ways: (1) the GC/MS response for phenolics is relatively low compared to many base/neutral compounds; (2) high concentrations of base/neutrals eluting at the same time in the chromatogram with the acid compounds may significantly raise detection limits; and (3) high concentrations of base/neutral constituents act to dilute acid as part of compounds in the extract. Isolation of acid compounds in the polar fraction was also considered but recoveries for these compounds might be low and subject to increased error.

COLUMN CLEANUP FOR OILY WASTES

When EPA's Office of Solid waste began its study of oily wastes from petroleum refining, it was confronted with the problem of identifying and quantifying target compounds in the base/neutral extract. The same interferences encountered with acid compounds (when not separated from the base/neutrals), were equally intense within the base/neutral extract for the target constituents. Detection limits were found to be unacceptably high.

In a typical sample of oily waste from petroleum refining, PNA's of

interest in a sample range in concentration from 1 to 100 ppm. The sample might contain 50 percent methylene chloride extractable material. This amount of extractable material would necessitate an injection size that overloaded the GC/MS detection system with aliphatics to achieve a detectable mass for a PNA. To alleviate this problem, the column cleanup method separates constituents in the base/neutral extract based upon their relative polarity. The separation is designed to isolate aliphatic, aromatic and polar constituents from one another. Chemical principles used in developing this method have been well-documented (1-3).

SUMMARY OF THE COLUMN CLEANUP METHOD

A discussion of the key elements of the column cleanup method is presented here. A 100 to 200 mg aliquot of the base/neutral extract is solvent exchanged into hexane. The final volume of the extract should be adequate to just solubilize semivolatile organic constituents. The dry hexane aliquot is applied to a neutral alumina column (70 to 230 mesh), and eluted with 13 mL of hexane. The hexane fraction, designated base/neutral aliphatics is collected. The aliphatic fraction is not generally analyzed but is retained should further analysis be indicated. The column is next eluted with 100 mL of methylene chloride. The fraction obtained is collected and labeled base/neutral aromatics. Finally the column is eluted with 100 mL of methanol, the fraction collected, and labeled base/neutral polars. The polar fraction is retained for later analysis if indicated. The volume of each fraction to be analyzed is reduced to 1 mL.

Ten percent (100 micrometers L) of the base/neutral aromatic fraction is evaporated to dryness and subjected to gravimetric analysis to determine the concentration of aromatics in the base/neutral fraction. Similar gravimetric analyses may be performed on the aliphatic and polar fractions should this information be desired. The final volume of the extract may be adjusted to achieve the desired concentration for injection, and the aromatic fraction is analyzed by Method 8270, GC/MS Method for Semivolatile Organics. Spectra for all target constituents are searched for in the chromatogram and the 10 major components of the aromatic fraction are identified. Figures 2 and 3 present typical chromatograms for the aliphatic and aromatic fractions. For most petroleum samples, the aliphatic fraction is quickly recognized because of its characteristic distribution of normal alkanes. The aromatic fraction does not show the organized distribution of alkanes present in the aliphatic fraction and may show a large undifferentiated peak along with the individual constituents.

SEPARATION OF ALIPHATIC AND AROMATIC CONSTITUENTS

Method 3570's primary objective is to eliminate interferences caused by high concentrations of aliphatics in petroleum refining wastes. Development of the method was directed toward achieving the split between aliphatics and aromatics. In this pursuit, the amount of hexane used to elute the aliphatic fraction was carefully considered.

Ultimately, an amount equivalent to one column pore volume was selected.

Figure 4 presents the single ion and reconstructed ion chromatograms for a base/neutral aromatic extract. The extracted ion current profile for the ion mass 57 is shown in the top chromatogram. This ion is characteristic of saturated hydrocarbons. The reconstructed ion chromatogram obtained for the same elution, with 13 mL of hexane used in the chromatographic cleanup, is shown in the lower portion of the figure. A 1 micrometer L injection of the sample extract was made, and a broad undifferentiated peak is readily visible in the lower chromatogram. The top chromatogram shows significant concentrations of saturated hydrocarbons, particularly in the latter portions of the run. A close examination of this profile demonstrates, however, that there is not an overwhelming presence of hydrocarbons. The normal alkanes (from approximately 20 carbon atoms to 35 carbon atoms) are indeed present in the sample. However, the elution of the major mass of the normal alkanes does not coincide with the peak of eluted material in the undifferentiated peak. The baseline upon which these alkanes appear is quite flat.

Figure 5 presents the relationship between amount of hexane used as the solvent for the aliphatic fraction, and the elution of three low molecular weight PNAs from the aromatic fraction. As shown in the figure, increasing the amounts of hexane used to elute "aliphatics" from the column tends to reduce naphthalene concentrations in the aromatic fraction. Presumably, large volumes of hexane act to elute naphthenics along with aliphatics. The aliphatic fraction was not evaluated in this study but has been examined in other evaluations. It has been found that, indeed, naphthalene is eluted in the hexane fraction when large volumes of the solvent are used. Table 2 presents a complete summary of the analysis of the aromatic fraction for the successive amounts of hexane used to elute the aliphatics. High molecular weight PNA's are not significantly affected by increasing the amount of hexane.

SURROGATES AND SURROGATE RECOVERIES

The column cleanup method employs surrogates that act as column performance indicators. The surrogates are added at the beginning of the analyses, preceding extraction, and are used to demonstrate recoveries for specific types of constituents. Surrogates used for Method 3570 are 2-fluorobiphenyl, nitrobenzene-d5, pyrene-d10, and terphenyl-d14. Phenol-d5 may be added immediately preceding application of the extract to the column if the polar fraction is to be analyzed. Good recoveries of 2-fluorobiphenyl, a low molecular weight diaromatic, indicates that the low molecular weight PNAs are eluted and recovered in the analysis. Pyrene-d10 and terphenyl-d14 are used to demonstrate recoveries for the higher molecular weight PNAs. These two surrogates elute in the later portion of the chromatogram. The surrogate nitrobenzene-d5 is used to demonstrate the extent to which relatively polar compounds are retained on the column during the methylene chloride wash. It has been found that

when no sample matrix interferences are present nitrobenzene-d5 is almost always retained on the column during the methylene chloride wash. That is, for blanks and other runs when only the surrogates are spiked, nitrobenzene-d5 is found in the polar fraction. When a sample is spiked with this surrogate and the column cleanup performed, however, nitrobenzene-d5 is found in the aromatic fraction. Matrix effects within the sample appear to alter polarities enough to elute nitrobenzene-d5. Recovery of nitrobenzene-d5 may, when more data have been obtained, be useful in making correlations between concentrations of specific types of polar constituents in the sample and elution patterns.

RECOVERIES OF TARGET CONSTITUENTS

For most studies of petroleum samples, polynuclear aromatics (PNAs) are the major constituents of concern. The column cleanup's performance for these compounds is within the recovery ranges given in SW-846. Column performance can be assessed by spiking known amounts of pure compounds onto the column. The compounds are spiked in a hexane solvent, and the cleanup and analysis sequences are performed as specified in the method. For the column performance evaluations presented here, only the aromatic fraction was analyzed. Table 3 summarizes the recovery of pure compounds spiked onto the column at an average mass of 500 micrometers g. A more extensive column performance evaluation was performed by another laboratory and the results are summarized in Table 4. For this study, each compound was spiked onto the column at a mass of 200 micrometers g. Recoveries in both studies were determined by single ion quantification compared to a calibration standard.

In the first study, recoveries of PNAs spiked at 500 micrometers g each were within the range of 90 to 110 percent. In the second study, the recoveries for the constituents spiked at 200 micrometers g were more variable. High molecular weight PNAs were recovered well, as they were in the previous study. Lower molecular weight hydrocarbon aromatics were inadequately recovered. The reasons for the low recoveries are unclear, since in other evaluations these compounds have shown good recoveries. This performance evaluation has not been repeated. It is possible that there is a matrix effect from the relatively high percentage of polar compounds in the spike or that some other effect is being seen. When this group of constituents was spiked into an oily waste sample containing high concentrations of aliphatics, recoveries for these low molecular weight compounds were significantly higher, and were within the ranges specified in SW-846, (discussed in the following subsection). For other sample constituents, including oxygenated compounds, amines, and nitroaromatics, the results were variable. The phenyl ethers and dibenzofuran are of intermediate polarity and showed good recoveries. Recovery of the most polar constituents was not reproduced, and did not meet the criteria specified in SW-846. The phthalic acid esters were recovered in amounts that indicate their appearance could be a result of contamination rather than recovery of the spike. Amines and nitroaromatics were not recovered. The phthalates, nitroaromatics,

and amines are expected to be eluted as part of the polar fraction. This fraction was not analyzed because it presents analytical problems that have not yet been resolved by Radian.

METHOD PERFORMANCE FOR OILY WASTE SAMPLES

Spiking pure compounds onto a column is an ideal situation; real samples can present a more complex analytical challenge. To determine the effect of the sample matrix, document laboratory repeatability, and demonstrate recoveries for target constituents, a methods study was performed. In the first phase of the study, aliquots of the sample were spiked with only the surrogates. The extraction-cleanup-analysis sequence (Methods 3540-3530-3570-8270) was performed on each aliquot, and the mean constituent concentrations are determined. In the second phase of the methods study, each target constituent was spiked into aliquots of the sample and the extraction-cleanup-analysis sequence repeated. Table 5 presents the results of the methods study (aromatic fraction) for constituents of interest spiked into an API Separator Sludge. Each constituent was spiked at a concentration of 200 micrometers g in a 1 gram aliquot. This spiking was performed preceding all sample extractions, and four aliquots of the unspiked sample and four aliquots of the spiked sample were analyzed. Mean constituent concentrations and standard deviations for each of the eight aliquots are presented in the table along with the mean percent recovery for each constituent.

The data show very good recoveries for the PNAs. Other constituents including the phthalates, amines, and nitroaromatics, are recovered poorly or not at all. These results are consistent with the results of the column performance check in Table 4. One interesting result of the methods study was that the low molecular weight aromatics were recovered better in this study than in the column performance evaluation. Additional work will be needed to investigate this apparent anomaly.

ANALYSIS OF POLAR FRACTION

Limited work has been performed on the polar fractions, data for target compounds are not available. There are two problems encountered with this fraction. First, the methanol solvent tends to promote degradation of the GC column used for analytical separation even when a bonded phase column is used. Second, it appears that in some cases methanol extracts material from the alumina, which in turn interferes with the GC/MS analysis.

SUMMARY

The column cleanup for oily wastes reduces interferences and lowers detection limits for constituents of concern in petroleum refining wastes. The method has been shown to perform well in combination with established SW-846 extraction and analysis methods. It is

particularly useful in reducing interferences from aliphatic hydrocarbons in the analysis of polynuclear aromatics (PNAs). Recoveries of PNAs subjected to the column cleanup are within the ranges established in SW-846, Method 8270, GC/MS Analysis of Semivolatile Organics. Other constituents have also been recovered within acceptable ranges. Highly polar constituents, believed to elute in the polar fraction, have not been extensively studied. Analytical problems with the evaluation of the polar fraction have limited study of recoveries for target constituents in this fraction.

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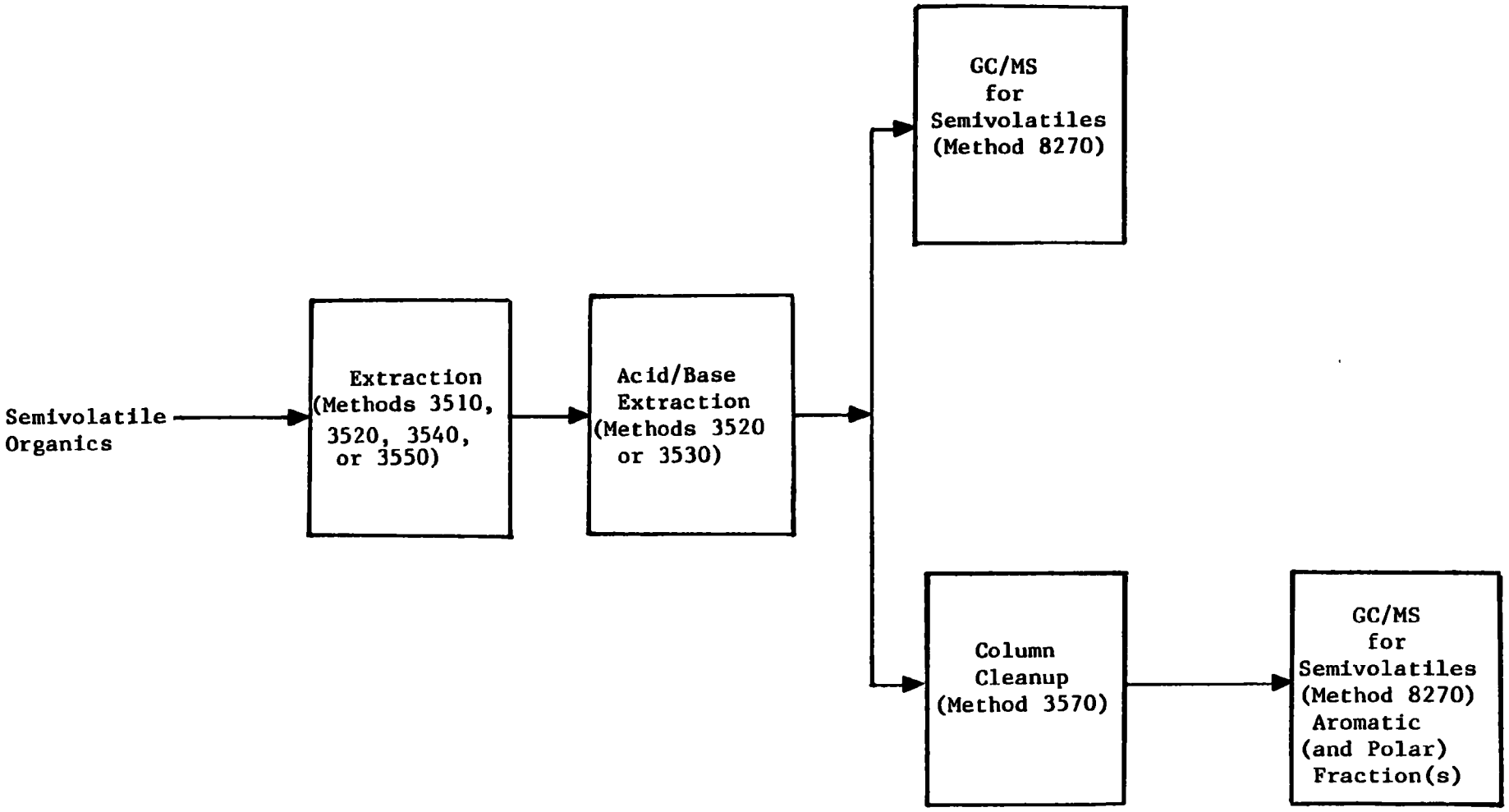

Figure 1

SCHEMATIC REPRESENTATION OF ANALYSES FOR SEMIVOLATILE ORGANIC CONSTITUENTS IN PETROLEUM REFINING SAMPLES

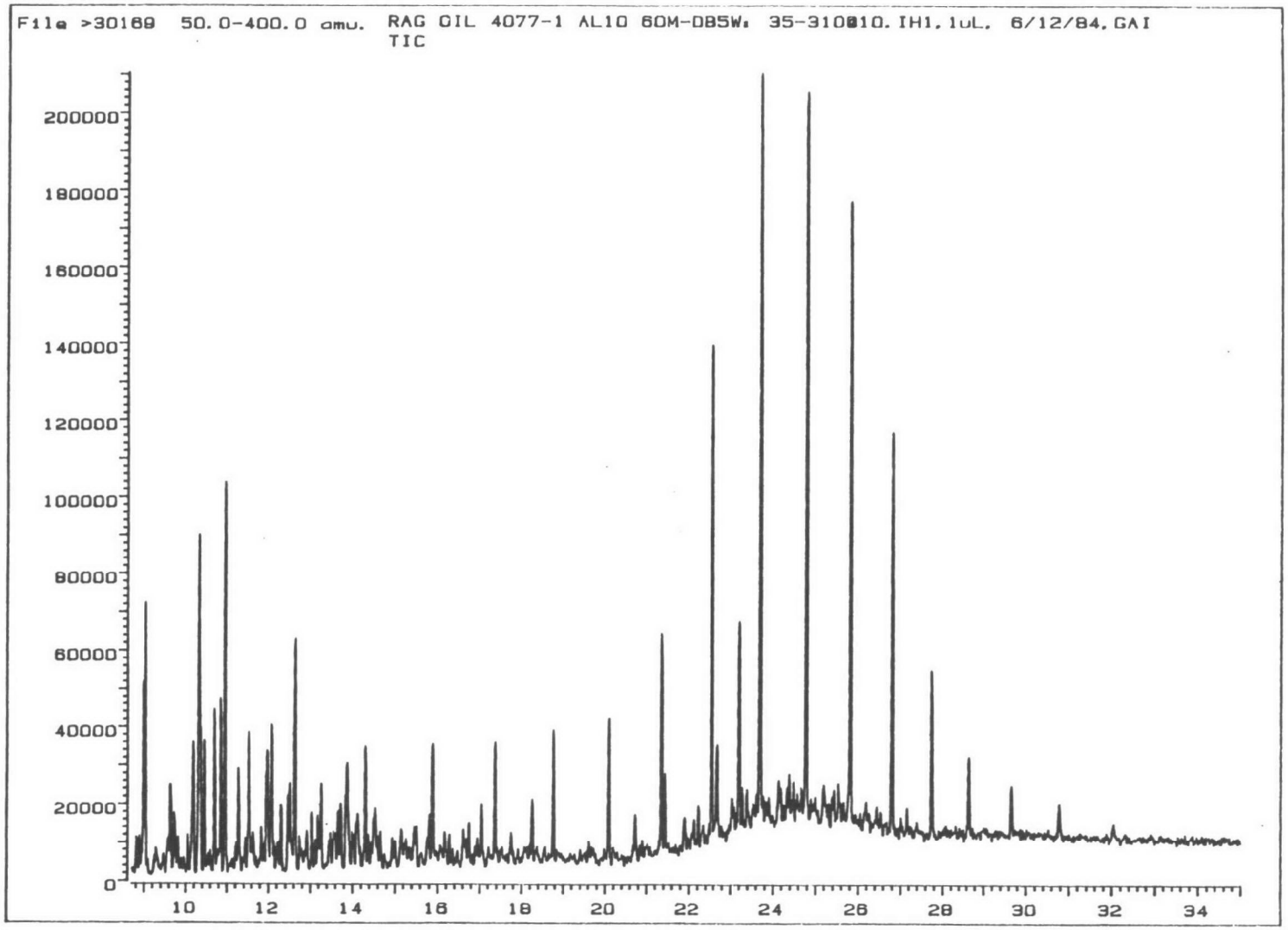

Figure 2

TYPICAL RECONSTRUCTED ION CHROMATOGRAM FOR THE ALIPHATIC FRACTION

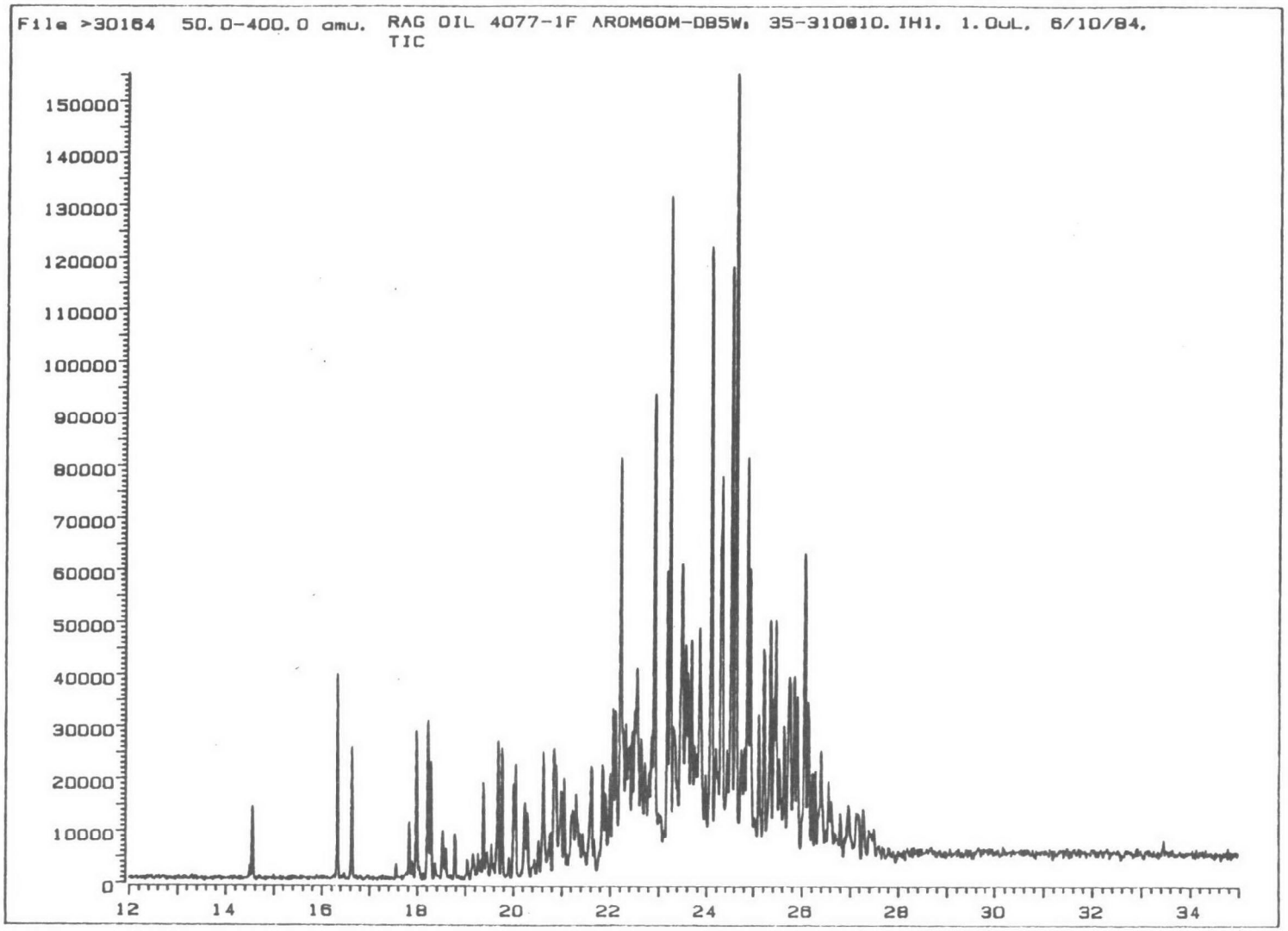

Figure 3

TYPICAL RECONSTRUCTED ION CHROMATOGRAM FOR THE AROMATIC FRACTION

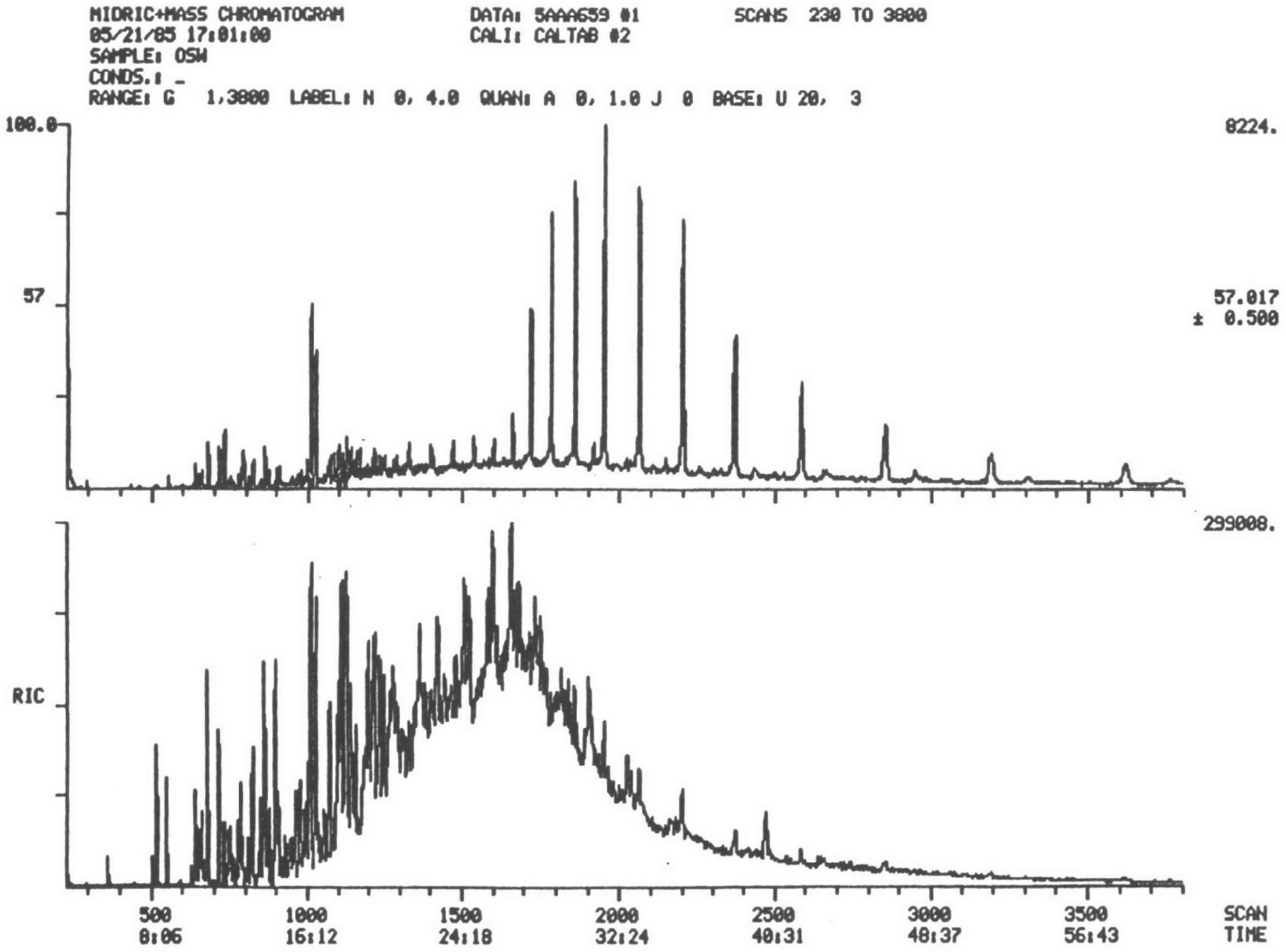

Figure 4

SINGLE ION CHROMATOGRAM SHOWING THE PRESENCE OF ALIPHATICS IN AN AROMATIC FRACTION

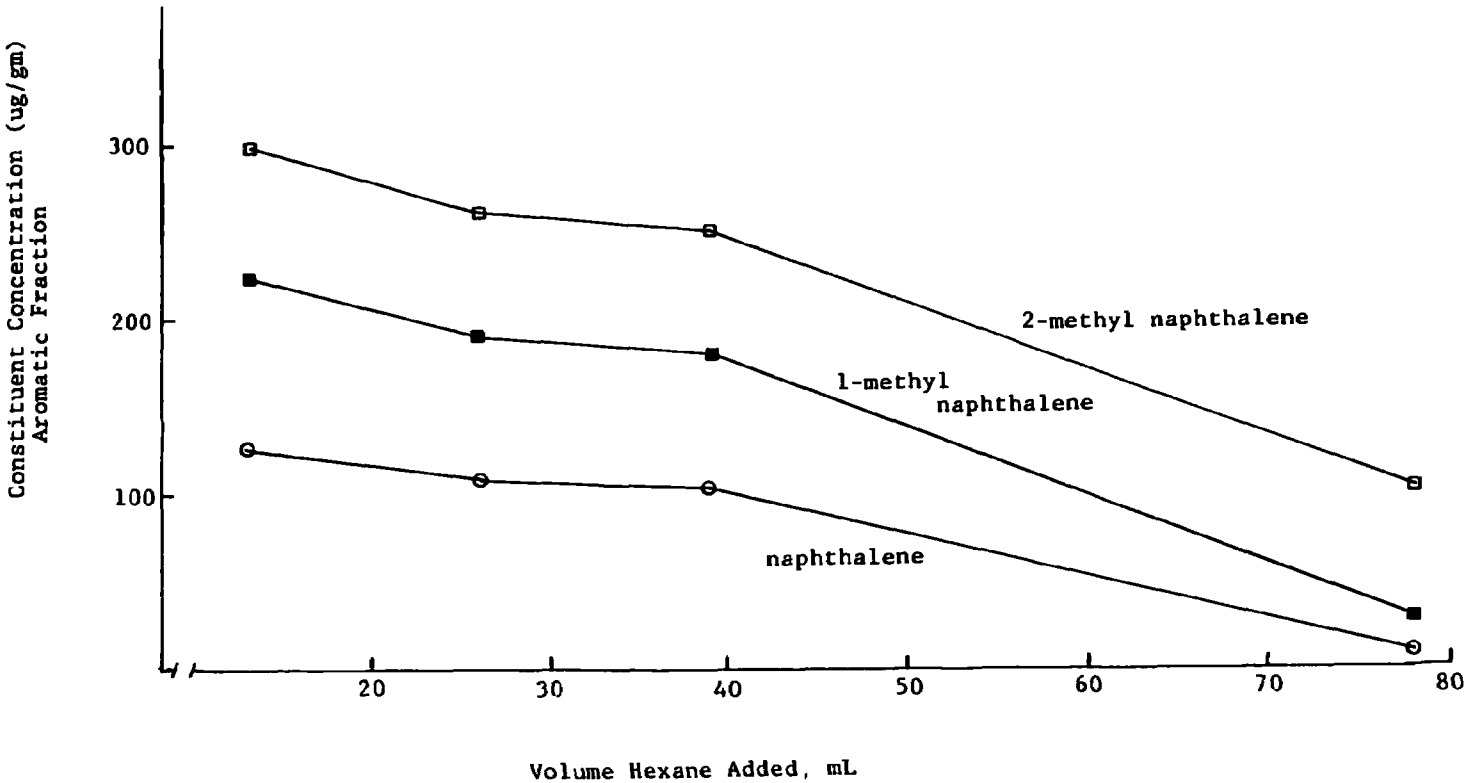

Figure 5

THE RELATIONSHIP BETWEEN HEXANE ELUTION IN THE ALIPHATIC FRACTION AND NAPHTHALENE CONCENTRATIONS IN THE AROMATIC FRACTION

Table 1

SEMIVOLATILE TARGET CONSTITUENTS ANALYZED IN THIS STUDY

Acid Extractables

Benzenethiol
p-Chloro-m-cresol
2-Chlorophenol
Cresols
2,4-Dimethyl phenol
4,6-Dinitro-o-cresol
2,4-Dinitrophenol
Nitrophenols
Pentachlorophenol
Phenol
Trichlorophenols

Base/Neutral Extractable

Aniline
Anthracene
Benz(c)acridine
Benz(a)anthracene
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Benzyl chloride
Bis(2-ethylhexyl) phthalate
Butylbenzyl phthalate
2-Chloronaphthalene
Chrysene
Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
7,12-Dimethylbenz(a)anthracene
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
Di-n-butyl phthalate
Dichlorobenzenes
Diethyl phthalate
Dimethyl phthalate
Dinitrotoluene
Di-n-octyl phthalate
Fluoranthene
Indene
Indeno(1,2,3-c,d)pyrene
Methylbenzo(c)phenanthrene
3-Methylcholanthene
Methylchrysene
1-Methylnaphthalene
Naphthalene
Naphthylamine
5-Nitroacenaphthene
p-Nitroaniline
Nitrobenzene
Phenanthrene
Pyrene
Quinoline
Styrene
Trichlorobenzenes
Trimethylbenz(a)anthracene

Table 2

CONCENTRATIONS OF TARGET CONSTITUENTS IN THE AROMATIC FRACTION WITH INCREASING AMOUNTS OF HEXANE TO ELUTE ALIPHATICS

Compound	A 13 mL Hexane	B 26 mL Hexane	C 39 mL Hexane	D 78 mL Hexane
indene	1.7 µg/g	1.2 µg/g	1.1 µg/g	NF
naphthalene	123.4	108.3	103.8	8.8 µg/g
2-methylnaphthalene	300.2	261.0	252.8	122.7
1-methylnaphthalene	224.6	192.4	181.8	27.0
acenaphthene	16.2	15.0	18.4	12.5
fluorene	32.6	23.0	27.0	34.9
phenanthrene	97.7	65.8	69.6	74.2
anthracene	5.8	5.3	5.9	5.2
di-n-butyl phthalate	0.4	0.5	0.3	0.3
fluoranthene	6.5	5.2	5.9	5.3
pyrene	31.5	27.9	27.3	33.7
chrysene	45.7	25.2	23.8	32.2
benzo(a)anthracene	53.7	39.6	43.2	54.2
bis(2-ethylhexyl) phthalate	1.4	5.5	1.2	2.7
benzo(b)fluoranthene	5.4	3.9	4.4	4.5
benzo(a)pyrene	7.9	6.3	7.8	8.7
dibenzo(a,h)anthracene	1.7	0.7	5.6	2.0
indeno(1,2,3-c,d)pyrene	0.9	1.6	4.5	4.6
dibenzofuran	3.2	5.0	5.3	10.4
benzo(k)fluoranthene	NF	NF	2.3	1.3
benzo(g,h,i)perylene	NF	NF	2.5	NF

Table 3

RECOVERY OF PNAs FOR METHOD 3570 COLUMN PERFORMANCE STUDY

Compound	Concentration, ug		% Recovered
	Spiked	Recovered	
Naphthalene	560	580	104
Acenaphthylene	630	600	95
Acenaphthene	540	490	91
Fluorene	500	520	104
Phenanthrene	540	550	102
Anthracene	570	550	96
Fluoranthene	560	600	107
Pyrene	530	590	111
Benz(a)anthracene	480	490	102
Chrysene	260	280	108
Benzo(b)fluoranthene	440	480	109
Benzo(k)fluoranthene	450	430	95
Benzo(a)pyrene	650	670	103
Dibenzo(a,h)anthracene	460	450	98
Indeno(1,2,3-c,d)pyrene	450	450	100
Benzo(g,h,i)perylene	390	380	97

Table 4

RECOVERY OF TARGET CONSTITUENTS FOR METHOD 3570
COLUMN PERFORMANCE STUDY

Compounds Observed in Standard	Blank ng/µL	Test #1 % Recovery	Test #2 % Recovery	Relative % Difference[a]
N-nitrosodimethylamine		NR	NR	--
Styrene		2	2	0
aniline		NR	NR	--
bis(2-chloroethyl)ether		NR	NR	--
m-dichlorobenzene		3	2	10.0
p-dichlorobenzene		3	4	7.1
benzyl chloride		NR	NR	--
benzyl alcohol		NR	NR	--
o-dichlorobenzene		6	5	4.5
indene		7	6	3.8
bis(2-chloroisopropyl) ether		NR	NR	--
N-nitrosodipropylamine		NR	NR	--
hexachloroethane		NR	NR	--
nitrobenzene		NR	NR	--
isophorone		NR	NR	--
bis(2-chloroethoxy) methane		NR	NR	--
1,2,4-trichlorobenzene		3	3	0
naphthalene	36.5	34	24	8.6
4-chloroaniline		NR	NR	--
hexachlorobutadiene		NR	NR	--
2-methylnaphthalene		29	21	8.0
hexachlorocyclopenta-diene		NR	NR	--
2-chloronaphthalene		35	26	7.4
3-nitroaniline		NR	NR	--
dimethyl phthalate		NR	NR	--
2,6-dinitrotoluene		NR	NR	--
acenaphthylene		26	18	9.1
4-nitroaniline		NR	NR	--
acenaphthene		31	22	8.5
dibenzofuran		80	67	4.4
2,4-dinitrotoluene		NR	NR	--
diethyl phthalate	0.4	NR	NR	--
fluorene		63	56	2.9
4-chlorophenyl phenyl ether		63	64	0.4
azobenzene		87	65	7.2
4-bromophenyl phenyl ether		101	78	6.4
hexachlorobenzene		10	9	2.6
phenanthrene	0.2	76	70	2.1
anthracene		92	73	5.8

Table 4 (Continued)

RECOVERY OF TARGET CONSTITUENTS FOR METHOD 3570
COLUMN PERFORMANCE STUDY

Compounds Observed in Standard	Blank ng/µL	Test #1 % Recovery	Test #2 % Recovery	Relative % Difference[a]
di-n-butyl phthalate	0.4	Trace	Trace	--
fluoranthene		104	80	6.5
pyrene	0.3	90	74	4.9
butyl benzyl phthalate		NR	NR	--
chrysene	0.3	104	71	9.4
benzo(a)anthracene	0.5	100	73	7.8
bis(2-ethylhexyl) phthalate	1.2	1	1	0
di-n-octyl phthalate		NR	NR	--
benzo(b)fluoranthene		84	52	11.8
benzo(k)fluoranthene		91	64	8.7
benzo(a)pyrene		73	59	5.3
benzo(g,h,i)perylene		69	61	3.1
dibenzo(a,h)anthracene		82	60	7.7
indeno(1,2,3-cd)pyrene		93	56	12.4
2-nitroaniline		NR	NR	--
naphthylamine		NR	NR	--

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[a] $\frac{[a - b]}{2(a+b)} \cdot 100$

NR = Not recovered.

Table 5

RECOVERY OF TARGET CONSTITUENTS SPIKED IN AN API SEPARATOR SLUDGE

	Concentration (ug/gm)				Average Percent Recovery
	Unspiked Sample		Spiked Sample[c]		
	$\bar{X}$[a]	SD[b]	$\bar{X}$[a]	SD[b]	
Styrene	--	--	54.6	19.6	27.3
m-Dichlorobenzene	--	--	123.2	14.5	61.6
p-Dichlorobenzene	--	--	124.0	16.6	62.0
o-Dichlorobenzene	--	--	122.3	14.7	61.2
Indene	1.7	0.3	67.0	25.3	32.6
Hexachloroethane	--	--	19.6	18.0	9.8
1,2,4-Trichlorobenzene	--	--	167.8	43.2	83.9
Naphthalene	62.4	13.8	163.4	29.2	50.5
Hexachlorobutadiene	--	--	7.9	10.0	3.9
2-Methylnaphthalene	110.6	22.6	223.9	44.2	61.6
2-Chloronaphthalene	--	--	194.4	29.0	97.2
Acenaphthylene	--	--	134.5	26.8	67.2
Acenaphthene	6.5	1.6	162.2	25.6	77.8
Dibenzofuran	2.8	0.8	189.4	45.1	93.2
Diethyl phthalate	0.3	0.2	0.3	0.1	0
Fluorene	17.7	4.2	189.1	36.8	85.4
4-Chlorophenyl phenyl ether	--	--	163.6	27.5	81.8
Azobenzene	--	--	176.3	28.0	88.2
4-Bromophenyl phenyl ether	--	--	170.0	18.3	85.0
Hexachlorobenzene	--	--	188.6	35.0	94.3
Phenanthrene	31.9	9.1	226.7	62.7	96.9
Anthracene	3.4	1.3	120.6	13.2	58.6
Di-n-butyl phthalate	0.5	0.2	0.5	0.1	0
Fluoranthene	1.2	1.0	149.2	37.7	73.6
Pyrene	6.9	1.9	129.5	21.1	61.2
Chrysene	4.1	0.9	187.8	35.5	91.8
Benzo(a)anthracene	9.0	2.0	176.2	29.7	83.4
Bis(2-ethylhexyl) phthalate	3.0	1.6	7.0	9.0	2.0
Benzo(b)fluoranthene	1.2	0.2	133.9	23.9	66.4
Benzo(k)fluoranthene	0.5	0.2	140.6	23.8	70.0
Benzo(a)pyrene	1.4	0.2	138.7	17.7	68.7
Benzo(g,h,i)perylene	--	--	131.1	27.2	65.7
Dibenzo(a,h)anthracene	--	--	155.0	34.4	77.5
Indeno(1,2,3-c,d) pyrene	--	--	155.0	25.8	77.5
Bis(2-chloroisopropyl) ether	--	--	0.8	1.7	0.4
Di-n-octyl phthalate	0.1	0.3	0.4	0.8	0.2
Butyl benzyl phthalate	0.4	0.8	NR	NR	0

Table 5 (Continued)

RECOVERY OF TARGET CONSTITUENTS SPIKED IN AN API SEPARATOR SLUDGE

	Percent Recovery			
	Unspiked Sample		Spiked Sample[c]	
	$\bar{X}$[a]	SD[b]	$\bar{X}$[a]	SD[b]
Naphthalene-d_8	52.5	10.5	56	11.8
2-Fluorobiphenyl	68.8	16.7	131	34.5
Nitrobenzene-d_5	23.2	27.2	NR	NR
Terphenyl-d_{14}	66.2	17.8	69	18
Pyrene-d_{10}	59.0	13.1	59	12.6

[a]Average of four analyses.

[b]SD = Standard Deviation
NR = Not Recovered

[c]Compounds spiked but not recovered:

Naphthylamine
Benzyl alcohol
Benzyl chloride
N-Nitrosodimethylamine
Aniline
Bis(2-chloroethyl) ether
N-Nitrosodipropylamine
Nitrobenzene
Isophorone
Bis(2-chloroethoxy)methane
4-Chloroaniline
3-Nitroaniline
Dimethyl phthalate
2,6-Dinitrotoluene
4-Nitroaniline
2,4-Dinitrotoluene
N-Nitrosodiphenylamine

QUANTITATIVE ANALYTICAL SCREEN FOR THE DETERMINATION OF THE APPENDIX VIII HAZARDOUS CONSTITUENTS

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ABSTRACT

On October 1, 1984, the Environmental Protection Agency proposed new Subtitle C testing requirements under RCRA. As part of these testing requirements many companies will be required to analyze groundwater and waste samples for the 375 Hazardous Constituents listed in Appendix VIII of 40 CFR Part 26 using methods in SW-846, "Text Methods for Evaluating Solid Wastes."

Due to a number of complex issues both in the proposed rule and in SW-846, RMAL prepared a report entitled "Evaluation of the Aplicability of the SW-846 Manual to Support All RCRA Subtitle C Testing." As part of this effort, RMAL identified, developed, and proposed an analytical strategy to determine effectively Appendix VIII consituents using the methods in SW 846.

This analytical strategy, designated as a Quantitative Analytical Screen (QAS), utilized 17 different methods based on ICP, AA, GC, AA, GC/MS and HPLC technology. The methods, consituents measured by each method and the general approach of the OAS will be discussed.

METHODOLOGY FOR THE ANALYSIS OF ORGANIC CHEMICALS IN PETROLEUM REFINING WASTES TO SUPPORT RCRA WASTE LISTING AND DELISTING AND LAND TREATMENT DEMONSTRATION PROGRAMS

DR. MARK J. CARTER, DR. MICHAEL P. PHILLIPS, AND JERRY L. PARR, ROCKY MOUNTAIN ANALYTICAL LABORATORY, ARVADA, COLORADO

ABSTRACT

In April, 1983, EPA initiated a study to re-evaluate the basis for listing the five regulated petroleum refining wastes. Subsequently, the American Petroleum Institute retained Rocky Mountain Analytical Laboratory (RMAL) to track this study. The scope of the study included the analysis of a subset of approximately 90 organic constituents drawn from the Appendix VIII list. From october 1983 to October 1984, EPA prepared three methods manuals, and in July, 1985 a guidance document concerning methods for analysis of petroleum refinery wastes was prepared.

The analysis of the volatile and semivolatile organics is based on SW-846 methods 8240 and 8270 with separation and clean-up steps to mitigate the interference from the aliphatic hydrocarbons. This paper will present the results of a study performed by RMAL of the recovery and detection limits of the "Skinner" organics in petroleum refinery wastes.

The EPA has recently released preliminary detection limit requirements for waste delisting. These limits are below the routine capability of some of the methods developed for the EPA waste listing study. Modifications of the methods necessary to obtain the lower detection limits will be reported.

DEVELOPMENT OF GROUNDWATER SCREENING PROCEDURES FOR USE IN MONITORING PROGRAMS: OBJECTIVES AND EXPERIMENT PROGRESS AT BATTELLE COLUMBUS LABORATORIES

S. V. LUCAS, BATTELLE COLUMBUS LABORATORIES, COLUMBUS, OHIO

ABSTRACT

Two of the Heirarchical Analysis Protocol (HAP) methods of SW-846 are currently the subject of laboratory efforts to establish their efficacy: Method 8610, "Total Aromatics by Ultraviolet Absorption," and Method 3560, "Reverse Phase Cartridge Extraction." A data base of physical and UV/visable spectroscopic properties has been established using a personal computer. For the 90 polar compounds in Method 8610, literature spectroscopic data were available for all but 10 compounds, and two or more sources of data were found for 70 of these compounds as well as for all 39 of the nonpolar analytes of the method. Using a Cary 17D spectrophotometer, it was found that the target detection threshold of 0.005 au was well within that instrument's capabilities of signal-to-noise ratio and spectrum reproducibility.

Evaluation of Method 3560 resulted in important modifications to the cartridge cleanup and elution procedures. Using reagen water and commercially available cartridges, a confident detection threshold of 0.02 au was estimated, and quantitative recovery of selected Method 8610 compounds at levels ranging from 15 to 3000 ug/L was obtained. When groundwater from actual site monitoring wells was used, the recovery of spiked compounds was apparently quantitative, but a substantial variability in the recovery of UV absorbing material in the groundwater itself prevented accurate quantification of spike recoveries. The groundwater matrix interference problem seemed to be associated with the presence of mineral particulate in these samples.

Work presently in progress is directed toward solving the Method 3560 problem of variability of recovery of UV absorbing material for groundwaters, and the status, to date, of this on-going work as well as the above described completed work will be presented.

This work is being conducted by Battelle Columbus Laboratories for the U.S. EPA Environmental Monitoring Support Laboratory (EMSL), Cincinnati, Ohio, under Contract 68-03-1760, Work Assignment 10. Dr. Fred K. Kawahara is the EPA Project Officer, and Mr. James E. Longbottom is the EPA Program Manager..

FOURTH SESSION

SAMPLING UNDER RCRA

1:00 pm - 4:30 pm

Thursday, July 25, 1985

Chairperson: Martin Meyers
Methods Program
Office of Solid Waste
U. S. Environmental
Protection Agency
Washington, D. C.

VOLATILE ORGANIC SAMPLING TRAINS FOR HAZARDOUS WASTE INCINERATORS: LABORATORTY VALIDATION

THOMAS J. LOGAN, ROBERT G. FUERST, AND M. RODNEY MIDGETT, U. S. ENVIRONMENTAL PROTECTION AGENCY, RESEARCH TRIANGLE PARK, NORTH CAROLINA; AND JOHN PROHASKA, PEI ASSOCIATES, INC., CINCINNAIT, OHIO

ABSTRACT

The measurement of volatile organic emissions from a hazardous waste incinerator is one of the more difficult source testing problems. Specific compounds called principal organic hazardous constituents (POHC) are to be identified and quantified at levels of 0.5 to 100 ppb in hot, wet incinerator exhaust gas, which may also contain high particulate and acid levels. The protocol, which describes the practices used by laboratories making these measurements, allows for several alternative designs and operating procedures. This paper describes an experimental program to evaluate under controlled conditions in the laboratory as many of the acceptable practices as possible. It describes the results of sampling at various concentration levels using two tube configurations, two moisture levels and other procedural variations. These results have led to conclusions about the specific VOST procedures to be followed during the field validation studies.

INTRODUCTION

The Code of Federal Regulation, Title 40, Part 264, requires that a destruction and removal efficiency (DRE) of 99.99 percent be achieved for each principal organic hazardous constituent (POHC) designated in the Trial Burn Permit (1). The calculation of DRE requires sampling and analysis to quantify POHCs in the waste feed material and stack gas effluent. The "Sampling and Analysis Methods for Hazardous Waste Combustion" manual provides information on methods that are applicable for collection and analyses of POHCs in process streams of hazardous waste incinerator units (2). The "Protocol for the Collection and Analysis of Volatile POHCs using VOST" (VOST Protocol) describes the Volatile Organic Sampling Train (VOST) used to measure POHCs in the stack gas effluent (3).

The purpose of this paper is to describe a laboratory study conducted by EPA to evaluate the VOST Protocol. This work was undertaken prior to the field validation to be sure that the best set of procedures would be validated in the field effort. The project was done under contract by PEI Associates in Cincinnati, Ohio, who developed the specific equipment and procedures for the laboratory study. The work was supported by the Quality Assurance Division (QAD), Environmental Monitoring Systems Laboratory, Research Triangle Park, NC

EXPERIMENTAL

Six volatile organic compounds were selected for use in the VOST laboratory evaluation. These compounds are listed in Table I. This table shows the compounds' boiling points and incinerability. Two of these compounds, carbon tetrachloride and chloroform, were included because of their expected frequent designation as principal organic hazardous constituents (POHC) in hazardous waste incinerator trial burns. Benzene was included because of the effect its historically high background levels has had on Tenax, which is the primary sample collection medium of the VOST. Tetrachloroethylene or perchloroethylene (commonly referred to as "perc") was included in the study to test recovery of a compound with a boiling point (121 C) near the high range of the protocol (approximately 100 C). Trichlorofluoromethane (TCFM) was selected because its low boiling point (24 C) challenged the recovery of the VOST. The final compound studied in this investigation was vinyl chloride (VC). VC was included even though its boiling point (-12 C) made it unlikely to be quantitatively recovered by the VOST. Except for TCFM, mixtures of these compounds at the ppb level were readily available as Group 1 gases through the QAD gas cylinder audit development program. The QAD's Group 1 gases were developed and certified by the National Bureau of Standards (NBS) and, therefore, concentrations of these mixtures could be traced to NBS for use in determining VOST recovery. A separate cylinder containing only TCFM and nitrogen was obtained, and the concentration of this cylinder was similarly traced to an NBS standard.

Test gas atmospheres for the laboratory study were generated by mixing gases from a cylinder of the five Group 1 gases (approximately 75 ppb each component, balance nitrogen), a cylinder of approximately 75 ppb TCFM in nitrogen, and a cylinder of ultra-pure zero air. At the conclusion of the project, the cylinders containing these compounds were analyzed independently by Research Triangle Institute (RTI), to verify labeled cylinder values and the stability of the low-level gases over the duration of the project. No values differed by more than 10 percent. The dilution system used to mix the gases was checked for leaks, levels of contamination and stability of operation and found to be acceptable before any test samples were collected.

The dilution system and cylinder gases were used to generate test gas concentrations of approximately 15 and 0.5 ppb. These two concentrations were considered to be within the range of normal hazardous waste incinerator POHC concentrations.

A quad (four-train) VOST was used to collect four samples simultaneously from a manifold purged with test gas of known levels of target compounds. Figure 1 shows a schematic of the quad VOST equipment in the laboratory evaluation. Figure 2 shows a more detailed description of a single VOST. Two types of VOST sample collection tubes are specified in the VOST Protocol. Figure 3 shows the two tube configurations in detail. The term "ST" is used in this report to designate the suspended tube design, which has numerous other names since it is the tube conventionally used in ambient air sampling with Tenax. The other design is designated "ND" for

neck-down tube. The VOST Protocol defines the ND the inside/inside tube configuration and the ST as the inside/outside tube configuration. Since one of the goals was to determine which design to use in field work, the quad VOST experiments were conducted with two ST-type trains and two ND-type trains.

All sampling activities were conducted in a mobile laboratory separate from the analysis and sorbent preparation areas.

The sorbent traps were all prepared from one lot of Tenax and one lot of charcoal and were prepared and conditioned as specified in the protocol. Preparation and conditioning of the traps were performed in a separate area of the laboratory in which no solvents are handled or stored. The exact handling of each trap during preparation and conditioning activities was documented in a log book.

Each pair of traps was blank-checked as a unit following conditioning and prior to use. The blanking procedure consisted of thermally desorbing the traps, concentrating the blank sample cryogenically, flash-vaporizing the concentrated sample, and analyzing the sample by gas chromatography/flame ionization detection (GC/FID). Because the GC/FID procedure gave only a general indication of blank levels, 1 of each 10 trap pairs was analyzed as a sample by gas chromatography/mass spectrometry (GC/MS) instead of GC/FID to determine actual blank levels of all the target compounds. Except for benzene, the blank levels for all other compounds were less than 10 nanograms per pair of traps.

All sorbent traps were analyzed in the same manner and in accordance with the protocol. Each sampled trap was spiked with an internal standard, thermally desorbed with organic-free helium gas bubbled through organic-free water and collected on an analytical sorbent trap. After the sample desorption steps, the analytical sorbent trap was rapidly heated and the carrier gas flow was reversed so that the effluent flow from the analytical trap was directed into the GC/MS. The volatile organics were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The mass of volatile compounds was calculated by the internal standard technique.

Unless specifically designated otherwise, all samples were analyzed within one week of collection.

The front (Tenax) and back (Tenax/charcoal) sorbent traps were analyzed separately for each sample run to determine in which portion of the train the target compounds were actually collected and to assess the potential for breakthrough.

RESULTS

In the course of performing the laboratory evaluation, several parameters were studied (sorbent tube design, moisture level in the sample gas and sample holding time).

The effects of tube design and moisture level varied from one component to the next and have been evaluated on a component basis. The following discussion describes the individual component data presented in Table II, which was summarized from eight quad VOST runs.

The sample means are simple averages of paired run data; standard deviations are pooled from paired run data. The percent relative standard deviation (RSD) values represent the pooled standard deviations expressed as a percent of the means. The percent expected value (EV) is the mean measured concentration expressed as a percent of the concentration of the target compound in the sampled gas stream. The statistical significance of the difference between the paired measurement results for each type of sampling train was determined by analysis of variance (ANOVA) for the dry test runs. The statistical significance of any difference between train types for the wet runs was determined by use of the t-test. Differences between train-types were determined to be statistically significant; if the respective test indicated there was less than a 10 percent probability the difference was due to chance.

VINYL CHLORIDE

An examination of the data at each test condition indicated that the ST sampling trains were ineffective in all cases. The maximum amount of vinyl chloride (VC) recovered by use of the ST train was 60 percent of the expected value for one of the wet runs at 15 ppb. Only the ND results at the 15 ppb dry test conditions were considered reasonable, with an average recovery of 91 percent EV. Unfortunately, subsequent experiments could not reproduce the 91 percent EV for VC. The presence of approximately 30 percent moisture in the test gas had a different effect on the two types of trains. The apparent effect on the ST results was to improve the average recovery. The effect of moisture was definitely detrimental to the ND train results at 15 ppb in that the average recovery was decreased from 91 to 48 percent EV.

RSD values were used as estimates of precision. The best and worst RSD values were for the ST trains at dry test gas conditions. These values, however, were considered nonrepresentative because of very low recoveries. Pooled precision values for the ND train type ranged from 7 to 10 percent RSD at 15 ppb.

TRICHLOROFLUOROMETHANE

The statistical tests showed a significant difference between the results determined with the two types of sampling trains for the high concentration of test gas (i.e., 15 ppb) for both wet and dry test gas conditions. In both cases the highest concentration of TCFM was reported for the ND sampling train. At the 0.5 ppb level, the results reported for the two types of sampling trains agreed quite well.

Examination of the TCFM data indicated that the presence of moisture

in the test gas affected only the ST trains at the 15 ppb level. The average recovery by the ST trains was 56 percent EV for the dry test runs versus 39 percent EV for the wet runs at 15 ppb. Conversely, the average recovery by the ND trains was approximately 75 percent EV for both wet and dry runs at 15 ppb.

The precision of the pooled data in each of the four test conditions ranged from 6 to 14 percent RSD for the ND trains. Precision of the pooled ST data was much more variable, ranging from 40-60% RSD.

CHLOROFORM

The statistical analyses indicate that the difference between the measurements made by the two types of sampling trains was significant only for the 15 ppb wet gas. For this test condition, the average concentration measured by the ND trains was 73.34 ng/liter compared with 65.31 ng/liter for the ST trains, for a difference of approximately 11 to 12 percent between the types of trains. Although the statistical comparison indicated the probability that this difference was due to chance was less than 5 percent, a difference of 12 percent does not seem significant when compared to overall results including other compounds.

An examination of the data sets indicated the presence of moisture in the test gas did not affect results obtained by the use of either type of train.

Precision of the pooled data sets at each condition for the ND trains varied between 4 and 23 percent RSD. Precision of the pooled data sets at each test condition for the ST trains varied between 3 and 15 percent RSD.

CARBON TETRACHLORIDE

The statistical analyses indicated that the results reported for the ND trains were significantly higher than those reported for the ST trains at all of the nominal test conditions except the 15 ppb dry gas.

An examination of the data sets indicated that the presence of approximately 30 percent moisture by volume in the test gas had no effect on the performance of the ND trains but definitely had an adverse effect on the recovery of the ST trains. The average recovery for the ST trains at 0.5 ppb was 71 percent EV dry test condition compared with 51 percent EV wet test condition, and at the 15 ppb test condition recoveries were 78 and 56 percent EV at dry and wet test conditions, respectively. By comparison, the average recoveries of the ND trains ranged from 85 to 92 percent EV for all test conditions.

Precision of the pooled data sets at each test condition for the ND trains ranged from 1 to 28 percent, RSD.

BENZENE

The statistical analyses determined that the difference between the results reported for the two types of sampling trains was not statistically significant at any of the four nominal test conditions.

An examination of the data at each test condition indicated that the presence of moisture in the test gas may have had some effect on the results measured by each type of train, but the differences between the dry and wet data were similar to the differences between train-types (which were determined not to be significant).

The very high recovery values obtained by both types of trains at the 0.5 ppb test conditions may be related to inherent benzene contamination, either because of inconsistent pretest conditioning effects or sorbent degradation after the conditioning procedure. The overall average recovery at 0.5 ppb conditions was approximately 150 percent EV. Average recoveries at the 15 ppb test conditions were not as high as those for the 0.5 ppb test gas and ranged from 100 to 116 percent EV.

The precision of the test results was also worse for the low-level tests than for the high-level tests. At 0.5 ppb, the precision of the pooled data sets varied between 2 and 44 percent RSD. For the tests conducted at 15 ppb, the pooled precision varied between 2 and 27 percent RSD.

TETRACHLOROETHYLENE

The statistical tests showed that there was no significant difference between the tetrachloroethylene (perc) concentrations reported for the two types of sampling trains.

An examination of the data at each condition indicated the presence of moisture in the test gas did not affect the ability of either type of sampling train to measure concentrations of perc. The average recovery values were higher at the 15 ppb test conditions than at the 0.5 ppb test conditions, ranging from 108 to 133 percent EV and from 100 to 109 percent EV, respectively.

Precision values ranged from 1 to 46 percent RSD for the pooled data sets at 0.5 ppb and from 3 to 25 percent RSD for the pooled data sets at 15 ppb.

EFFECT OF SAMPLE HOLDING TIME

All samples for quad Runs Q1, Q2, and Q3 were analyzed in the laboratory within less than one week after sample collection. Samples from quad Run Q4 were analyzed two weeks after sample collection and those from quad Run Q5 were analyzed five weeks after collection. All of these samples were collected during the same week of sampling and

at the same nominal test conditions, 15 ppb concentration of target compounds in a dry gas stream. The measured concentration data were analyzed statistically by ANOVA to determine if the difference between results obtained at the three sample holding times was significant. For example, the average concentration of VC for Run Q5 (5-week holding time) was compared with the average concentration of VC for Run Q4 (2-week holding time) and for Runs Q1, Q2, and Q3 (holding time less than 1 week). If the difference between the concentration was significant, the effect of holding time was significant. A summary of the results of the analysis of the effect of holding time is presented in Table III.

As can be seen from Table III, there was an overall tendency toward a decrease in the reported concentration of each target compound as the time between sample collection and sample analysis was increased. The value obtained for any compound on either type of trap, except VC on ST traps, was the highest when analysis was completed within 1 week. This apparent effect of sample holding time was statistically significant for vinyl chloride and trichlorofluoromethane, the two lowest-boiling compounds studied.

For TCFM, a decrease in concentration of approximately 25 percent within two weeks of collection for the ND trains indicates that samples should be analyzed as soon as possible after collection. Again, the ST trains were not very effective because of low recovery (-56% EV as shown in Table II). The similarity between results at the 2- and 5-week holding times seems to indicate that any significant loss of TCFM occurs within the first two weeks.

It should be noted that these results are for high-level (-15 ppb), dry samples, which may be "ideal" samples. The effect of sample holding time will also be investigated for actual field samples.

CONCLUSIONS

The laboratory evaluation indicates that the precision and accuracy of the VOST protocol depends on the target compound and on the type of sorbent trap used. In some cases, the precision and accuracy may also be affected by the moisture content of the sample stream and the amount of compound collected on the sorbent trap. The amount collected is a function of the concentration in the sample stream, the sampling rate, the sample volume, and the sampling time.

The most obvious conclusion of the laboratory tests is that neither the ND- nor ST-type of sorbent trap designs produced acceptable results for vinyl chloride.

The precision and accuracy for the ND and the ST types of sorbent traps varied for each compound and must, therefore, be described individually. For example, of the three compounds--chloroform, carbon tetrachloride and tetrachloroethylene--only carbon tetrachloride showed differences in precision and accuracy between the ND and ST traps. For carbon tetrachloride, the ST traps also showed differences

between wet and dry conditions. The ND traps showed no differences between wet and dry conditions.

Benzene results must be considered separately because of the inherent problem of benzene presence in the Tenax sorbent. At concentrations of 15 or 0.5 ppb, no distinguishable effect was observed for trap type or moisture condition, but the amount collected had a definite effect. Average benzene recoveries were 108 and 155 percent, with corresponding precision estimates of 16 and 35 percent, for collections of approximately 1,000 and 50 ng, respectively. Precision and accuracy results for benzene were not comparable to those for the other compounds when less than approximately 50 ng were collected in the sample.

The ND data for trichlorofluoromethane and carbon tetrachloride and all the data for chloroform and tetrachloroethylene indicate that average recoveries for the four compounds ranged from 75 to 121 percent. Precision (expressed as the pooled RSD of the replicate pairs) varied between 8 and 23 percent at the two different concentrations under both wet and dry conditions when approximately 50 ng or more of each compound was collected.

With the possible exception of benzene, the estimates of accuracy obtained during this laboratory study (75 to 121 percent) were better than that given in the VOST Protocol (50 to 150 percent). The precision estimates (23 percent or better) are considered good. Because these estimates were obtained on a clean air matrix, they cannot be considered typical of actual test site precision and accuracy.

In general, the results indicate that the ND traps were superior to the ST traps. The ND traps are less complicated in design and handling and have a positive forced flow during desorption. Therefore, their performance should be as good as or superior to that of the ST traps for other, untested, compounds.

A trend toward lower recoveries with prolonged holding times was observed for all compounds included in this study. Excluding vinyl chloride, the only compound for which the lower recovery could be considered significant was trichlorofluoromethane, which showed approximately a 30 percent decrease on both types of traps when samples were analyzed 2 weeks after collection. Again, these results were obtained on a matrix of clean, dry air; the effect of holding time may increase under actual field conditions.

RECOMMENDATIONS

The recommended changes to the VOST Protocol have been described in detail in the PEI Laboratory Report on the VOST. Recommendations for minor modifications to the VOST Protocol were made in the following areas:

- Calibration procedure for the dry gas meter.

- Field blank handling.
- Substitution of methanol instead of pentane for extraction of glass wool.
- Elimination of methanol extraction of charcoal.
- Prescreening of charcoal prior to its use in traps.
- Prescreening of each lot of Tenax.
- Predrying of Tenax before it is placed in the vacuum oven.
- More specific procedures for sorbent trap conditioning to enhance consistency of blank levels, including longer conditioning time and maintenance of positive flow during heating and cooling.
- Specific procedures for handling conditioned traps to minimize ambient air contamination.
- More sensitive and specific calibration for blank checking.
- More specific procedures for blank checking.
- Quality control for blank checking, including system blanks and recovery checks.
- Different sample desorption flow rate.
- Development of a procedure for evaluating performance of the analytical trap in the purge and trap apparatus.
- Addition of a recovery check procedure for the analytical system.
- Development of procedures for determining acceptable analytical separation to assist in column selection and other GC conditions.
- Development of procedures for determining appropriate calibration levels.

Overall, the laboratory evaluation accomplished all of its stated objectives.

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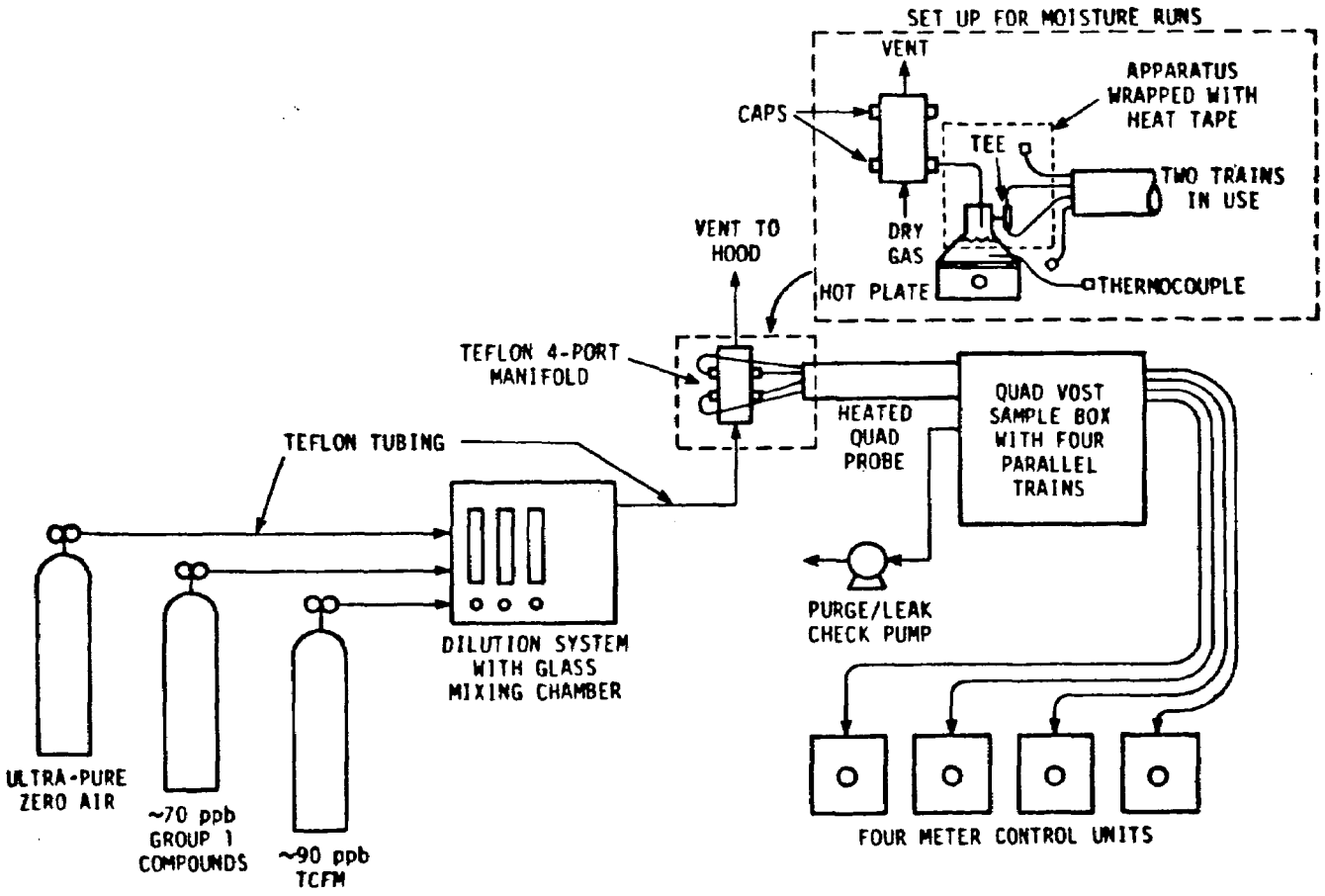

Figure 1. Schematic of sampling arrangement for laboratory evaluation.

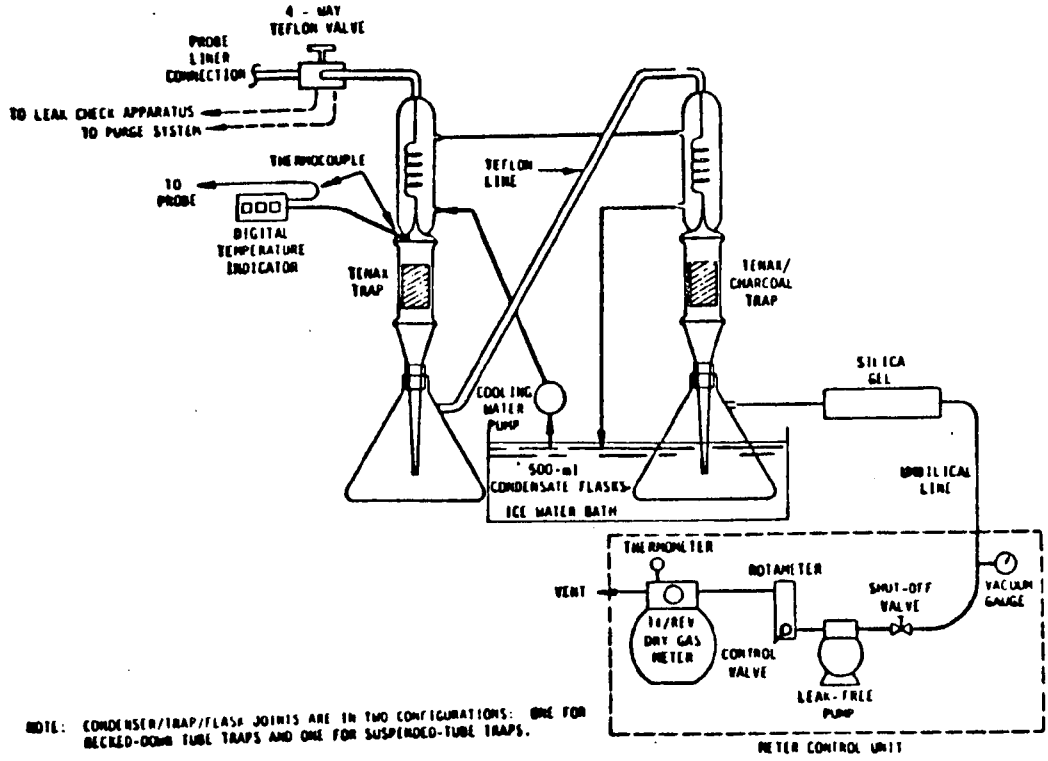

Figure 2. Schematic of single volatile organic sampling train (VOST).

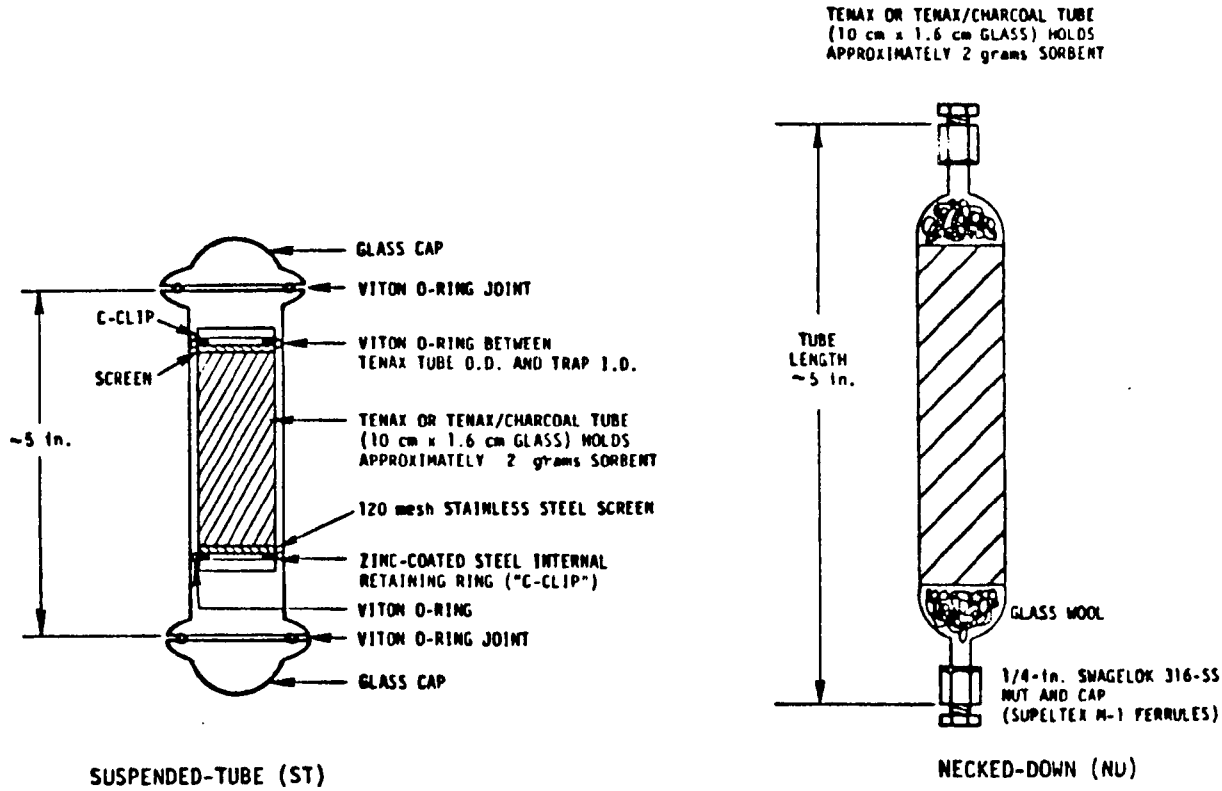

Figure 3. Sorbent trap configurations.

TABLE I. LIST OF COMPOUNDS SELECTED FOR VOST PROTOCOL VALIDATION

Compound	Boiling point,[b] °C	Incinerability[a] ranking		Comments
		ΔH[c]	T 99.99/2[d]	
Tetrachloroethylene	121	15	1	Group 1 compound;[e] potential recovery problem
Benzene	80	282	23	Group 1; historical Tenax blank problem
Carbon tetrachloride	77	4	2	Group 1; frequently selected as a POHC
Chloroform	61	10	44	Group 1; common lab solvent.
Trichlorofluoromethane	24	1	NL[f]	Lower limit of acceptable boiling point range
Vinyl chloride	-12	58	26	Group 1; potential breakthrough problem

[A] A ranking of 1 is the most difficult to incinerate.

[b] The general target range in the VOST Protocol is 30° to 100°C.

[c] Based on the heat of combustion table for 283 RCRA Appendix VIII constituents.

[d] Based on the temperature required to achieve 99.99 percent destruction at a residence time of two seconds (list of 55 compounds compiled by J. J. Cudahy of IT Enviroscience, September 1983).

[e] Group number refers to the QAD gas cylinder audit program.

[f] Not listed.

TABLE II. SUMMARY OF PRECISION, ACCURACY, AND TRAIN-TYPE COMPARISON RESULTS[a]

Nominal test conditions	Parameter	Vinyl chloride		Trichloro-fluoro-methane		Chloroform		Carbon tetra-chloride		Benzene		Tetrachloro-ethylene	
	Trap type	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST
0.5 ppb, dry[b]	$\bar{x}_c$, ng/liter	0.60	0.17	2.22	2.37	1.90	1.94	2.22	2.28	2.87	2 55	3.69	3.91
	σ_c, ng/liter	0.09	0.01	0.31	1.42	0.08	0.11	0.14	0.26	1.04	1.13	0.03	1.79
	% RSD[c]	15.0	5.9	13.9	55.9	4.2	5.7	5.1	11.4	36.2	44.3	0.8	45.8
	% EV[d]	42	12	78	83	83	85	85	71	175	155	103	109
Significant difference?[e]		Yes		No		No		Yes		No		No	
0.5 ppb, wet[f]	$\bar{x}$, ng/liter	0.53	0.36	2.74	2.53	2.02	1.84	2.71	1.63	2.48	2.01	3.79	3.55
	σ, ng/liter	0.13	0.09	0.17	1.0	0.12	0.27	0.39	0.32	0.75	0.03	0.15	0.40
	% RSD	24.5	25.0	6.2	39.5	5.9	14.7	14 4	19.6	30.2	1.5	4.0	11.3
	% EV	38	26	97	89	89	81	85	51	153	124	107	100
Significant difference?[g]		Yes		No		No		Yes		No		No	
15 ppb, dry[h]	$\bar{x}$, ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	88.23	75.55	57.03	53.01	130.2	117.1
	σ, ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.51
	% RSD	7.5	41.5	6.3	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
	% EV	91	12	76	56	116	106	92	78	116	107	121	108
Significant difference?[e]		Yes		Yes		No		No		No		No	
15 ppb, wet[i]	$\bar{x}$, ng/liter	20.32	19.98	64.47	33.84	73.34	65.31	86.46	53.43	52.64	49.35	143.4	139.2
	σ, ng/liter	2.10	3.71	4.55	6.62	2.89	6 12	1.13	2.39	1.10	3.45	4.16	3.51
	% RSD	10.3	18.6	7.1	19.6	3.9	9.4	1.3	4.5	2.1	7.0	2.9	2.5
	% EV	48	47	75	39	107	95	90	56	107	100	133	129
Significant difference?[g]		No		Yes		Yes		Yes		No		No	

[a] Includes data from quad Runs Q1 through Q3 and Q6 through Q8 and paired Runs W1 through W8. No data are corrected for blank values.

[b] Quad Runs Q6 through Q8, including all data except Run Q7, Sample No. L.5ST112 values for all compounds.

[c] Standard and relative standard deviations are pooled from paired run data.

[d] Percent of expected value = $(\bar{x}/EV) \times 100$, where EV is the average for applicable runs taken from the summary table of dilution system data and expected concentrations in ng/liter.

[e] Difference between train types based on analysis of variance at 10% probability level.

[f] Paired Runs W5 through W8, including all data The moisture content of the sampled gas stream was approximately 30%.

[g] Based on t-test statistic at 10% probability level, difference between train types

[h] Quad Runs Q1 through Q3, including all data except Run Q2, Sample No. L15ND121 values for vinyl chloride and trichlorofluoromethane.

[i] Paired Runs W1 through W4, including all data The moisture content of the sampled gas stream was approximately 30%.

TABLE III. SUMMARY OF SAMPLE HOLDING TIME RESULTS[a]

Sample holding time[b] (weeks)	Parameter	Vinyl chloride		Trichlorofluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloroethylene	
	Trap type	MD	ST	MD	ST	MD	ST	MD	ST	MD	ST	MD	ST
1[c]	$\bar{x}_d$, ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	80.23	75.55	57.03	53.01	130.2	117.1
	σ^d, ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.5
	% RSD	7.5	41.5	6.1	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
2[e]	$\bar{x}$, ng/liter	15.21	7.28	47.56	31.16	70.72	67.74	75.55	72.33	53.04	47.80	116.0	99.5
	σ, ng/liter	2.11	0.23	4.29	2.25	0.76	9.19	0.18	6.29	3.31	2.65	2.19	7.50
	% RSD	13.9	3.2	9.0	7.2	1.1	13.6	0.5	8.7	6.2	5.5	1.9	7.5
Difference,[f] %		-61	39	-25	-33	-11	-7	-14	-4	-7	-10	-11	-15
5[g]	$\bar{x}$, ng/liter	10.70	6.42	50.02	29.60	70.42	68.26	81.86	70.29	50.68	50.20	126.1	112.2
	σ, ng/liter	5.64	5.03	0.40	4.64	6.02	5.20	3.09	3.27	1.28	1.02	20.93	12.30
	% RSD	52.7	78.3	0.8	15.7	8.5	7.6	3.8	4.7	2.5	2.0	16.6	11.0
Difference,[f] %		-72	22	-22	-37	-17	-7	-7	-7	-11	-5	-3	-4
Significant difference,[h]		Yes[i]		Yes		No		No		No		No	

[a] All samples collected at a nominal target compound concentration of 15 ppb in a dry gas stream. All data were used from Runs Q1 through Q5 except for Run Q2, Sample No. L15MD121 values for vinyl chloride and trichlorofluoromethane. No data are corrected for blank values.

[b] Time between sample collection and analysis. All samples were stored in refrigerated cans containing charcoal.

[c] Runs Q1 through Q3.

[d] Standard and relative standard deviations are pooled from paired run data.

[e] Run Q4.

[f] Difference between mean concentrations at indicated holding time and initial values,

$$\% = \frac{\bar{x}_f - \bar{x}_{initial}}{\bar{x}_{initial}} \times 100$$

[g] Run Q5.

[h] Difference between holding times based on analysis of variance at 10% probability

[i] The effect of sample holding time is significant for the MD train but not for the ST train.

PRACTICAL CONSIDERATIONS FOR IMPROVING SAMPLING ACCURACY AT GROUNDWATER TEST WELLS

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INTRODUCTION

The RCRA groundwater monitoring program requires accurate, representative, and consistent measurement of contaminants at very low levels. In most existing groundwater monitoring programs, the sampling component of the monitoring process represents the greatest existing potential gap in the quality assurance chain. This presentation discusses ways in which field conditions, operator variability, sampling procedure, and sampling device design may impact sample accuracy. Particular emphasis is given to sampling problems due to cross-well contamination, well head environmental contamination, operator technique, inadequate equipment cleaning, and sampling under extreme climatic conditions.

The lack of adequate attention to basic questions of sample quality control in the past has already resulted in very serious problems of data accuracy and validity in the nation's newly developing groundwater monitoring programs. Many recent EPA and private reports suggest that problems of sample quality may be so serious within RCRA monitoring programs that they could jeopardize the successful implementation of many subsequent phases of the RCRA program which will depend on the results of this monitoring data. (1, 2, 3, 4) That an important, costly new environmental program, such as RCRA, should founder for lack of adequate attention to a program component so basic and easily manageable as sample quality control is unfortunate, for the sampling process is the least expensive step in the whole data handling train. To do the job right costs no more than doing it the wrong way, and in either case, the cost of achieving a good reliable groundwater sample is insignificant when compared to overall monitoring program costs or to other monitoring components such as sample analysis or well construction.

Yet despite the fact that good sample quality is instrumental to the success of RCRA groundwater monitoring efforts, there are as yet few uniform standards or minimum State requirements to ensure the minimum levels of accuracy and consistency these sophisticated new programs demand.

Currently, sampling procedures in most State groundwater monitoring programs represent a surprisingly haphazard hodgepodge of everything from high speed production pumps engineered originally to keep basements dry to slight modifications of Biblical era methods designed originally to bring water in a bucket at the end of a rope to the surface of the ground as a means to the furtherance of livestock raising. While these techniques were certainly adequate in the past to their originally intended function, they are hardly appropriate for

the controlled, consistent collection of groundwater samples to be chemically analyzed reliably for parts-per-billion of volatile organics or toxic contaminants, as is now required by today's RCRA groundwater monitoring programs.

Although we understand that good progress is now underway at EPA to address the sampling issue, in the past sampling has taken a decidedly back seat to analytical methods in EPA efforts to build quality assurance into the groundwater monitoring process. Consequently the situation which is now emerging in most State groundwater monitoring programs is this: an extraordinarily expensive and elaborate set of high-resolution analytical testing procedures are now being required by the states, but little attention so far has been given to the basic means by which these carefully analyzed samples are collected. Under these circumstances, the success of the monitoring process is jeopardized far more by poor sample quality than by poor analytical procedure. (4)

One of the most admirable and clearly stated goals of EPA's RCRA monitoring program is to ensure that its sampling and analytical procedures will provide "accurate, consistent, and comparable testing results—year to year, facility to facility, and region to region." The statement of this goal immediately poses three questions for us regarding sampling: First, is this goal now being achieved in EPA's groundwater monitoring programs? We believe that most people would agree that it is not. Secondly, can this goal be achieved in the sampling component of the monitoring process? We believe the answer is yes, and that it can be achieved with existing technology and knowledge. Thirdly, if it can be achieved, then what, from a practical point of view, can state RCRA programs do to achieve consistency and accuracy in their sampling? In the time we have here, we would like to discuss, from a practical viewpoint, four interrelated areas that should receive attention if this goal is to be met:

- Dedication of sampling equipment
- Sampling device design
- Materials
- Minimizing operator variability

DEDICATION OF SAMPLING EQUIPMENT

Accuracy and consistency of groundwater sampling can be greatly enhanced by dedication of the groundwater sampling equipment to each well. This offers enormous benefits in terms of sample quality and minimizes the amount of time and manpower needed to obtain unbiased samples. By dedicating sampling equipment to each well, most of the problems of cross well sample contamination, exposure of sampling equipment to well head environmental contaminants, and the inadequate cleaning of multi-well sampling equipment can be overcome. In most

field condition situations, it is extremely difficult, as a practical matter, to avoid the risk of introducing significant contamination into a sample well when using multi-well equipment. Mud, ice, dust or dirt are always present at the well head during the sampling process, in the pick-up truck, and in the shop where equipment is stored. Long lengths of wet, unwieldy tubing, cables, pumps, etc., easily pick up contaminants from use and transport in the field. Elaborate and expensive procedures usually prescribed for cleansing portable sampling equipment and tubing with repeated acidic baths and rinses of distilled water prior to use and between well sampling episodes are frequently only perfunctorily observed, at best, under actual field conditions. During winter sampling in the northern half of the United States, such procedures are not only unrealistic to carry out, but the well contamination problem is further compounded by the instant accumulation of ice on all downwell portions of nondedicated sampling systems.

Nondedicated monitoring approaches are also extremely vulnerable to operator abuse and variability, as they generally require more care and training on the part of the operator. Problems in training, employee turnover, and lack of conscientiousness can become significant sources of sample error with many nondedicated monitoring approaches. Although the dedicated approach cannot overcome such potential problems entirely, they can be greatly mitigated.

Health and safety are other good reasons for requiring the dedicated approach for groundwater monitoring. As the operator is not regularly handling the down-well components of the sampling equipment on a dedicated sampling system, the operator's exposure to potentially hazardous down-well contaminants is significantly reduced.

SAMPLING DEVICE DESIGN

As mentioned, there is a wide range of groundwater sampling devices being used in the field at this time to collect RCRA groundwater samples. The most commonly used are:

- The bailer
- The electric submersible pump
- The positive displacement gas pump
- The suction pump
- The positive displacement bladder type "squeeze" pump

A short description of each sampling device and its advantages or disadvantages follows.

Bailers

The bailer has traditionally been widely employed for well sampling. It is simply a long cup-like cylinder with a line attached to it. The bailer is lowered into the groundwater sampling well, water enters by means of check valves or through an opening in the top, much like a bucket, and then the bailer and the water it contains is manually pulled to the surface. There are several serious risks associated with the use of a bailer for well purging and collection of samples, however, and the following precautions should be noted regarding sampling with bailers:

- The bailer, if not used with extreme care, can easily disturb well contents during the sampling process. The piston action of the bailer entering and exiting the well creates a surging action that can stir up sediment, move fine particles into the well, aerate the sample and/or strip dissolved gases from the sample.

- The bailer contacts the walls of the well during raising or lowering, potentially scraping precipitated contaminants or well casing material off the inside of the casing and into the well or the sample.

- Bailer operator technique has been demonstrated to greatly affect sample precision. (5,6,7,8,9) Two different trained field personnel sampling the same well on the same day can obtain significantly different samples, particularly when analyzing for volatile organic constituents.

- Purging four volumes from a "typical" 100 foot deep well with 75 feet of standing water requires approximately 200 repetitions of bailer lowering, filling, raising, and emptying, thereby multiplying the deleterious effects of bailer use on sample quality.

- The bailer lift line is very difficult to keep clean. The tendency is to either wrap the line around one's arm or to coil it on the ground. When the bailer is raised and lowered repeatedly during the lengthy purging process, the opportunity for contamination to be transferred to the well is extremely high. Cleaning of the bailer lift line from one well to the next is very difficult. (10) This problem is further exacerbated by the braided construction of most lift lines which encourages water to become trapped and inaccessible to casual cleaning efforts.

- The bailer exposes field personnel to contaminants due to the intimate handling of wetted components and splashing and dripping of bailer contents.

- Care must be exercised during the transfer of a sample from the bailer to a sample bottle. (7,9) In particular with volatile organic constituents, the

loss of significant fractions can occur if the sample is not transferred with extreme care.

- It should be a fundamental assumption that personnel and environmental conditions will not remain constant throughout the duration of a sampling program. Due to the overwhelming lack of precision with the bailer, it is a poor choice of sampling equipment when the objective is early detection or tracking of contaminants over an extended period of time. (5)

Electric Submersible Pumps

It is important to separate the conventional electric submersible, well water delivery type pumps from designs built for sampling small diameter monitoring wells. In addition to the problems regarding the need for external power, the presence of many inappropriate materials, and difficulty with deploying the conventional electric submersible pump, there are some other difficulties that should be mentioned:

- Conventional electric submersible pumps are limited to 4-inch or larger diameter wells that are more expensive to install than 2-inch wells, less amenable to hollow stem auger drilling methods, and require substantially greater purge volumes.

- Studies have shown that the turbulence and pressure change caused by a rotating impeller can influence the accuracy of volatile organics sampling. The work also indicates that the tendency to strip volatiles out of the sample is variable among pump designs. (11,12)

- Appropriate flow control of a conventional electric submersible pump is not available. Attempting to do so by valving the discharge can result in further turbulence and volatile organics loss, due to impeller cavitation and to a spray nozzle type effect from the sudden pressure drop across the throttling valve. (9)

- The difficulty in cleaning these pumps is significant as it is often impossible to fully access the internal wetted surfaces and components of the pump in the field. (7)

- Purging at very high flow rates with electric submersible pumps can disturb local conditions in the aquifer and alter the quality of water in the well, due to induced turbidity and flow from other horizons. (6)

- The small diameter specialty electric submersible pump is a recent development that still shares the basic design problems the conventional electric submersible has with regards to the loss of volatile organic

parameters due to induced turbulence and use of the sample for cooling the pump mechanism. Because of this point it is not recommended that the small diameter electric submersible be used for volatile organic sampling. (11)

Positive Gas Displacement Pumps

Due to the use of compressed gas applied directly to the sample, the positive gas displacement pump is not recommended for sampling. The application of the gas will directly affect any dissolved gas-sensitive or volatile components in the sample. (11,12,8) Altering dissolved gases can also alter pH, which will affect low level metals analysis.

The positive gas displacement type pump is applicable for well purging due to the high flow rates available with it, the ability to pump sediments without harming pump components, the simplicity of the design, relative ease of cleaning and portability.

Suction Pumps

The suction pump is only useful to purge wells that are shallower than 25 feet It has been demonstrated that the changes of altering both volatile organices, pH, and metals levels in a sample are high when sampling with this type of pump. (11,13,8,9,14) Thus, use of the suction pump should be prohibited as a sampling device.

Positive Displacement Bladder-Type Squeeze Pumps

This is the most highly regarded sampling device in the field today. It was specifically designed to sample groundwater. Its efficient use of compressed gas to raise water to the surface also allows it to be used effectively as a well purging device. The gas operated squeeze pump is also the only device tested and proven effective in both purging and sampling.

The gas operated squeeze pump has been very highly rated as a sampling device in nearly all recent studies for several reasons. These include:

- The squeeze pump is the most accurate way to sample for volatile organic parameters. (11,12,8,15) This is the direct result of a design that separates the drive gas from the sample or purge water. As volatile organics are among the most difficult constituents to accurately sample for, using a method adequate for volatile constituents ensures that all parameters of interest are also being sampled for in the best way possible.

- Its simple design allows it to be economically constructed

of materials most acceptable for groundwater sampling. Squeeze pumps constructed entirely of TeflonR are available at modest cost.

- It is possible to pump turbid waters without damaging the pump. In contrast to other pump designs that include delicate, close-fitting parts, most squeeze pump designs do not include complex moving parts that can be damaged by particles associated with turbidity.

- It is possible to sample from extreme depths with the squeeze pump. Standard squeeze pumps have been used successfully as deep as 1,000 feet.

- Adjustable low flow rates are possible with this pump, even down to the 100 mul suggested as the optimum flow rate during the sampling procedure by the U.S.G.S.

- Filtration is easily accomplished with this pump design by simply applying more pressure to the pump and installing an in-line filter on the pump discharge line. (16,9)

- The squeeze pump is very portable when used with a small compressed gas cylinder.

- Since the drive air is separated from the well water, any drive gas, including ambient air, may be used.

- The squeeze pump may be pumped dry without harm.

- The flow rate on a gas-operated squeeze pump can be easily controlled by simply changing the drive gas pressures. This allows easy flow control for slowly filling sample containers.

- Because the movement of water into a squeeze pump by the existing hydrostatic head minimizes turbulence, it is one of the few designs that can accurately sample from a discrete location in the well. The ability to sample at a particular depth is valuable for sampling many parameters; dedicating the squeeze pump to the well is especially effective in ensuring sampling at a discrete level.

- The squeeze pump's simplicity, accuracy, reliability, and cost make it highly advantageous for dedication to the well, thus also achieving dedication's concomitant benefits of consistency of method and elimination of cross-well contamination. Thus, the positive-displacement bladder-type squeeze pump represents the best currently available technology for groundwater sampling; its use should be encouraged for RCRA program monitoring applications wherever possible.

Construction Materials for Sampling and Purging Devices

Sufficient information is now available on material properties and performance for groundwater monitoring to provide specific guidance on their selection. (11,10,17,18)

The objectives of groundwater monitoring programs demand the usage of inert materials (e.g., particularly TeflonR, and to a lesser extent, stainless steel) for sampling equipment; their cost-effectiveness is supported on the basis of the assurance of representative samples they provide and their low cost relative to total monitoring program costs.

TeflonR offers the unique advantage of near universal chemical inertness to organics and inorganics, along with minimizing sorption effects. Its use should be strongly encouraged.

At a very minimum, the use of demonstrated detrimental materials, such as silicone rubber and carbon steel, should not be allowed. This same prohibition should certainly extend to unranked materials, such as the numerous commercial variations of plastics formulations in existence, unless performance equivalency to acceptable materials has been demonstrated (19).

CONCLUSION

Serious problems with accuracy and comparability of groundwater data will result if improper sampling procedures are permitted at the outset of the RCRA groundwater monitoring program. It is estimated that only a very small percentage of the RCRA sites nationally have begun the groundwater monitoring they will be required to conduct under state and national guidelines. During the next year, a large percentage of the remaining sites will begin their monitoring programs. Without adequate guidance at this time from state and federal regulatory authorities regarding sample accuracy, standardization and quality control, large sums of money may be pointlessly spent as very expensive groundwater programs get under way with little consistency or quality control in the sampling process. The rare opportunity to build meaningful, scientifically valid, statistically comparable statewide data bases for groundwater quality will be lost. What a shame it will be if we now undertake this expensive new groundwater monitoring effort, only to end up with reams of scientifically useless data that do not permit statistically meaningful aggregation at the state or national level due to the lack of attention to accuracy and consistency in the most basic and least expensive part of the quality assurance chain, the sampling procedure.

When the sampling methods employed during the monitoring programs are inadequate, whole classes of important contaminants (such as volatile organic compounds) may go undetected. The groundwater monitoring program thus fails in its primary purpose. Good sampling practices

should be instituted at the beginning of the program or, if the program has already started, as soon as possible. Just because bad practices are "already under way" in a groundwater monitoring program is no reason why such practices should be maintained throughout the rest of the program.

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THE RELATIONSHIP BETWEEN THE DESIGN OF WELLS AND SAMPLING IN COMPLIANCE MONITORING FOR GROUNDWATER UNDER RCRA

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INTRODUCTION

The goal of the RCRA groundwater monitoring regulations is to ensure that owner/operators of land disposal units evaluate and monitor the impact of their facilities on the aquifer(s) underlying their sites. The objective of groundwater quality monitoring programs, therefore, is to obtain samples representative of depth discrete, in-situ fluid for analysis. A number of factors can influence whether or not a sample is representative. Two of the most crucial elements of the monitoring program are the design of the wells and the sampling methodology.

WELL DESIGN

Two types of wells are of use in a groundwater monitoring program: observation and monitoring wells. Observation wells are commonly installed during the characterization phase of the site investigation to provide geological data as well as data on water level or potentiometric head. Observation wells can be constructed of PVC or any other such material since the parameters to be measured are physical, not chemical, aquifer characteristics. They are temporary and are not to be used for regulatory sampling. Monitoring wells, on the other hand, must be designed and constructed to satisfy the criteria summarized in Table 1.

Table 1. Criteria for Evaluating Monitoring Well Design

Does the design allow the following tests?:

- measurement of total depth;
- measurement of depth to static water level;
- determination of the existence of nonaqueous phase liquids (e.g. dense and light);
- discrete sampling of nonaqueous phase liquids; and
- the taking of a water sample with the least amount of agitation and loss of volatiles.

Is the well?:

- constructed of materials suited for monitoring any or all of the Appendix VIII constituents in a particular hydrogeologic environment (e.g. non-reactive, non-sorbitive,

non-releasing);

- constructed to function through the active life and post closure monitoring period for the facility; and

- constructed in a way as to be secure from tampering or accidental collision.

Monitoring wells are used to evaluate the chemical quality of water within the aquifer(s). Two factors that must be considered in the design of monitoring wells are the chemical characteristics of the liquids in the saturated zone and the physical characteristics of the formation (i.e. depth) being monitored.

A variety of construction materials have been used for the casings and screens of wells including, teflon, steel (stainless, black, galvanized), PVC, polyethylene, epoxy biphenol and polypropylene. Many of these materials may, however, affect the quality of groundwater samples and may not have the long-term structural characterstics required for RCRA monitoring wells. For example, steel casing deteriorates in corrosive environments; PVC deteriorates when in contact with ketones, esters and aromatic hydrocarbons; polyethylene deteriorates in contact with aromatic and halogenated hydrocarbons; and polypropylene deteriorates in contact with oxidizing acids, aliphatic hydrocarbons and aromatic hydrocarbons. In addition, steel, PVC, polyethylene and polypropylene may adsorb and leach constituents that may affect the quality of ground-water sample quality. Presently the Agency is advocating the use of either stainless steel or teflon as construction materials (in the saturated zone) and for well screens. Teflon is generally inert to chemical attack, has low leach potential and is relatively non-sorptive. Table 2 provides some insight into the adsorption characteristics of Teflon. It is a particular good construction material for use in corrosive situations where inorganic contaminants are of interest.

Table 2. Exposure of Teflon Resins to Solvents, Acids and Bases

Solvent	Weight Increase %
Hydrochloric acid (10%)	0.0
Nitric acid (10%)	0.0
Sulfuric acid (30%)	0.0
Sodium hydroxide (10%)	0.0
Ammonium hydroxide (10%)	0.0
Ethyl alcohol (95%)	0.0
Acetone	0.3
Toluene	0.3
Ethyl acetate	0.5
Carbon tetrachloride	0.6

Notes:

. Exposure temperature 25 C (77 F)
. Exposure time 12 months
. These are essentially equilibrium test values: additional exposure times would not increase the values significantly.
. Weight changes less than 0.2% are not considered to be experimentally significant.
. Values are test averages only and are not for specification purposes.

Stainless steel is also durable corrosion-resistant material. A number of various types of stainless steel exist. The types used in casings and screens are listed in Table 3 along with their chemical make-up. It is particularly useful construction material in situations where organic leachate will be encountered.

Table 3. Composition of Stainless Steels in Use for Groundwater Monitoring

Designation or type	Composition, %*								
	C	Mn	Si	Cr	Ni	P	S	Mo	Al
304	0.08	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.03	-------	---------
316	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0	---------
405	0.08	1.00	1.00	11.5-14.5	---------	0.04	0.03	-------	0.10-0.30
410	0.15	1.00	1.00	11.5-13.0	---------	0.04	0.03	-------	---------

*Single values are maximum unless otherwise noted.

The Agency does allow for combinations of materials (composite designs) so long as Teflon or stainless steel casing and well screen is used in the saturated zone and the different construction materials in the upper casing (i.e., casing above the saturated zone). Allowable materials for use as upper casing include steel, PVC, polyethylene and polypropylene. Where different metals are used an evaluation, and possible provision, should be made for galvanic reactions. Plastic pipe sections must be flush threaded or have the ability to be connected by another mechanical method that will not introduce contaminants such as glue or solvents into the well. All well casing and screens must be cleaned prior to emplacement to ensure that all oils, greases and waxes have been removed.

Once the material for the casing is chosen, the depth of the wells becomes the determining factor for design. The preference for all wells is roughly as follows:

. Four (4) inch ID casing.

. One screen per well.

- No screen to exceed ten (10) feet, except the upper screen in the surfical aquifer which can be of sufficient length to cover fluctuations of the water table caused by seasonal or pumping affects.

- Lowest screens to sit on top of aquitards or aquicludes with no gravel pack beneath the screen.

- Gravel packs not to exceed screen length by more than two feet.

- Gravel or sand packs.

- Only rough-grit, pure Bentonite, certified not to produce a pH change in a leachate, to be used below the water table to seal the annulus.

- A Bentonite-cement mixture is to be used above the bentonite to the surface.

- PVC, black iron, or other reactive mateials may be used in the zone above the water table. Anti-glavanic devices required for mental composites.

- Concrete apron at surface.

- Bumper guards.

- Locking caps.

- All purging and sampling is to be by dedicated bailers, with the latter to be bottom filling types.

An example of such a well is provided in Figure 1.

When a larger diameter well is preferred or when the well must be very deep (i.e., greater than 150 ft.), six (6) inch wells may be installed with sealed casings and dedicated, down-the-hole, positive displacement pumps. These pumps may be used to purge the well and sample disolved constituents. A two (2) inch ID casing will be mounted against the inside of the six inch casing, extending through the cap to the bottom of the screen. It is in this casing that sampling for light phase, heavy phase and if required dissolved constituents will be made, as well as the determination of the existence of phases and the water-level reading. This sampling will be made by bailers. The lower sample to be taken by bottom filling bailer. An example of this well is provided in Figure 2.

It should be noted that in each figure the design is different from anything previously presented by the Agency. The primary difference is the addition of a section of casing 8"-12" in length, below the screen, which serves as a trap, or collecting cap, for heavy phase

compounds. Ideally the bottom of the screen should be placed at the top of a less permeable horizon, if one exists. This modification is particularly important if the facility receives dioxin compound, PCB's or wastes known to produce precipitates with a change in pH.

SAMPLING

There is a series of activities to be accomplished in any sampling effort. First, a protocol for sampling of monitoring wells must be developed and implemented which fulfills the following criteria: allows for the removal of stagnant/standing water from the well before sampling; does not affect the chemical quality of the sample (i.e., degassing, absorption); allows for depth discrete sampling (i.e., heavy or light immissible phases); and minimizes human error. An example of sequence of operations that should be used when sampling a monitoring well is provided in Table 4.

Table 4. Sequence of Operations to be Followed When Sampling a Monitoring Well

1. Remove the locking cap, and protective cap.
2. Sample the air above the well head with HNU or OVA, record reading if any.
3. Use an interface probe to determine the presence of any light and/or dense phase immissible.
4. Use a bottom filling bailer(s) to obtain a sample of the immissible(s).
5. Use a manometer, or acoustical sounder, to measure the static water level and record measurement.
6. Measure the record the total depth.
7. Calculate the volume of water in the casing.
8. Determine how best to evacuate the well based on volume and recharge characteristics. This step may be already determined by dedicated, down-the-hole equipment.
9. Remove three (3) volumes of water from the well from the center of the screened zone, if possible.
10. Dispose of the purge water in accordance with the RCRA regulations and operating procedures at the facility, (away from the well head).

The water found standing in a well prior to sampling may not be

representative of in-situ ground-water quality. Therefore, the standing water in the well must be removed so that water which is representative of the formation can replace the standing water. The sampling and analysis program must include detailed step-by-step procedures for the well evacuation procedures. Prior to well evacuation, water level measurements must be taken so the volume of standing water in the well can be calculated. These measurements must include depth of standing water and depth to intake bottom measurements taken to 1/100 of a foot. Each well should have a survey point from which its water level measurement is taken. The device to be used for water level measurements and the procedure for water level measurement should be specified. Before evacuating the well, the sampling personnel must check if there is material floating on the surface of the water. If there is, it must be sampled and if appropriate, its thickness measured. The evacuation procedure should ensure that all stagnant water is replaced by new formation water upon completion of the process.

The procedure used for well evacuation depends on the yield of the well. (The yield also is a factor in determining what type of dedicated, down-the-hole equipment to use.) When evacuating low yield wells, the wells should be evacuated to dryness once. As soon as the well recovers, the plan must require that the first samples removed are the ones to be tested for pH, oxidation reduction and/or volatilization sensitive parameters. During long recovery times volatilization may occur, hence, under no circumstances should these samples be taken more than three hours into the recovery period (i.e., after evacuation of dryness). Whenever full recovery exceeds three hours, the remaining samples must be extracted in order of their volatility as soon as sufficient volume is available for a sample for each parameter. Parameters that are not pH sensitive or subject to loss through volatilization, (such as nonvolatile or nonreactive organics) should be drawn last. For higher yielding wells, withdrawal of 3 casing volumes is required. Detailed field logs of the evacuation procedure must be kept to ensure that any equipment malfunction or other problems are described. An example of an allowable option of purging equipment in the case of a deep, rapidly recharging well is shown in Figure 3. Devices used for sample withdrawal must not alter or contaminate the sample during withdrawal. Devices must be dedicated to a specific well or capable of being fully disassembled and cleaned between events. Procedures for cleaning the sampling equipment must be documented.

When used properly, the following are acceptable sampling devices for all parameters:

- Teflon bladder pumps with adjustable flow control;
- Bottom valve bailed (Teflon or stainless steels); and
- Syringe bailers (Teflon or stainless steels).

Appropriate operating precautions for each type of sampling device

include, but are not limited to:

- Bladder pumps must be operated in a continuous manner so that they do not produce pulsating samples that are aerated in the return tube or upon discharge;
- Check valves must be designed and inspected to assure that fouling problems do not reduce delivery capabilities or result in aeration of the sample;
- Sampling equipment (e.g. especially bailers) must never be dropped into the well because this will cause degassing of the water upon impact;
- Bailers will be extracted from the well at a uniform speed. (recommend boom and crank);
- The contents of a bailer must be transferred to a sample container in a way that will minimize agitation and aeration; and
- clean sampling equipment must not be placed directly on the ground or other contaminated surfaces.

Detailed field logs of each sampling event must be made to ensure that prescribed procedures were followed and that unusual events (e.g., slow recharge rates, malfunction of equipment, possible contamination of samples, etc.) are noted.

When sampling for parameters are not sensitive to volatilization, pressure differentials, or oxidation/reduction reactions, the following devices are acceptable:

- Peristaltic pumps;
- Gas lift devices;
- Centrifugal pumps; and
- Venturi pumps;

Sampling equipment must be constructed of materials that will not affect the quality of the sample. This applies to all down-hole equipment including the cable to lower it into the well. Equipment with neoprene fittings, PVC bailers, tygon tubing, silicon rubber bladders, neoprene impellers, polyethylene, and vitron are not acceptable. Equipment must be made of fluorocarbon polymers (i.e. teflon) or when appropriate, 316 stainless steel, or other "proven" inert material. When using bailers, "Teflon" coated wire, single strand stainless steel wire or monofilament must be used to raise and lower the bailer. The use of braided cables, polyethylene, nylon or cotton cords is prohibited.

When dedicated equipment is not used for sampling (or well evacuation), procedures must be included for disassembly and cleaning of equipment before each use. If the constituents of interest are inorganic, the first rinse must be a dilute hydrochloric acid or nitric acid and the second and subsequent rinses must be distilled water or deionized water. Dilute hydrochloric acid is generally preferred to nitric acid when cleaning stainless steel because nitric acid may oxidize stainless steel. When organics are the constituents of concern, the equipment must be steam cleaned, then followed by a rinse with a solvent (e.g. hexane) and finally with rinsed distilled or deionized water. Acetone is discouraged due to its proven reaction with Teflon.

When collecting samples for analysis, pumping rates must not exceed 100 milliliters/minute. Higher rates can increase the loss of volatile constituents and can cause fluctuation in pH and pH sensitive analytes. Sampling plans must specify sampling rates and field logs must document sampling rates.

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Figure 1.

GENERAL WELL DESIG

(Applicable for Portable Purging System)

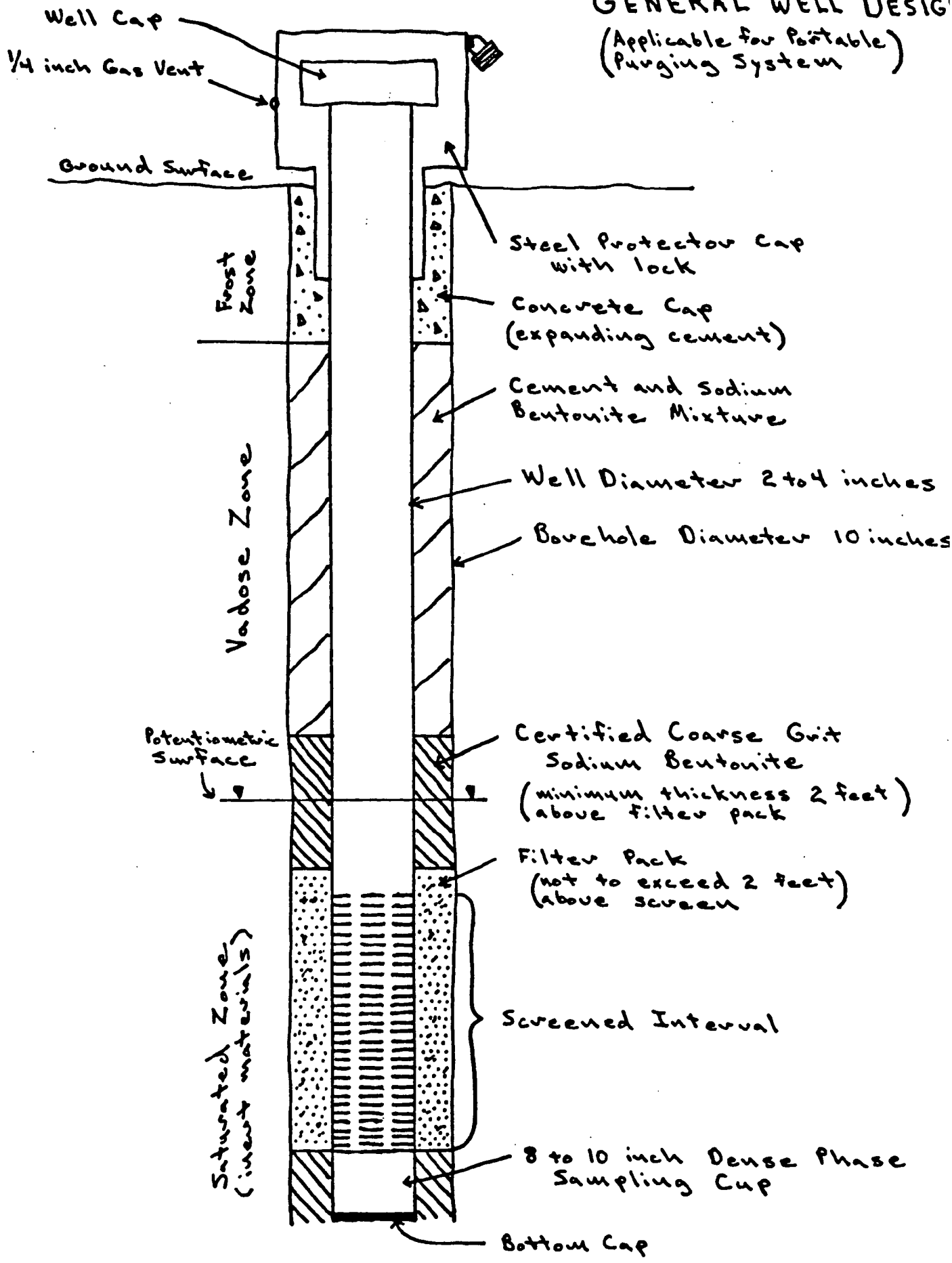


Figure 2.

MONITORING WELL DESIGN,
DEDICATED BLADDER PUMP
(depth 150 to 400 feet)

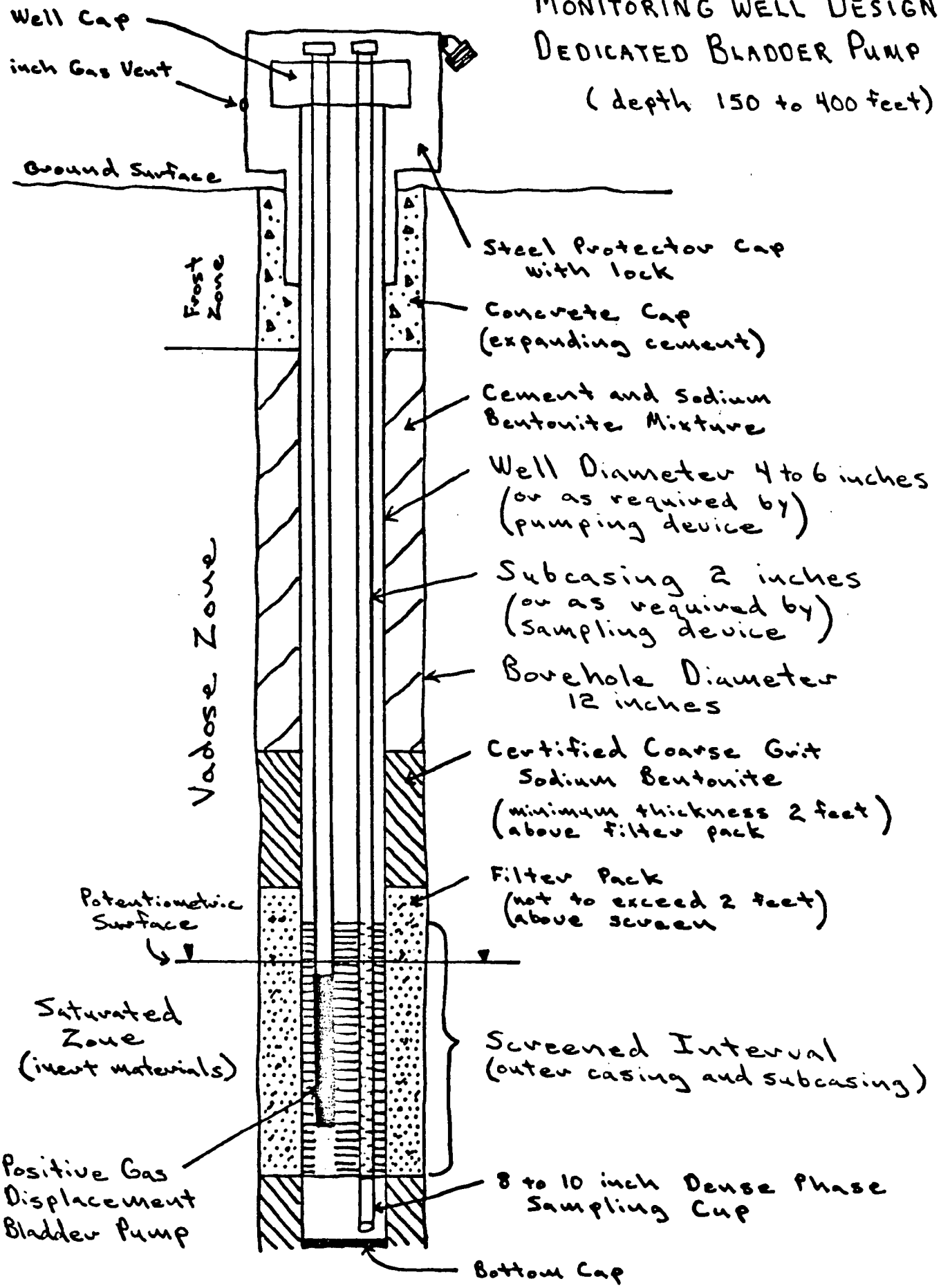
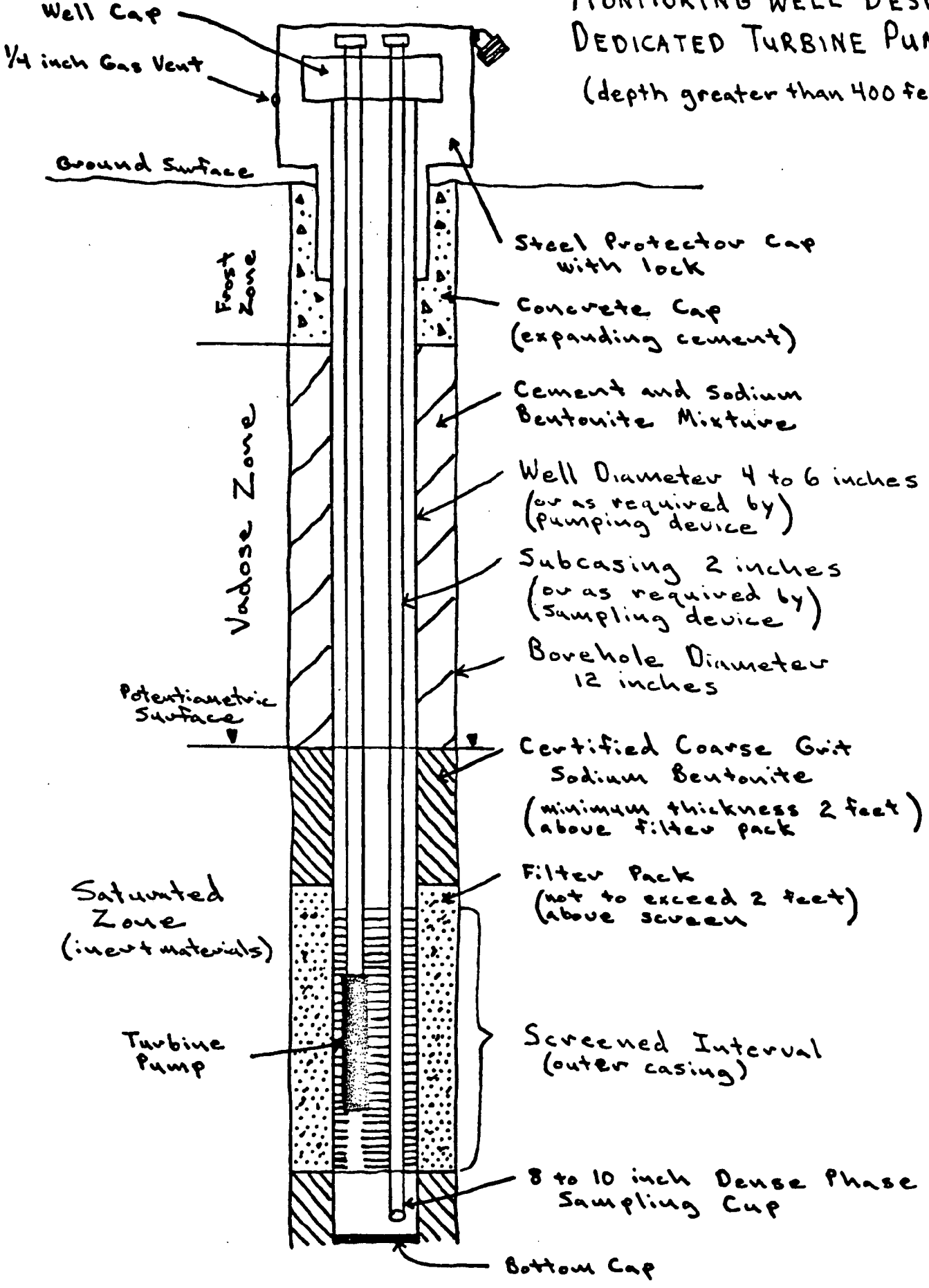


Figure 3.

MONITORING WELL DESIGN,
DEDICATED TURBINE PUMP
(depth greater than 400 feet)



SAMPLING TECHNIQUES FOR RISK MANAGEMENT: A DIOXIN CASE HISTORY

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ABSTRACT

In late May, 1983, a site with high levels 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin) was discovered in the ironbound section of Newark, New Jersey. Meetings were immediately convened among the U.S. Environmental Protection Agency (EPA), the Centers for Disease Control (CDC), New Jersey Department of Environmental Protection Agency (DEP), the New Jersey Department of Health (DOH), and representatives from the New Jersey Governor's Science, Advisory Committee to address this issue. This body of scientific experts developed a conceptual framework for monitoring programs and overall data quality goals required to develop information for effective risk management. A particular concern was that data meet criteria established by CDCs analytical specialist for medical decisioin-making purposes. CDC has previously developed monitoring program quality assurance requirements from prior experience working with dioxin problems in Missouri.

This paper will describe procedures used to develop a data base for dioxin in the Newark area. Preliminary conceptual planning and work plan development will be described that allowed for a phased approach to project planning. This phased approach allowed for evaluation of analytical results as they related to site conditions prior to development of additional site assessment phases. Topics that will be described include:

- Development of an environmentally bound dioxin standard soil reference material,
- preparation of a QA data base by selectively batching samples to be included in analytical runs,
- development of quality control charts to track various contractor laboratories,
- data statistical evaluation criteria to determine false positive and negative results at a 95 percent confidence level,
- evaluation of introlaboratory bias, and
- data management and data presentation methods.

The monitoring procedures implemented on over 25 distinct sampling phases will be described. The end result of this monitoring program was the stabilization of on-site high level contamination areas, the remediation of all offsite contamination areas over one part per

billion and the identification and remediation of a nearby satellite disposal site.

DESIGN AND IMPLEMENTATION OF SAMPLING PLANS FOR RCRA LISTING AND DELISTING PROGRAMS

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Although the title of this speech specified RCRA programs, in general the content should be applicable to any sampling effort. It should also be mentioned that the content of this talk is aimed at a level of expertise which falls between that of the uninitiated and the experienced sampler. The first slide presents an outline of the topics to be discussed. These topics start with the importance of defining the objectives of the sampling effort; the actual design of a sampling plan including statistical, waste, and site-specific factors; the selection of equipment; a brief discussion of quality assurance, health and safety, and chain-of-custody considerations; and lastly a discussion of implementation of the sampling plan and the conpositing of samples.

One can correctly assume that the need for a sampling program would naturally be defined prior to spending time and money on sampling. Once the need for a sampling program is established, the next step is to define the objectives. This step, the defining and understanding of the objectives of a sampling program, is often not given proper attention. In fact, it is understood that a substantial number of unsuccessful sampling efforts fail not because of problems encountered during sampling but because of a poor understanding of the objectives.

In summary, when management requests someone to sample a waste, this request establishes a need for sampling but it does not establish the objectives of a sampling effort. By investigating the reasons that the sampling effort was requested one will be able to define the objectives.

The primary objective for waste sampling is to obtain information which will be used to evaluate a waste. To further define the objectives one must question which waste is to be sampled:

- The waste as generated?
- The waste as prior to or after mixing with other wastes or stabilizing agents?
- The waste prior to or after aging in a drying lagoon?
- The waste just prior to disposal?

Also, should the sampling effort be restricted to recently generated waste or should it also include the sludge disposed of over the last 20 years in the onsite landfill?

Ask what parameters the waste samples are to be analyzed for. Determine why these parameters, and not others, were chosen.

If, after having the previous questions answered, you still don't know why you are collecting samples, ask. There are numerous reasons to

collect samples and often the sampling has to be modified to accommodate these different reasons. This slide lists a few reasons why sampling may be required.

If you have been chosen to collect samples, it is probably as a result of your knowledge of the waste; your input may have a substantial effect on the success of the sampling program. Therefore, before collecting samples, determine what the objective are and whether the proposed sampling plan should be modified.

In the opposite situation, where you are delegating sampling responsibility, make sure that those performing the sampling are well aware of the sampling objectives.

A few years ago, ENSECO's laboratories were assisting a chemical engineer at a latex company to eliminate a certain phthalate from his waste. Let's call this undesired phthalate, phthalate B. The engineer had changed to raw materials which contained phthalate A and therefore expected that phthalate B would disapear from his waste stream. However, 24-hour composite samples continuously found phthalate B present at a lower concentration. The engineer tried to find an explanation but could not solve his mass-balance equations.

The engineer's dilemma was solved months later when the nightshift started wondering why they had to collect all these darned samples. It happened that the nightshift was run by some oldtimers who were very cost conscious. Instead of discarding the old phthalate raw material, they decided to save the company some money and blended the old raw material in with the new. This was a situation where informing the sampling team of the program objectives not only affected the sampling plan but changed the manufacturing process.

In summary, be sure to define the objectives of a sampling program and make sure that everybody participating in the sampling effort is aware of them.

Once the general objectives of a sampling program are defined, then one must concentrate on specific objectives. Specific sampling, analytical, and data objectives will be best defined by studying the end-use of the generated data base.

For example, let us consider a situation where the primary objectives are identical--that is, to determine if the concentration of barium is less than the regulatory threshold; but the specific objectives will vary and have a substantial effect on the sampling. To present this situation, two figures have been excerpted from Section One of SW-846, and lightly modified.

In this first figure limited information has indicated that the average concentration of barium is 50 ppm. Let us assume that this is true and that the concentration of barium is normally distributed around 50 ppm, which is substantially different from the regulatory threshold of 100 ppm.

In this second case, historical data indicated an average concentration of 90 ppm. The specific objective for this situation is to discriminate between 90 and 100 ppm, while in the first case the specific objective is to discriminate between 50 and 100 ppm. Greater accuracy and precision will be required to discriminate between 90 and 100 ppm and this will affect the number and size of samples collected and analyzed. Thus, specific sampling, analytical, and data objectives must be defined along with primary objectives to ensure the success of a sampling program.

Following the definition of the program objectives, the second step in a sampling program can commence. The second step is the design of a sampling plan.

A sampling plan is usually a written document which describes the sampling and analytical tasks that will be performed to achieve the primary and specific objectives of the program.

To ensure that the sampling plan is designed properly, it is wise to have all aspects of the effort represented. For example, an end-user of the data should be involved because he will be using the data to attain the program objectives and thus will be best prepared to ensure that these objectives are understood and incorporated into the sampling plan.

An experienced member of the field team that will actually collect the samples will be able to offer hands-on insight into potential problems and solutions and, having acquired a comprehensive understanding of the entire sampling effort during the design phase, will be better prepared to implement the sampling plan.

Most sampling plans are actually sampling and analytical plans since the analytical requirements for sampling, preservation, and holding times will be factors that the sampling plan will be written around. A sampling effort cannot succeed if an improperly collected or preserved sample or an inadequate volume of sample is submitted to the laboratory for chemical, physical, or biological testing. The appropriate analyst should be consulted on these matters.

If a complex manufacturing process is being sampled, it will be necessary to have a representative of the appropriate engineering discipline present to optimize sampling locations and to ensure that all waste-stream variations are accounted for.

A statistician should be available to review the sampling approach to verify that the resulting data will be suitable for any required statistical calculations or decisions.

Lastly, a quality assurance representative should determine the number of blanks, duplicates, spike samples, and other steps that will be required to document the accuracy and precision of the resulting data base.

Preferably, at least one person will be familiar with the site to be

sampled. If not, then a presampling site visit should be arranged to acquire site-specific information. If no one is familiar with the site and a presampling site visit cannot be arranged, then the sampling plan must be written so that it can address contingencies that may occur.

It is not coincidental that sampling and statistics are discussed interchangeably. This occurs since the goal of sampling and statistics is identical, that is, to make inferences about a parent population based upon information contained in a sample.

Thus it is not surprising that waste sampling relies heavily upon the highly developed science of statistics and that a sampling/analytical effort usually contains the same elements as a statistial experiment. The Harris pollster connects opinions from randomly chosen people while we collect waste from randomly chosen locations or times. The pollster analyzes the information into a usable data base; laboratories analyze our sample and generate data. Then this unbiased data base is used to make inferences about the entire population which, for the Harris pollster, may be the voting population of Yonkers, New York, or, for those involved in waste sampling, the entire population may mean the entire contents of a hazrdous waste landfill.

During the implementation of a sampling plan or a statistical experiment an effort is made to maximize the possibility of making correct inferences by obtaining samples which are representative of a population.

The term "representative sample" is commonly used to denote a sample which (1) has the chemical and physical properties of the population from which it was obtained and (2) has these properties in the average proportions that they are found in the population.

In regard to waste sampling, it should be noted that the term "representative sample" can be misleading unless one is dealing with a homogeneous waste from which one sample can truly represent the whole population. In most cases it is best to consider a "representative data base" generated by an evaluation of more than one sample, which defines the average properties or composition of a waste.

Statisticians have developed a number of strategies, such as random or stratified random sampling, to obtain samples which are unbiased and collectively representative of a waste. These strategies, which are discussed in SW-846, can help your sampling plan withstand scrutiny for purposes of quality control or litigation. Thus, prior to sampling, study Section One of SW-846 and consult your resident statistician.

The sampling plan must also address other factors in addition to statistical considerations. Regarding the waste itself, one must consider the physical state of a waste. Can that sludge waste support the weight of sampling personnel or will a boat or some other means of accessing the waste be required?

What is the volume of waste which has to be represented by the samples you collect? How you approach the sampling of a 40-square-foot lagoon as compared to a 40-acre lagoon will vary substantially in terms of logistics and number of samples collected.

Safety and health precautions and methods of sampling and shipping will very dramatically with the hazardous properties of the waste.

The homogeneity of waste composition and the required degree of variance information needed to achieve program objectives will affect the number of samples to be collected.

Facility-specific factors must be considered when designing a sampling plan. For example, the plan will have to address the accessibility of waste at the chosen sampling locations.

The waste generation process will have to be understood, and the sampling plan will have to address inconsistencies in waste production such as batch processing that may require the sampling to occur at a specified time or at a number of different times to account for waste-stream variation.

The sampling plan should address whether waste generated during startup or maintenance transients should be sampled or avoided.

The sampling plan must also specify climatic and hazard conditions that must be overcome. Field personnel have to be prepared for excessive heat or cold as well as sampling in confined areas such as manholes.

An obvious step in the design of a sampling plan is the choice of sampling equipment and sample containers. The choice of this equipment will be very dependent upon the previously described waste and site considerations.

The analyst will necessarily plan an important role in the selection of sampling equipment. He will be aware of interactions between sampling equipment material and the parameters to be measured and other factors which can affect the integrity of a sample.

By choosing the proper equipment, the analyst will be able to minimize negative contamination, which is the loss of a parameter of interest by volatiliation or adsorption onto container or sampling equipment. The proper choice of equipment will also minimize positive contamination which occurs when leaching from container walls or particle fallout or gaseous air contaminants artificially increase the concentration of a parameter in a waste sample.

The analyst will also assist in choosing sampling equipment that is easily cleaned or is disposable so that cross contamination between samples is minimized.

The chosen sampling device will also have to accommodate the

collection of the required sample volume for analysis.

Deciding factors between sampling devices will be the ease of use and the degree of hazard associated with deployment under the conditions that will be encountered on-site.

Lastly, the cost of sampling devices and the labor costs associated with their deployment must be considered.

Quality assurance can be briefly defined as the process for ensuring that all data and decisions based on these data are technically sound, statistically valid, and properly documented. Quality control procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

Typical quality control procedures that come to mind are:

- trip and field blanks to measure sample contamination during sampling and shipment;
- laboratory blanks to determine contamination during analysis;
- reagent blanks to determine background levels in acids and solvents;
- spike samples to identify and characterize matrix effects;
- field duplicates and spiked duplicates to determine precision;
- check standards to verify calibration throughout the analysis of a sample batch;
- the use of standard reference materials to verify the accuracy of the analytical protocol; and
- surrogate and internal standards to account for sample-to-sample variation.

In addition a good quality assurance program will be responsible for authoring standard operating procedures which will ensure that an essential step is not overlooked during implementation. These standard procedures should cover a sampling effort from the definition of objectives to the submission of samples to the laboratory, at which time the samples will be subjected to the laboratory's standard operating procedures.

Safety and health must also be considered when implementing a sampling plan. A comprehensive health and safety plan has three basic elements: monitoring the health of field personnel, routine safety procedures, and those procedures that one follows when an emergency occurs.

At ENSECO, where employees routinely collect samples in the field and are routinely exposed to chemicals in the laboratory, we have a medical examination at the initiation of employment and annually thereafter. This exam is performed and evaluated by a team of medical doctors that specialize in industrial medicine. The exam consists of those elements of a rigorous physical exam as well as a comprehensive blood chemistry analysis to detect any bodily response to chemical exposure.

Regarding safety procedures, personnel should be instructed in the proper use of safety equipment such as Draeger tube air samplers to detect air contamination as well as the proper use of protective clothing and respiratory equipment. Protocols should also be defined regarding when safety equipment should be employed and the designation of safe areas where facilities are available for washing, drinking, and eating.

Even when the utmost of care is taken, an emergency situation can occur as a result of an unanticipated explosion, electrical hazard, a fall, or exposure to a hazardous substance. To minimize the impact of an emergency, field personnel should be aware of basic first aid and have immediate access to a first aid kit. Thus immediate attention to the injured person can occur while waiting for medical assistance.

Phone numbers for both police and the nearest hospital should be obtained prior to entering the site. Directions to the hospital should also be obtained so that when someone suffers a minor injury they can be taken to the hospital for treatment.

Chain-of-custody procedures document the history of samples and maintain their legal integrity. Unless the sampling is done only for internal use and there is no chance that someone will later want to use the data for other purposes, then you should employ chain-of-custody procedures. Chain-of-custody procedures can be helpful, even when sampling is done only for internal use, since proper chain-of-custody protocols will document pertinent sampling and sample information.

If chain-of-custody procedures are to be followed, then you are responsible for implementing those procedures while the sample is in your possession.

When do you possess a sample? You possess a sample when you are holding it, looking at it after you have been holding it, or you have it locked or sealed in your Igloo cooler, or you have stored it in a secured area which has limited access to authorized personnel.

Where do chain-of-custody procedures start? They start during the design of the sampling plan. The sampling plan must accommodate the time, materials, and labor effort that will be consumed to comply with the documentation protocols.

A minimum chain-of-custody effort would start in the field, when field personnel document in their field notebooks where, why, and how a particular sample was or is to be sampled.

Next the sampler completes a sample label by describing the sample, the sample location, the sampler, and the time and date of collection.

The sample should then be secured under lock. If a lock is not available a seal should be attached to the sample or a cooler in such a fashion that it will have to be broken if anyone tampers with the sample.

Chain-of-custody records must be completed, documenting sample information and all transfers of possession from the time of sample collection up to and including receipt in the laboratory.

Upon receipt in the laboratory, the sample manager will be responsible for completing the chain-of-custody record with a signature, date, and time. He will then inspect the samples for temperature, any unauthorized tampering, and any breakage or leakage. He will record this information and also cross-check the sample descriptions on the chain-of-custody record with those on the individual sample labels. All of this information will then be properly filed for further reference. The samples will be logged into the laboratory's sample management system and stored in a secured area at the appropriate temperature. The analysis of samples will also be confined to restricted access areas.

Now following all that preparation it is time to implement the plan. This is best started with a mental walk through the sampling plan, starting with the preparation of equipment, to the time when samples are received at the laboratory. This mental excursion should be in as much detail as can be imagined. Consider the little things, because these are most frequently overlooked.

It can be guaranteed that by employing this technique you will add at least one more item to your equipment list and may uncover a major oversight in the process.

Next, take a second mental excursion through your sampling plan and try to anticipate what can go wrong. Then decide how you will solve these problems if they do occur. Add to your equipment list the materials necessary for solving these problems.

The equipment list should be comprehensive and leave nothing to memory. The categories of materials that should be considered are:

- personnel equipment, which will include boots, raingear, disposable coveralls, face masks and cartridges, gloves, etc;
- safety equipment such as portable eyewash stations and a first aid kit;
- and field test equipment such as pH meters and Draeger tube samplers.

Regarding the containers, have an ample supply to address the fact that once in the field you may want to sample 50% more samples than originally planned, or you may want to collect a liquid sample while the sampling plan had only specified solids.

Include not only shipping equipment you plan to use, but additional sampling equipment that may be useful if a problem arises. Also include a tool kit.

Shipping and office supplies include items such as tape, labels,

shipping forms, chain-of-custody forms and seals, field notebooks, random number tables, scissors, pens, etc.

After weeks of preparation, the team finally arrives in the field. After towing a boat and trailer 200 miles the sampling team finds that the boat is not necessary since the lagoon to be sampled doesn't contain 2 feet of water as they were led to believe. Worse yet, the lagoon sludge which is to be sampled cannot support the weight of the sampling team.

What can be done? Going home is one alternative but somebody will probably send them back the following week. However, going home and coming back the next week may actually be the optimum solution, if in talking to the facility operators they discover that next week is when the facility plans to excavate the lagoon contents. In this case the sampling team could return the following week and randomly sample buckets of the sludge as it is transferred to trucks.

If the facility is not going to excavate the lagoon, there may be other alternatives. For example, if in touring the facility a crane with a clam shell bucket is discovered, the crane could possibly be employed to collect samples at random locations throughout the lagoon.

If the sampling team determines that the lagoon is not going to be excavated and a crane is not located, another alternative is to randomly sample the perimeter of the lagoon.

This latter approach may actually allow one to meet the objectives, but what you cannot say is that the lagoon has been sampled. The sampling team only randomly sampled that part of the lagoon which is adjacent to the perimeter and the resulting data base is only representative of that sludge. However, if one knows how the lagoon was filled and the properties of the waste as it was disposed you can possibly make some assumptions about the remainder of the sludge.

Regarding the compositing of samples, ENSECO has found it very useful and cost effective to collect component samples in the field and composite aliquots of each sample later in the laboratory. Then after reviewing the data, if any questions arise you can recomposite the samples in a different combination, or analyze each component sample separately to better determine the variation of waste composition over time and space or to better determine the precision of an average number.

SLIDE #1

Definition of Objectives
Sampling Plan Considerations
- Statistical
- Waste
- Site
- Equipment
- QA/QC
- Health and Safety
- Chain of Custody

Sampling Plan Implementation
Compositing

SLIDE #2

DEFINITION OF OBJECTIVES

Need → Objectives

SLIDE #3

WASTE
- As Generated?
- Prior to Mixing?
- Prior to Aging?
- As Disposed?
- Recent vs. Historical?

SLIDE #4

PARAMETERS
- Why?
- Why Not Others?

SLIDE #5

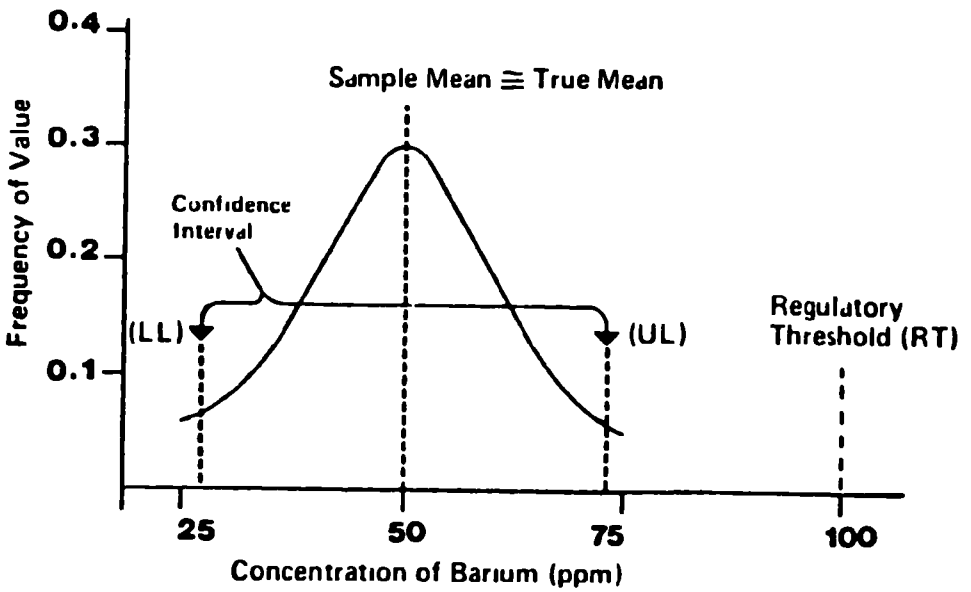
WHY - Delisting Petition
- Monitoring
- Characterization
- Litigation

SLIDE #6

?

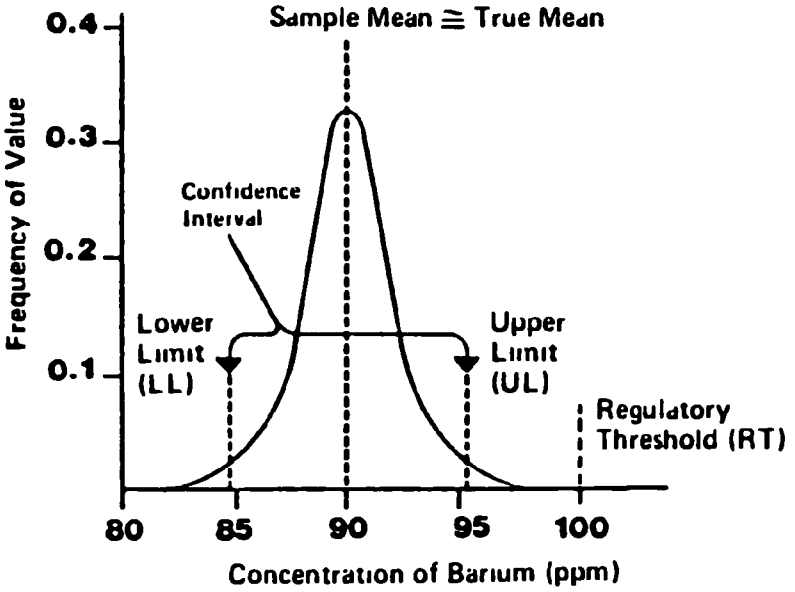
Latex + Phthalate A = Latex + Phthalate A + Phthalate B

SLIDE #7



Distance of true value from regulatory threshold requires less accuracy and precision.

SLIDE #8



Proximity of true value from regulatory threshold requires more accuracy and precision.

SLIDE #9

SAMPLING PLAN: DOCUMENTATION OF OBJECTIVES AND SAMPLING TASKS

Designed by:
- End-User of Data
- Field Team Member
- Analytical Chemist
- Engineering Representative
- Statistician
- Quality Assurance Representative

SLIDE #10

STATISTICAL/SAMPLING CONSIDERATIONS

- Data/Waste Collection
- Data/Waste Analysis
- Inferences

SLIDE #11

REPRESENTATIVE SAMPLE/REPRESENTATIVE DATA BASE

- Chemical and Physical Properties
- Same Proportions

SLIDE #12

WASTE CONSIDERATIONS

- Physical State
- Volume
- Toxicity, Ignitability, Corrosivity, and Reactivity
- Homogeneity Over Time and Space

SLIDE #13

FACILITY/SITE CONSIDERATIONS

- Accessibility
- Type of Waste Generation
- Transitory Events
- Climate
- Hazards

SLIDE #14

SELECTION OF SAMPLING EQUIPMENT

- Negative/Positive/ Cross Contamination
- Sample Size
- Ease of Use
- Safety
- Cost

SLIDE #15

QUALITY ASSURANCE

- Technically Sound
- Stastically Valid
- Properly Documented

SLIDE #16

QUALITY CONTROL PROCEDURES

- Trip/Field/Lab/Reagents Blanks
- Spiked Samples
- Field Duplicates and Spike Duplicates
- Check Standards
- Standard Reference Materials
- Surrogate and Internal Standards

SLIDE #17

STANDARD OPERATING PROCEDURES

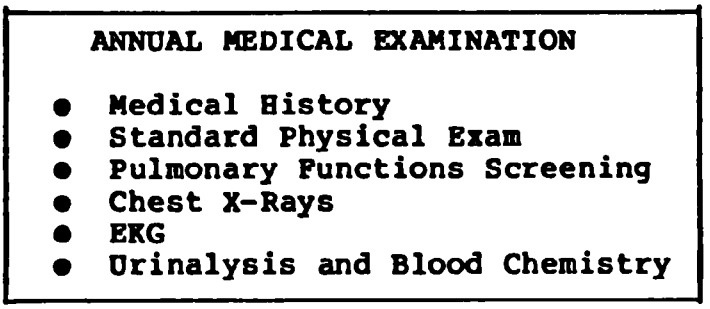
- Definition of Objectives
- Design of Sampling Plan
- Preparation of Containers and Equipment
- Maintenance, Calibration, and Cleaning of Field Equipment
- Sampling Preservation, Packaging, and Shipping
- Chain-of-Custody

SLIDE #18

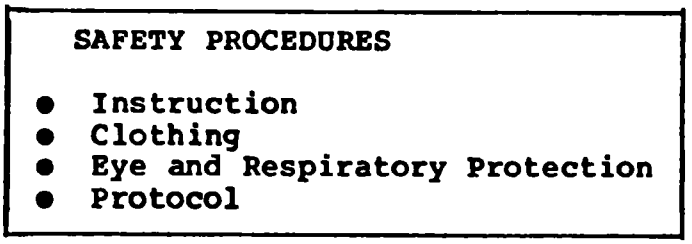
ELEMENTS OF A SAFETY AND HEALTH PLAN

- Health Monitoring
- Safety Procedures
- Emergency Procedures

SLIDE #19



SLIDE #20



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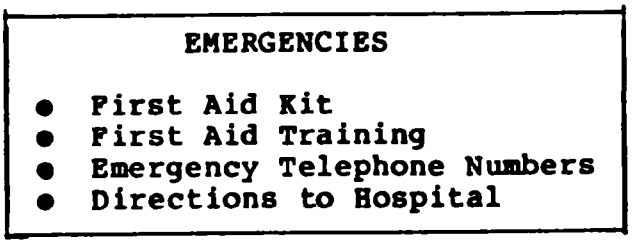

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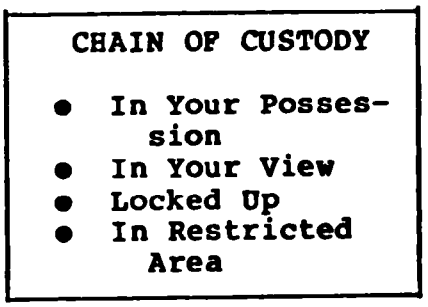


SLIDE #23

CHAIN-OF-CUSTODY SAMPLING PROCEDURES

- Field Notebooks
- Sample Labels
- Seals/Locks
- Chain-of-Custody Forms

SLIDE #24

CHAIN-OF-CUSTODY LABORATORY PROCEDURES

- Receipt and Inspection
- Maintenance and Information
- Sample Logging
- Storage

SLIDE #25

SAMPLING PLAN IMPLEMENTATION

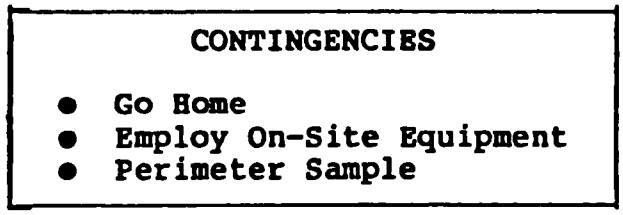
Mental Excursion

SLIDE #26

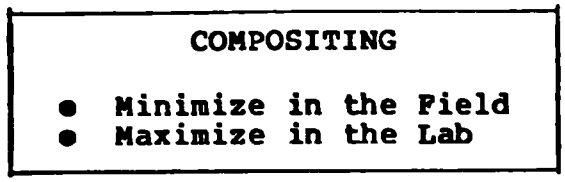
EQUIPMENT LIST

- Personnel Equipment
- Safety Equipment
- On-Site Test Equipment
- Sample Container
- Sampling Apparatus
- Shipping and Office Supplies

SLIDE #27



SLIDE #28



PRACTICAL STATISTICAL CONSIDERATIONS IN DESIGNING A SAMPLING PLAN

JOHN WARREN, OFFICE OF POLICY, PLANNING, AND EVALUATION, U. S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, D. C.

INTRODUCTION

The intent of this paper is to show how differing variabilities at various stages of collecting and analyzing groundwater data can result in a variety of sampling plans. Slides will be used throughout to help the audience visualize the points being made.

PROGRAM STANDARDS

Both standards and interim status standards are found in 40 CFR 264-265:

40 CFR 264 Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities

40 CFR 265 Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities

Sampling and statistics appear in subsections:

264.97 General Ground Water Monitoring Requirements

264.98 Detection Monitoring Program

264.99 Compliance Monitoring Program

264.97 Instructs owner/operator to:

- Install sufficient wells to characterize the background and flow through the site,
- Document a quality assurance program,
- Perform a minimum sampling requirement,
- Use a particular statistical test,
- Or use an equivalent statistical procedure (with permission of the Regional Administrator).

264.98 Instructs the owner/operator to:

- Determine if a statistically significant change

in ground water parameter has occurred.

- Follow the requirements of 264.97.
- Resample the wells if a significant change detected.
- Go to 264.99 if still significant.

264.99 Instructs the owner/operator to:

- Determine if certain concentration limits have been exceeded.
- Follow the requirements of 264.97.
- Resample the wells if a significant difference between sample and concentration limit is found.
- Go to a Corrective Action Program if still significant difference.

But What's the PROBLEM?

Misclassifying a site in either the detection monitoring program or the compliance monitoring program.

False Positive

The site is classified as leaking when in reality it is secure. This is a key concern of owner/operators as further testing to refute the false positive result is expensive and time-consuming. There is also the community-relations problem of disabusing the public of fears of health hazards from a contaminating site.

False Negative

The site is classified as not leaking when in reality it is leaking. This is the key concern of the EPA and the environmentalists.

An ideal test procedure (statistical or otherwise) would have zero false positive/false negative rates. In a less-than-ideal world, a balance has to be struck between the concern of owner/operators - false positives, and the concern of environmentalists - false negatives.

Sources of Variation in Ground Water Monitoring

- Spatial
- Temporal

- Well Construction
- Sample Collection and Chain-of-Custody
- Analytical

Spatial Variation

- Geologic properties of the site.
- Hydraulic flow of ground water.
- Proximity of site to lakes or rivers.
- Proximity of site to other waste sites.
- Multiplicity of aquifers at the site.

Temporal Variation

- Seasonal effects.
- Long-term cycles and trends.
- Floods, rainstorms, and irrigation effects.
- Temperature differences.

Well Construction

- Contamination from drilling.
- Variation in casings (teflon, stainless steel, etc.).
- Screen construction.

Sample Collection and Chain-of-Custody

- Purge and recharge of well-water.
- Rate of removal.
- On-site handling and storing of sample.
- Field quality assurance.

Analytical Variation

- Method of analysis.
- Laboratory contamination.
- Operators/analyst experience.
- Calibration.
- Minimum detection/quantification limits.
- Data reporting requirements.
- Intra/inter laboratory differences.

How Can Variability Be Reduced?

- Spatial variability — Use multiple wells
  - * High cost of construction.
- Temporal variability — Take readings over time.
  - * Difficult as historical records may not exist.
- Well construction — Ensure similarity in well characteristics.
  - * Relatively inexpensive, but needs planning.
- Sample Collection — Ensure consistency in quality assurance plans.
  - * Inexpensive, but needs planning.
- Analytical — Ensure a rigorous laboratory quality assurance plan.
  - * Inexpensive, but needs planning.

Short-Term Improvement in Data Quality by Reducing Variabilities

- Ensure all wells have the same physical characteristics (or as close as possible the same).
- Consistently collect and handle samples in the same fashion (i.e., ensure a good field quality assurance).

- Make sure the laboratory has a rigorous quality assurance plan.
- Try to use the same laboratory for all the analyses.
- Ask the laboratories to use the Minimum Detection Limit procedure as outlined by the American Chemical Society (1980).
- Check the performance of the laboratory by sending identical samples to different laboratories and comparing the results for consistency.
- Plot the data on a graph and visually look for trends in the data.

Background Readings of Barium

(Micrograms Per Liter)

Contractor A

January	84	600	January	85	530
		590			480
		650			470
		620			450
April	84	300	April	85	420
		400			400
		300			470
		390			480
July	84	400	July	85	450
		500			480
		380			430
		450			460
October	84	560	October	85	600
		540			580
		500			540
		540			570

Illustration of How Differing Variables Affect the Characteristization of Groundwater

For illustration, suppose 32 readings are taken on a site by two different contractors:

Contractor A: Takes four samples every 12 weeks from a background

well for 2 years.

Contractor B: Takes two samples every 6 weeks from a background well for 2 years.

The problem an owner/operator must face is which set of readings characterizes the background ground water flow best (recall the requirements under 264.97).

(It is understood the Contractor B will cost more than A due to the extra expense of visiting a site to collect samples not being completely off-set by the increased expense of more sample analyses per visit.)

Long-Term Improvements in Data Quality by Reducing Variabilities

- Increase the number of background and monitoring wells (and therefore reduce spatial variability by better characterizing the flow of groundwaters).

- Increase the frequency of sampling (and therefore reduce temporal variability).

- Improve laboratory effectiveness by sending multiple samples to laboratories (this will reduce the inter-laboratory variability).

- Improve analytical precision and accuracy by demanding the laboratories' use of the Agency's Data Quality Objective Program (and so reduce the intra-laboratory variability).

Background Readings of Barium

(Micrograms Per Liter)

Contractor B

January	84	610	January	85	490
		630			520
March	84	430	February	85	590
		390			620
April	84	370	April	85	400
		310			470
May	84	540	June	85	530
		570			510

July	84	420 430	July	85	460 480
September	84	480 490	August	85	510 520
October	84	540 500	October	85	540 610
November	84	600 630	December	85	460 440

Comparing the Two Contractors

- Contractor A gives more information on laboratory variability than Contractor B (four readings per sampling date as opposed to two readings).

- Contractor B gives more information on temporal variability than Contractor A (sixteen sampling dates as opposed to eight sampling dates).

The "Trade-Off"

- The laboratory variability can be estimated with 24 degrees of freedom (a statistical term) for Contractor A, and with 16 degrees of freedom for Contractor B.

- The temporal variability can be established with 7 degrees of freedom for Contractor A but 15 degrees of freedom for Contractor B.

Statisticians can show that when estimating variabilities; 24 degrees of freedom do not yield that much better answers than 16 degrees of freedom, but 15 degrees of freedom is much more superior than 7 degrees of freedom. The guiding light is that the more variable something is, the more degrees of freedom it needs to "control it."

IN SUMMARY

In purely terms of variability, the probable greatest-to-smallest ordering would be:

- Temporal
- Spatial

- Analytical
- Sample Collection and Chain-of-Custody
- Well Construction

Moral: Owner/operators should concentrate on "reducing" variability by designing sampling plans with the help of a statistician!

FIFTH SESSION

QUALITY ASSURANCE ISSUES

8:00 am - Noon

Friday, July 26, 1985

Chairperson: Florence Richardson
Methods Program
Office of Solid Waste
U. S. Environmental
Protection Agency
Washington, D. C.

DOCUMENTING THE EQUIVALENCY OF PROPOSED METHODS TO APPROVED TEST METHODS FOR EVALUATING SOLID WASTE

Dr. L. R. WILLIAMS, U.S. ENVIRONMENTAL PROTECTION AGENCY-EMSL, LAS VEGAS, NEVADA

ABSTRACT

The U.S. EPA, in its quest for environmental data of known high quality, has proposed formal processes for validating standardized measurement methods and for demonstrating the equivalency of alternative procedures. This paper addressed the method equivalency process.

Just as method validation procedures are driven by the data quality objectives of the client office (e.g., the Office of Solid Waste), so too are the procedures for demonstrating the equivalency of methods proposed as alternative to those methods currently in "Test Methods for Evaluating Solid Waste" (SW-846). Several factors govern the degree of complexity and formalism that an equivalency testing program shall take. These depend upon the purpose and extent of the intended use of the method and the amount of existing information that supports the petitioner's claim for equivalency. Appropriate experimental designs and statistical prpocedures are discussed. Minimum data requirements for establishing equivalency are presented and discussed.

USE OF PERFORMANCE BASED QUALITY CONTROL CRITERIA IN THE SUPERFUND CONTRACT LABORATORY PROGRAM

GARETH PEARSON, U. S. ENVIRONMENTAL PROTECTION AGENCY-EMSL, LAS VEGAS, NEVADA; AND MICHAEL T. HOMSHER AND FOREST C. GARNER, LOCKHEED ENGINEERING AND MANAGEMENT SERVICES COMPANY, INC., LAS VEGAS, NEVADA

ABSTRACT

Performance based quality control criteria are quality control criteria developed from the data generated through the actual use of a specific analytical protocol under actual operational conditions. When applied to contract analytical laboratories providing analytical services to the usepa's superfund contract laboratory program (CLP), these criteria can be used to assess data quality and evaluate laboratory and method performance. The rationale, development, calculation, and use of performance based quality control criteria in the clp will be presented. A detailed discussion of the development and use of performance based surrogate recovery criteria for the GC/MS analyses of volatile and semivolatile organic compounds in water and soil/sediment will be presented. The benefits and application to additional quality control criteria will be discussed. .

A NATIONAL VOLUNTARY LABORATORY ACCREDITATION PROGRAM FOR ENVIRONMENTAL MEASUREMENTS

PETER S. UNGER, NATIONAL BUREAU OF STANDARDS, U. S. DEAPRTMENT OF COMMERCE, GAITHERSBURG, MARYLAND

ABSTRACT

The State of Indiana Environmental Management Board requested that the National Bureau of Standards (NBS) establish under its National Voluntary Laboratory Accreditation Program (NVLAP) a laboratory accreditation program (LAP) for hazardous waste analysis in accordance with methods approved by the U.S. Environmental Protection Agency (EPA). Under the NVLAP procedures, NBS is requesting public comments on the need for a LAP which may eventually include the whole range of environmental measurements. A decision will be made later in 1985 on whether to proceed with development of a LAP.

This paper provides an overview of NVLAP, summarizes the comments on the State of Indiana request, reviews related accreditation efforts in the environmental testing field, and indicates the role that NVLAP might play.

INTRODUCTION

The Department of Commerce, National Bureau of Standards (NBS) administers the National Voluntary Laboratory Accreditation Program (NVLAP). NVLAP was established in 1976 to serve government and industry needs for evaluating laboratories and accrediting those found competent to perform specific test methods in certain fields of testing.

NVLAP's goals are to:

- Provide national recognition for competent laboratories;
- Provide laboratory management with a quality assurance check;
- Identify competent laboratories for laboratory users; and
- Provide laboratories with guidance from technical experts to improve their performance.

NVLAP is comprised of a series of laboratory accreditation programs (LAPs) established based on requests and demonstrated need. More than 160 laboratories are currently participating in the nine LAPs that have been established. Although NVLAP has primarily been involved with narrowly-focused product testing laboratory accreditation, NBS is able to establish broadly-defined LAPs. NBS is not restricted to a

product-by-product approach in the normal definition of that term. The NVLAP procedures are flexible enough to adjust to government and industry needs as they may arise. The acoustical testing services LAP and the commercial products LAP, which are established and operational, are two examples of broadly-defined LAPs. For the topic at hand, the LAP could cover the full range of environmental testing services.

If a LAP is broadly defined, this does not mean that we will offer a broad-brush, general, or subjective accreditation. We insist on having a credible, quality program based on documentation and accreditation to established standards and test methods. Each laboratory is accredited for its capability to perform one or more specific test methods offered within each LAP. This approach is the fundamental basis of our bilateral mutual recognition agreements with three foreign national laboratory accreditation systems.

NVLAP accreditation is granted based on conformance with generic criteria published in the Code of Federal Regulations as part of the NVLAP procedures (15 CFR Part 7). The criteria are similar to those found in the International Organization for Standardization (ISO) Guide 25: "General Requirements for the Technical Competence of Testing Laboratories." The criteria address a laboratory's quality system, staff, facilities and equipment, calibration procedures, testing procedures, records, and test reports. Specific technical requirements are developed for each LAP to address the particular testing technologies involved. Participation in workshops to develop specific LAP requirements is open to all interested parties.

NVLAP ACCREDITATION PROCESS

Accreditation is granted following successful completion of a process which includes submission of an application and payment of fees by the laboratory, on-site assessments (similar to laboratory system audits conducted by the U.S. Environmental Protection Agency (EPA)), successful participation in proficiency testing (similar to performance audits administered by EPA), resolution of any identified deficiencies, and periodic technical evaluation and administrative review for initial and renewed accreditation.

For a more detailed description of the NVLAP accreditation process, see Appendix I.

STATE OF INDIANA REQUEST

Under the NVLAP procedures, a LAP can only be established in response to a formal written request and based on demonstrated need. In a letter of August 24, 1984, the State of Indiana Environmental Management Board requested that NBS establish a LAP for hazardous waste analysis. After informally consulting with EPA personnel, NBS decided to publish the request for public comment. The notice appeared in the Federal Register on February 20, 1985. EPA requested

an extension of the 60-day comment period beyond the date of the Solid Waste Testing and Quality Assurance Symposium (July 24-26, 1985) to give symposium participants the opportunity to express and submit their views. Accordingly, NBS deferred its decision regarding the need for and development of a LAP until after the symposium.

SUMMARY OF COMMENTS RECEIVED TO DATE

A total of 33 letters (representing 29 organizations) commenting on the need for a LAP were received as of July 9, 1985. Of the 29 organizational comments, 24 are positive, four are conditionally positive, and one is negative. The positive respondents cite the role the LAP could have in improving the consistency of the testing and resultant test data, integrating the various efforts of the states, and supporting regulatory decisions. The conditionally positive respondents agree with the need for a LAP, but have reservations or suggest alternatives. The one negative respondent states that current efforts by EPA and the states are in place and work satisfactorily. Table 1 shows the number of comments by type of organization:

Type of Organization	Positive	Conditionally Positive	Negative
Prof./Trade Association	4	3	
Testing Laboratories	5	1	1
Private Industry	6		
State Government	9		
Total	24	4	1

Of particular significance, the nine states that responded all support establishment of a LAP. Seventeen of the total number of respondents indicated that there is a need for an accreditation program to cover all environmental measurements. An identification of the 29 organizations and excerpts from their comment letters are set out in Appendix II.

RELATED EFFORTS CONCERNING ENVIRONMENTAL LABORATORY ACCREDITATION

Approving or accrediting laboratories to perform measurements related to environmental protection is not a new issue. Over the past decade, questions of both a general and specific nature have been raised, though they are not limited to the hazardous waste area. In 1975, the American Public Health Association (APHA) issued a policy statement expressing concern over the need for the establishment of standards of performance for environmental laboratories. The policy statement discussed the various efforts being made to evaluate environmental laboratories and concluded by saying:

> The efforts underway, comparable though they may be, differ

> in specific approach, in definition of environmental laboratories, especially in types of laboratories included, in voluntary versus compulsory regulation, and in regulatory agency, that is, professional society or state and federal government. If a non-integrated approach continues, a chaotic condition will no doubt result. The history of all regulatory actions emphasizes the need for a uniform solution to a common problem.

In the view of some, this prognosis has come to pass.

APHA sponsored a National Conference on the Establishment of Standards of Performance for Environmental Laboratories on May 1-3, 1978. The conference participants "overwhelmingly voted approval of the 10 recommendations to establish a mandatory system." Excerpts from four of the recommendations are noteworthy:

1. Standards should be developed as a national level in order to provide uniformity and to eliminate duplication of standards and inspection.

2. A single federal agency should be responsible for standards for all environmental laboratories...

4. Implementation and administration of national standards should be carried out at the state level...

9. The administration of standards should be carried out in a manner which eliminates duplication of activity and provides reciprocity among all the states.

The first official EPA recognition that approval must be given to laboratories to ensure valid results for compliance testing came with the National Interim Primary Drinking Water Regulations, proposed in 1975. These regulations require laboratories testing for compliance under the Safe Drinking Water Act be performed by laboratories approved either by EPA or those states with primary enforcement responsibility (primacy states). The EPA program is described in the "Manual for the Certification of Laboratories Analyzing Drinking Water," which was first published in May, 1978. This manual serves as a guide to the states for implementing "laboratory certification programs" for drinking water. There are no comparable EPA manuals for other types of environmental testing. The criteria and critical elements for drinking water laboratory certification in the EPA manual are similar to what NBS prepares when developing a LAP under NVLAP. Similar documentation is needed for hazardous waste analyses and other types of environmental testing.

Several states have established water laboratory approval programs (as early as 1950 in the case of the State of California) and have established or are developing programs for other types of environmental testing. A recent example is the rule proposed by the State of Wisconsin Department of Natural Resources, currently undergoing public comment, which will establish a "laboratory

certification/registration program...applicable to commercial, municipal, and industrial laboratories that analyze wastewater, groundwater, surface water, hazardous substances, hazardous waste and sediments." The comment period on the proposed rule is scheduled to end on July 29, 1985.

The status of reciprocal recognition agreements among the states for their programs has not been ascertained by this author, but it is a major issue. The American Council of Independent Laboratories (ACIL) has indicated that many commercial laboratories need approval from many of the states in which they offer their services. Each state program can require its own formal application, fee payments, proficiency testing, and on-site assessments. ACIL has indicated that these multiple accreditation programs are a costly and unnecessary duplication of effort and that a credible national system is needed that can be accepted by the states in lieu of their own systems.

Two organizations submitted comments to NBS identifying themselves as alternative laboratory accreditation systems that can operate on the national level. The National Sanitation Foundation (NSF) indicated that it is implementing a drinking water laboratory accreditation program and plans to develop programs in waste water and solid waste. NSF submitted documentation to NBS on its program procedures and requirements for drinking water laboratories. NSF staff has indicated that the necessary documentation for hazardous waste laboratories has not been developed yet, but have indicated an intent to do so.

The American Association for Laboratory Accreditation (AALA) indicated that it has accredited laboratories for water quality testing and is available to offer accreditation in other areas of environmental testing. However, AALA did not respond to an NBS request for written documentation on its accreditation program for environmental testing laboratories so we are unable to assess how its program might meet the need.

HOW A LAP MIGHT OPERATE

NVLAP staff has had several informal discussions with EPA officials about the State of Indiana request and how best to proceed. A concept for a joint EPA/NBS effort to develop and administer a LAP is set out in Table 2. The estimated annual costs for operating a LAP, based on NBS experience, range between $2,300 to $3,400 per laboratory. Table 2 shows:

I. EPA/NBS Joint Role

- Develop technical requirements for accreditation to ensure that they are consistent with environmental laws and regulations.
- Determine desired frequency of on-site assessments (system audits).
- Design assessment protocols, checklists, etc.

- Recruit, select, and orient technical experts to perform assessment and evaluation functions and schedule assessments.
- Determine frequency of proficiency testing (performance audits) and pass/fail criteria.

II. EPA Role

- Administer proficiency testing (performance audits).
- Evaluate assessment (system audits) reports and proficiency test results.
- Formulate accreditation recommendations.

III. NBS Role

- Prepare announcements about the LAP and distribute application forms, handbooks, and other information about the LAP.
- Receive and process applications and fees from participants.
- Disburse funds to cover costs of assessment, proficiency testing, evaluation and other administrative costs of the LAP.
- Receive recommendations and issue accreditation certificates.
- Publish directories of accreditated laboratories and supplements.

CONCLUSION

Based on the comments on the State of Indiana request received so far, there appears to be a need for a national laboratory accreditation system for hazardous waste analysis. There is also an indication that such a program should cover all types of environmental testing. Whether NBS proceeds to fill this need by developing a LAP will depend on a final analysis of comments received as well as the position that EPA takes on the matter. If appropriate, NBS is willing to enter into an interagency agreement with EPA or make suitable arrangements with the states which are interested in using NVLAP for their own programs. NBS is prepared to host public workshops to develop the technical requirements for such a LAP.

The integrated approach to solve the problem of recognizing competent environmental laboratories, suggested by the American Public Health Association 10 years ago, has not been realized. Some would argue that ten years later we are no further along to a "uniform solution to a common problem" and that we have a "chaotic condition" as a result. We cannot fully support this view. Our country is a pluralistic society which enables it to create several solutions to common problems. We believe that NVLAP can be one of these solutions.

REFERENCES

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Letter from the American Association for Laboratory Accreditation, signed by Foster C. Wilson, Chairman of the Board, to Stanley I. Warshaw, Director, NBS Office of Product Standards Policy, March 20, 1985.

Appendix I

THE NVLAP ACCREDITATION PROCESS

BACKGROUND

The U.S. Department of Commerce, National Bureau of Standards (NBS) administers the National Voluntary Laboratory Accreditation Program (NVLAP). NVLAP's function is to accredit public and private testing laboratories based on evaluation of their technical qualifications and competence for conducting specific test methods in specified fields of testing. Accreditation is granted based on conformance with criteria published in the Code of Federal Regulations as part of the NVLAP procedures (15 CFR Part 7).

NVLAP accreditation is available to commercial laboratories, manufacturer's in-house laboratories, university laboratories, Federal, State, and local government laboratories. Foreign-based laboratories may also be accredited by NBS if they meet the same requirements as domestic laboratories and pay any additional fees required.

NVLAP is comprised of a series of laboratory accreditation programs (LAPs) established based on requests and demonstrated need.

NVLAP accreditation means recognition of a testing laboratory's competence to perform specific test methods in specified fields of testing. It means that the laboratory's quality system, staff, facilities and equipment, calibration procedures, test methods and procedures, records, and test reports, have been evaluated and found to meet NVLAP criteria. NVLAP accreditation does not mean a guarantee (certification) of laboratory performance or product test data; it is a finding of laboratory competence.

For accreditation to be meaningful, it must be granted by a clearly credible organization. NVLAP provides an unbiased third party evaluation and recognition of performance as well as expert technical assistance to upgrade laboratory performance.

OVERVIEW

Accreditation is granted following successful completion of a process which includes submission of an application and payment of fees by the laboratory, on-site assessments, resolution of identified deficiencies, participation in proficiency testing, and periodic technical evaluation and administrative review for initial and renewed accreditation.

APPLICATION AND FEES

An Application Package is sent to a laboratory on request. It includes: General Application Forms, a Fee Calculation Sheet, and one or more LAP Handbooks, which describe the requirements of the LAPs. The General Application Form must be completed and signed by an authorized representative of the laboratory. The authorized representative is one who can act on behalf of the laboratory and commit it to fulfill the NVLAP requirements. Before completing and signing the application, the authorized representative should review all documents and become totally familiar with NVLAP requirements. Although other laboratory staff may be designated to perform activities, such as handling proficiency testing or receiving an assessor, the authorized representative is the only one who can authorize a change in the scope or nature of the application.

In general, the accreditation fee is composed of several parts, some of which are fixed while others depend on the scope of accreditation desired and the specifics of the LAP. The total accreditation fee must be paid before accreditation can be granted.

The laboratory will be scheduled for an on-site assessment after payment of all required fees and will be notified of any additional information which must be supplied and of any applicable proficiency testing requirements which must be completed for the technical evaluation.

APPROVED SIGNATORY

Under NVLAP criteria, an accredited laboratory must have one or more individuals or laboratory positions designated as having responsibility for signing "all test reports endorsed with the NVLAP logo." This is the person(s) to whom NVLAP, laboratory clients, or others would go in case of questions or problems with the report.

There is no formal requirement for nomination or approval of persons or laboratory positions designated as approved signatories. The laboratory should inform NVLAP of its appointments by completing the appropriate sections in he application for accreditation. Approved signatories should be: persons or positions with adequate responsibility or authority within the organization, with adequate and appropriate technical capabilities, and without conflict of interest.

Laboratory test reports carrying the NVLAP logo need not be signed individually by the approved signatory. Test report forms may be preprinted with the required information. Forms that are electronically or computer generated may have the information printed along with the test results.

TECHNICAL EXPERTS

NVLAP uses Technical Experts (TEs) as assessors and evaluators. These are individuals knowledgeable in the testing field being evaluated.

They may be engineers or scientists currently active in the field, consultants, college professors or retired persons. They are selected on the basis of their professional and academic achievements, experience in the field of testing, management experience, and tact in dealing with people. Their services are generally contracted as required; they are not NVLAP staff members.

Assessors are TEs selected to conduct an on-site assessment of a particular laboratory on the basis of how well their individual experience matches the type of testing to be assessed, as well as absence of conflicts of interest. The laboratory has the right to appeal the assignment of an assessor and may request an alternate.

Evaluators are TEs selected to review the record of the laboratory as a whole, including the application, assessment report, deficiencies, corrections to deficiencies, and proficiency test results and, based on this record, to recommend whether or not a laboratory should be accredited. The evaluators are matched to the type of testing being evaluated and are selected to avoid conflicts of interest.

ON-SITE ASSESSMENT

Before initial accreditation and periodically thereafter, an on-site assessment of each laboratory is conducted to determine compliance with the NVLAP criteria. The assessment is conducted by one or more NVLAP assessors selected on the basis of their expertise in the field of testing to be reviewed. Assessors use checklists developed by NVLAP so that each laboratory receives an assessment comparable to that received by others. However, assessors have considerable latitude to make judgments about a laboratory's compliance with the NVLAP criteria, depending on the assessor's experience and the unique circumstances of the laboratory.

Each laboratory will be contacted to arrange a mutually agreeable date for an assessment. The time needed to conduct an assessment varies, but two days is the norm. Every effort is made to conduct an assessment with as little disruption as possible to the normal operations of the laboratory. During the assessment the assessor will carry out the following functions:

- Meet with management and supervisory personnel responsible for the laboratory's activities (for which accreditation is being sought) to review the assessment process with the individuals involved and to set the assessment agenda.

- Examine the quality assurance system employed by the laboratory. The assessor may select and trace the history of one or more samples from receipt to final issuance of test reports. The assessor will conduct a thorough review of the laboratory's quality manual or equivalent, evaluate the training program, examine notebooks or records pertaining to the samples, check sample identification and tracking procedures, determine whether the appropriate environmental

conditions are maintained, and examine copies of completed test reports.

- Review records of periodic internal audits, use of check samples or participation in round robin testing or other similar programs.

- Review personnel records including resumes and job descriptions of key personnel, competency evaluations for all staff members who routinely perform the testing for which accreditation is sought, calibration or verification records for apparatus used, test reports, and sample control records.

- Observe demonstrations of testing techniques and discuss them with the technical personnel to assure their understanding of the procedures.

- Examine major equipment, apparatus, and facilities.

At the conclusion of the assessment, the assessor will conduct an exit briefing to discuss his or her observations with appropriate laboratory staff and call attention to any deficiencies uncovered. A written summary of any deficiencies discussed will be left at the laboratory. The assessor will forward the assessment forms and a written summary to NBS.

If deficiencies have been noted, the laboratory must, within 30 days of the date of this notification provide NVLAP with documentation or certification, by the authorized representative, that the specified deficiencies have been corrected or that specific actions are being taken to correct the deficiencies.

A laboratory applying for initial accreditation may request an extension to complete required corrections.

If any deficiencies are noted at laboratories which are currently accredited, such deficiencies must be corrected within 30 days after notification or the laboratory may face possible revocation, suspension, or expiration of its accreditation. Any test equipment that is identified as out-of-calibration, should not be used until corrective action has been completed. All deficiencies noted for corrective action will be subject to thorough review and verification during subsequent assessments and technical evaluations.

MONITORING VISITS

In addition to regularly scheduled assessments, monitoring visits may be conducted by assessors or by NBS staff at any time during the accreditation period. Monitoring visits may occur for cause or on a random selection basis. These visits serve to verify reported changes in the laboratory's personnel, facilities, and operations or to explore possible reasons for poor performance in proficiency testing.

The scope of a monitoring visit may range from checking a few designated items to a complete review. Failure to cooperate with NVLAP assessors will be grounds for initiation of adverse accreditation action. No additional fee is required for the monitoring visit.

PROFICIENCY TESTING

Proficiency testing is an integral part of the NVLAP accreditation process. Demonstration of appropriate facilities, equipment, personnel, etc. is essential, but may not be sufficient for the evaluation of laboratory competence. The actual determination of test data using special proficiency testing samples provides NVLAP with a way to determine the overall effectiveness of the laboratory.

Proficiency testing is a process for checking actual laboratory testing performance, usually by means of interlaboratory comparisons. Each LAP has unique proficiency testing requirements. The data are analyzed by NVLAP and summary reports of the results are sent back to the participants.

For many test methods, results from proficiency testing are very good indicators of a laboratory's testing capability. Information obtained from proficiency testing helps to identify problems in a laboratory. When problems are found, NVLAP staff members work with the laboratory staff to solve them. If problems with the test method are suspected, NVLAP provides information to the appropriate standards-writing bodies.

TECHNICAL EVALUATION

After a laboratory has completed all the technical requirements of a LAP and is ready for an accreditation action, a final technical evaluation is conducted by experts chosen for their experience and knowledge of the pertinent test methods. They review records on each applicant laboratory and base their evaluation on:

- information provided on the application;
- on-site assessment reports;
- actions taken by the laboratory to correct deficiencies;
- results of proficiency testing; and
- information from any monitoring visits of the laboratory.

If the technical evaluation reveals additional deficiencies, written notification describing them will be made to the laboratory. The laboratory must respond within 30 days of such notification and

provide documentation or certification by the authorized representative that the specified deficiencies have been corrected. Clarification of some issues may be requested by telephone. All deficiencies must be corrected before accreditation can be granted or renewed.

ADMINISTRATIVE REVIEW

After the technical evaluation has been completed, the NVLAP staff prepares an administrative recommendation that the laboratory either be granted or denied accreditation. This recommendation is based on a review of the technical evaluation and other records to ensure that all NVLAP technical, financial and administrative obligations have been satisfied.

ACCREDITATION ACTIONS

Acting for the Director of NBS, the Director of the NBS Office of Product Standards Policy makes the following decisions:

Accreditation	If accreditation is recommended, the recommendation forms the basis for granting accreditation. A Certificate of Accreditation will be issued to the laboratory.
Denial	If denial is recommended, the laboratory is notified of a proposal to deny accreditation and the reason(s) therefor.
Suspension	If a laboratory is found to have violated the terms of its accreditation, the accreditation can be suspended. The laboratory will be notified of the reasons for and conditions of the suspensions and the action(s) that the laboratory must take to have accreditation reinstated.
Revocation	If a laboratory is found to have violated the terms of its accreditation, the laboratory is notified of a proposal to revoke accreditation and the reasons therefor. The laboratory may be given the option of voluntarily terminating accreditation. If accreditation is revoked, the laboratory must return its Certificate of Accreditation and cease use of the NVLAP logo on any of its reports, other correspondence, or advertising.

If denial or revocation has been proposed, the laboratory may request a hearing, under United States Code 5 U.S.C. 556, within 30 days of the date of receipt of the notification. If a hearing is not requested, the action becomes final upon the expiration of that 30-day period.

After a participant's accreditation has been terminated, whether voluntarily or through adverse action, the accreditation certificate must be returned to NVLAP. If a laboratory elects not to renew or wishes to voluntarily terminate its accreditation at any time, the notification of such intention should be forwarded to NBS in writing.

ACCREDITATION PERIOD

Accreditation is granted for a period specified for each LAP (usually one year). The accreditation period begins on one of four dates: January 1, April 1, July 1, or October 1. Once a laboratory has been assigned an accreditation date, it retains that date as long as it remains in the program. Accreditation expires and is renewed on that date.

RENEWAL

Each participating laboratory is sent a renewal application package, well in advance of the expiration date of its accreditation, to allow sufficient time to complete the renewal process. The renewal application contains the same forms used for initial application, and the laboratory need only indicate where changes have occurred from the previous period in personnel, equipment, facilities, or the scope of accreditation desired.

With the exception of an initiation fee for new applicants, the technical requirements and fees are the same as for initial accreditation. The application and fees must be received by NBS prior to expiration of the laboratory's current accreditation to avoid a lapse in accreditation.

SUMMARY AND EXCERPTS OF COMMENTS
ON
PROPOSED LABORATORY ACCREDITATION PROGRAM FOR HAZARDOUS WASTE ANALYSIS

On February 20, 1985, the National Bureau of Standards published in the Federal Register (50 FR 7095-7096) a request from the State of Indiana Environmental Management Board to establish a laboratory accreditation program (LAP) for hazardous waste testing laboratories. The notice requested that public comments on the need for the proposed LAP be sent to NBS by April 22, 1985. The U.S. Environmental Protection Agency requested that the comment period be extended beyond the July 24-26 symposium on solid waste testing and quality assurance to allow symposium participants the opportunity to consider the need for laboratory accreditation in this area. The comment period was extended at least one month beyond the symposium.

NBS has received letters from 29 organizations commenting on the need for the proposed LAP. Twenty-four of the responses are positive, four are conditionally positive, and one is negative. The positive responses emphasize the role the LAP will have in improving the consistency of interpretation of the test technology and resultant test data, integrating the various efforts currently underway, and supporting regulatory decisions. The conditionally positive responses agree with the need for a LAP, but have reservations or suggested alternatives. The negative response indicates that current efforts by EPA and the states are in place and work satisfactorily.

The following are excerpts of the 29 responses received so far.

Positive Responses (24)

International Association of Waste Management Professionals
--"supportive of the concept" -- of an accreditation program

Grocery Manufacturers of America, Inc.
--such a LAP would be "important to maintain laboratory performance, to ensure the interlaboratory consistency of analytical results, and to assure the public that they can have confidence in the analytical data available for regulatory decisions."
--"The proposal...describes an important need for accredited analytical services...Since no system of accreditation presently exists, NBS should establish the requested LAP..."
--"immediate priority should be given to the LAP for hazardous waste analysis. The scope can be expanded to other environmental concerns at a later date."

National Environmental Health Association
--"the general concept of the proposal appears to be consistent with what this professional society has been recommending in

the way of practices designed to improve the quality of our environment."

Wabash Valley Environmental Association, Inc.

—"An environmental LAP developed and administered at a national level would be a benefit and a service to the regulator, the regulated community and the public. Administration at the national level is necessary since environmental analysis is conducted as interstate commerce."

—"development of an environmental LAP by NBS will lead to sounder environmental control and will provide a much needed assurance...that the analytical results on which so many environmental decisions are based are made on valid analytical results."

—"a LAP should be developed first for the area of hazardous waste...The hazardous waste program has at its heart specific and detailed analytical and sampling protocols on which the critical decisions to include or exclude a waste in the hazardous waste system hinge. The liabilities both financial and health-related incurred by an incorrect decision based on analysis using incorrect protocols demand the development of a hazardous waste LAP as a top priority."

—"A LAP for hazardous waste is also important with the recent expansion of RCRA to include small quantity generators. These individuals will undoubtedly have to rely on commercial laboratories for analytical support."

EMS Laboratories, Inc.

—"wholeheartedly support the concept of laboratory accreditation ...The need for a greater degree of uniformity and credibility in all areas of environmental testing manifests itself more each day."

—"Many of the test methods for the analysis of solid and hazardous wastes are similar or identical to those for the analysis of water and wastewater. It seems appropriate, therefore, to develop a LAP which could encompass "the whole range of environmental measurements" as has been proposed..."

—"such a program would save time for State and Federal regulatory personnel and would save money for users of laboratory services. Frequently, we are called upon to generate and submit a variety of ancillary data with our laboratory reports and the generation and review of this data is time-consuming for everyone concerned. It also increases the cost."

National Laboratories, Inc.

—"strongly support the request..."

—"it is entirely conceivable that many violations can be attributed to unreliable analytical data. A requirement of certification of analytical data, accompanied by the certification number of the laboratory could have a salutory effect on business for those laboratories that are serious in their efforts to provide reliable, reproducible data."

—"Whatever the cost, and however it is accomplished, it should be done by an agency which is independent of the regulatory

agencies and of the private laboratories. Under the present (non) system, it is easy for hearing officers to ignore any facts which are in opposition to the regulatory agency's position."

Northern Laboratories, Inc.

—"development of an accreditation program for the analysis of hazardous materials would be of great benefit to the laboratories performing the analysis and users of these laboratories alike to assure that reproducible results can be obtained regardless of where or when the analysis is performed. Laboratories would have greater confidence in their procedures and users of these laboratories could be confident that the work they are having performed would be acceptable to regulatory agencies."

—"Accurate and consistent test results achieved by approved laboratories are a necessary first step in the design of a comprehensive program of hazardous waste site evaluations and clean-ups."

Environmental Consultants

—"the request...has merit and should be considered."

—"The need is clearly present to consolidate all external laboratory evaluations under one program, where all interested laboratories can participate."

—"Most important to the commercial laboratory services industry is a well-defined protocol for becoming an accredited laboratory in environmental analyses, and it will equally be beneficial to State environmental programs to be able to identify those facilities which are qualified."

—"would benefit the commercial laboratory industry by eliminating the current confusion over 'Certified' reporting."

Pollution Control Systems Incorporated

—"voice our support..."

—"would standardize the procedures being used for the analysis of hazardous waste and decrease interlaboratory variations in procedures and results."

—"standardize the interpretation of 40 CFR Part 261."

Chevron U.S.A., Inc.

—"strongly endorse NBS rapidly establishing a LAP for waste analysis."

—"would ensure the quality control of local laboratories..."

—"could provide monitoring of waste analysis data quality and provide a statistical database to develop real precision statements for the EPA SW-846 methods."

—"would weed out incompetent laboratories and improve day-to-day documentation and practices for quality laboratory measurement."

—"would be an incentive for laboratories to develop and sustain a high level of performance."

—"EPA and some states have proficiency testing for RCRA and CERCLA, however, these programs are not developed for general waste characterization on a national scale."

—"NBS is the proper disinterested third party to develop a LAP."

Cummins Engine Company, Inc.

—"it would be very desirable for both producers and consumers of analytical services if there were a universally recognized national accreditation program which would help assure that the analytical results produced in support of solid waste management activity are as accurate as possible."

—"it would be desirable to expand the scope of any accreditation program beyond the limit of solid waste procedures to include all aspects of environmental analytical testing."

Dow Chemical U.S.A.

—"laudable to verify the consistency and equivalence of testing being performed throughout the country."

—"encourages use of standards from ASTM D-34."

Duke Power Company

—"such a program is warranted and would offer many advantages."

—"would assure that analytical results for hazardous wastes throughout the country were obtained using consistent and equivalent methods."

—"Present variability between laboratories performing these analyses would be decreased. Interpretation of test methods found in 40 CFR Part 261 would also become more consistent."

—"the burden and the subsequent liability of selecting and/or not selecting a reputable laboratory, would be diminished for the generator of hazardous wastes."

SOHIO The Standard Oil Company

—"support expanding NVLAP into the area of environmental testing."

—"a real need for this type of program in all of the environmental testing subgroups (air, wastewater, drinking water, solid waste, etc.). However, each should be addressed independently."

Sylvania Chemicals/Metals

—"would welcome the opportunity for accreditation..."

—"Our interest...would be best served by a modular approach..."

State of Connecticut Department of Environmental Protection

—"supports...proposal to establish an environmental testing laboratory accreditation program (LAP)..."

—"would prefer that such a program not be limited to hazardous waste analyses, but rather also include air and wate analyses for specific toxic compounds..."

—"such a program 'should' be at least partially supported by user fees."

—"such a LAP would fill an existing nationwide need and would be a giant step toward consistency in state and federal hazardous waste and toxic pollutant analyses policies."

State of Delaware Department of Natural Resources & Environmental Control

—"fully supports the request..."

—"would serve two valuable purposes: assurance of the accuracy of data so that the environment may be effectively protected, and assurance that laboratories will take the safety precautions appropriate to protect their employees, the general public, and the environment from the consequences of the testing process itself."

State of Florida Department of Environmental Regulation
—"concurs with the...request..."
—"support the suggestions to expand the laboratory accreditation program to include air, water, and solid waste, as well as hazardous waste."

State of Georgia Department of Natural Resources
—"wishes to add its support to a voluntary laboratory accreditation program (LAP) to be promulgated by the National Bureau of Standards. The need is urgent and the problems are diverse."

Commonwealth of Kentucky Natural Resources and Environmental Protection Cabinet
—"wholeheartedly support a national accreditation program for hazardous waste laboratories."

State of Maine Department of Environmental Protection
—"express this Bureau's support for the laboratory accreditation program for hazardous waste...also urge that consideration be given to expanding the concept to include accreditation for analyses needed to comply with or administer other EPA programs in addition to RCRA."
—"This Bureau has had undesirable experiences, including non-productive use of our resources and misunderstandings... resulting from questionable analyses for hazardous waste parameters."
—we are "considering the creation of a State approval system... there is a widespread perception that some such program is needed."
—"Clearly it would be desirable to have a nationally uniform system of accreditation, even if there were to be significant state participation. Having uniform criteria, evaluation instruments, audit sample programs and so forth would better ensure an effective program and consistency and facilitate reciprocity."

State of Maryland Department of Health and Mental Hygiene
—"there is a need to support such a program so proper and uniform methodologies and procedures would be used nationwide in the testing of hazardous wastes."

Missouri Department of Natural Resources
—"An accreditation program encompassing all environmental measurements as well as hazardous waste would be a welcome activity from our perspective...from the perspective of the regulated community."

--"We in the environmental regulatory field depend heavily on analytical data to make informed decisions. Our ability to make sound, uniform and fair decisions is no better than the data on which the decisions are based. Our years of experience in other environmental control areas has taught us that there is a wide spectrum of quality found in the laboratory marketplace. In the absence of control, whether it be regulated or voluntary, the quality of laboratory services tends toward the lowest common denominator because of the competitive advantage of reduced overhead which in many cases means reduced quality."

State of New Mexico Environmental Improvement Division
--"strongly support the concept of a laboratory accreditation program (LAP) for environmental testing laboratories, to be developed by the National Bureau of Standards cooperatively with the Environmental Protection Agency (EPA). The intent of the quality assurance (QA) programs required by EPA for any state-delegated program receiving EPA funds would be addressed in large part of having a nationwide LAP covering chemical analysis for all environmental parameters. Such a LAP might follow the format of the existing EPA Manual for the Certification of Laboratories Analyzing Drinking Water...but should be expanded..."

Conditionally Positive Responses (4)

American Association for Laboratory Accreditation
--"have no objections to NVLAP developing a program in these fields in competition with AALA..."

American Council of Independent Laboratories, Inc. (ACIL)
--"the need for a national program for laboratory accreditation definitely exists in the environmental (hazardous waste) field. And as the notice hints that might well be expanded to the areas of air, water and solid waste."
--"while the testing methodology to support accreditation currently exists, the non-technical issues are very complex. For example: the need for the LAP to be self-supporting. Another issue is whether EPA will replace its current system with NVLAP and the time for such a transition. Another issue concerns the reciprocity needed between states to have a NVLAP program successful. Finally, the question of whether or not the American Association for Laboratory Accreditation (AALA) might not offer a viable altenative to NVLAP, in this environmental area, needs to be considered."

National Sanitation Foundation
--"The need is evident, and NSF can provide a viable third-party alternative to official regulation."
--"Drinking water is the first area of laboratory accreditation where NSF will offer services. When the DWLA program is established, we plan to expand accreditation services to wastewater laboratories and ultimately to hazardous waste

laboratories."

Lancy Laboratories
--"in cooperation with the USEPA, develop a program that would cover water, wastewater, solid and hazardous wastes."
--"The only negative comment...Unless a large majority of certifying agencies accept this program in lieu of their own, this will just be another certification burden that many laboratories would have to maintain."

Negative Response (1)

Analyte Laboratories, Inc.
--"do not feel the environmental issue should be addressed by the NBS."
--"First, the EPA, through EMSL, has a well-established library and distribution network for documentation, especially current methodology. Second, EPA also maintains a repository for hazardous material and performance evaluation materials. This program is more than adequate to provide laboratories with quality guidance measures. Third, as part of normal interaction with private business, contract laboratories are routinely and thoroughly inspected for their capabilities. The intensity of their investigation is noteworthy. The EPA also performs ongoing research within its laboratories to maintain the above programs."
--"EPA...is more capable of readily instituting or modifying any type of LAP...see no need for NBS to expand its LAP and unnecessarily duplicate an established program."

CONTROLLING AND COPING WITH UNWANTED VARIANCE IN GROUNDWATER MONITORING DATA: QUALITY CONTROL AND STATISTICS

BURNELL W. VINCENT, PROGRAM MANAGER, GROUNDWATER PROGRAM, OFFICE OF SOLID WASTE, U. S. ENVIRONMENTAL PROTECTION AGENCY, WASHINGTON, D. C.

INTRODUCTION

Establishing an appropriate statistical comparison program in accordance with the RCRA regulations may be one of the most vexing tasks facing a permit writer. The purpose of requiring statistical comparisons is to provide a standard protocol for determining whether differences between up- and down-gradient ground-water quality values are due to facility effects. There are many sources of variance in the data which are not related to the facility. Some are representative of actual differences in ground-water quality, such as near by sources of contamination or naturally occurring special variability; others are due to measurement error or to bias introduced by sampling methodology. A good statistical protocol will accommodate anticipated variance and selectively identify the type of variances which do indicate facility impact.

Many of the problems addressed by other speakers at this conference contribute variance in the data reported to a facility's permit writer: the problems in obtaining standards, in laboratory certification, and in many of the aspects ordinarily considered in a quality assurance program. The reason that a statistical comparison technique is such a vexing problem to the permit writer at this point in development of the state of the art is that these various sources are all confounded in the data. "Statistics" or the selection of a statistical comparison technique has been given a bum rap. It is blamed for false positives by owners and operators and false negatives by environmentalists when, in fact, it does just what we ask of it.

Rather, the point of this presentation is that false positives are much more directly due to violations of the requirement for representative samples than they are due to faults of the regulation. Failure to implement adequate quality assurance programs introduces variance which can be orders of magnitude greater than the concentrations representing lethal doses of some of the constituents of concern. Equally important, there are gaps in the technology of ground-water sampling. Some devices commonly in use have potential but undocumented influence on sample quality.

The objective of this presentation is to discuss two initiatives at EPA which promise to bring some short term relief to the permit writer who must draft the statistical and quality assurance provisions of permits. The first of these is an effort to improve guidance directives specifying quality control. It should be familiar to many of you who have read our draft Technical Enforcement Guidance Document, the topic of address by Murphy and Gilbertson at yesterday's session. The second is an initiative to develop guidance for a

simple, workable statistical package which satisfactorily complies with the regulation.

THE PROGRAM

The regulations generally require owners and operators to prepare a ground-water monitoring program capable of detecting any influence from the facility on ground-water quality. This program, as specified in both interim status and permit requirements, must include consistent sampling and analysis procedures that are designed to ensure monitoring results that provide a reliable indication of ground-water quality. The regulatory intent was to express only the performance standard in the promulgated text, and to develop the details for meeting that performance standard in guidance documents. Unfortunately, the comparison technique specified in the regulations assumes that replicate values are as independent of each other as the between-quarter values are.

Typically, there are three levels of guidance materials: the first is quasi regulatory, such as SW-846, which will be incorporated by reference into the regs. The second is interpretative or policy guidance, such as the permit writers' guidance manuals and the Technical Enforcement Guidance Document. These manuals contain "rules of thumb" and other specific normative criteria by which regulatory officials and owners and operators can decide whether particular methods or techniques are seen by the Agency as satisfying the performance standards as promulgated. The third level of guidance doucments are scientific research reports and technical resource documents describing the state of the art techniques, but not prescribing sufficiency from a regulatory standpoint.

We are currently seeing the technical resource documents and research reports come to maturity. In the midst of the ongoing research, however, it is clear that a large portion of the variance is correctable simply by standardizing the materials and procedures for sampling. Therefore, this second body of guidance documents, the rules-of-thumb, are being redrafted in an effort to foster such standardization. Upon finalization of these documents, those rules which are hard and fast and well-supported by science will become mandatory as requirements in SW-846.

Several technological gaps have been identified over the last several years. These are just now appearing in the third level of guidance documents. One such issue for example is the choice of non-interactive sample contact surfaces in sampling equipment. The wells and pumps used to bring samples to the surface must be designed to overcome many physical obstacles. Some of the best engineering materials, chosen for durability, flexIbility, and cost, are made of materials which are directly of concern or interactive with constituents of concern as contaminants. Until very recently, the agency has not begun to quantify the influence of the methods and materials of sampling on the resulting ground-water quality data.

In the midst of ongoing research, and for the sake of consistency, quality control, and fairness to the regulated community, the Agency is drafting a list of criteria for the methods and materials of sampling.

SPECIFIC PROBLEMS

The output of detection monitoring is the determination that there is or there is not a facility-induced difference between the background and the potentially affected ground water. With the dozens of sources of variance which are becoming identified, it is becoming increasingly apparent that the lack of difference between these values could be due simply to the artifacts and the real concentrations cancelling each other (a false negative). Alternatively, sharply differing values due to reinforcing artifacts could result in a false positive.

The two initiatives previously mentioned are a beginning, in the near term, to provide controls for the most controllable influence and to accommodate variances which are not controllable. Over the longer run, as more and more ground water quality data becomes available, more sophisticated analyses of sources of variance will help our understanding of variances which by their nature are so confounded as to appear inseparable. An example is an apparent seasonality of volatile constituents which in fact is a bias introduced by sampling error. When samples to be analyzed for volatile constituents are exposed to the air during the sample acquisition, preservation, and containment, the reported values may be influenced by sun, humidity, and temperature of the season in which they are sampled. Separating the influences due to these two sources of variance is not now amenable to statistical methods.

The initiative to quantify and control the controllable influences is coordinated between RCRA enforcement offices and a Task Force, the Hazardous Waste Ground-Water Task Force, which was established this year to accomplish the two major goals of determining whether regulated facilities ground water requirements and to identify and evaluate causes of poor compliance. That Task Force will evaluate approximately 60 regulated facilities. The dual objectives of the Task Force's effort are to determine whether the facilities are leaking and to document the difficulties which have made that determination so elusive, heretofore.

The Office of Waste Programs Enforcement, using panels of experienced Agency enforcement officials and researchers, is compiling a set of criteria which will standardize well design and construction and sample taking techniques for new wells, and set standards for acceptability of existing wells. The Task Force is fully integrated with this effort. Task Force protocols for inspection of the 60 facilities to be evaluated are consistent with enforcement findings; new issues identified by the task force will be incorporated into the guidance if they are resolvable issues. Non-resolvable issues will be prioritized for accelerated research.

The Enforcement standards for controlling sampling induced error are expressed in the Technical Enforcement Guidance Document which is currently available in draft for public comment. This manual presents standard techniques designed to resolve a lengthy list of commonly encountered but easily resolvable sources of error. For instance, it is not uncommon for enforcement officials to observe that wells have been sealed using neat cement. Such seals, in proximity to well intakes, can have a major impact on pH and through pH on the mobility and solubility of many of the constituents of concern. The manual identifies this problem and forbids the use of neat cement.

Steel and plastic in corrosive or solvent environments is identified as a source of error (due to interaction), as well as a loss of stability in background data (the loss and the replacement of old wells which have corroded away can destroy continuity of historic background data).

Typically, drilling techniques have been developed for water supply wells or petroleum industry use. Commonly, drilling muds or fluids are injected ahead of drill bits to loosen or dislodge the cuttings. While introduction of fluids for high volume production wells is of little concern, these muds can have a devastating impact on a detection monitoring program. Similarly, wells for residential use are commonly field slotted. Rather than purchasing expensive screens uniformly slotted to a size which excludes packing and aquifer materials, the well driller will simply use a hacksaw to slot the well casing, resulting in newly cut surfaces of interactive material, and in wrong-sized openings which allow passage of sediment along with the water sample. The experts advising the Agency on "rules-of-thumb" have suggested that when highly turbent samples are encountered and no information on well construction can be provided, the guidance must call for the wells to be replaced.

Filter packs are commonly inserted between the aquifer material and the well screen; they are designed to keep soils and sediment away from the screen. Improperly sized and/or interactive materials in a filter pack, of course, can affect values measured at that well. Guidance will likely reflect these factors.

The draft document identifies allowable drilling methods. A wide variety of drilling methods have been developed for various purposes in various geologic settings. Several of these should be prohibited because of known effects on monitoring objectives. Guidance documents should present drilling methods which are acceptable according to geologic settings. Practices and precautions for their use should be identified in order to further control the effects on the resulting data.

The problem of interactive sample contact surfaces is one which requires considerable further research. Meanwhile, for standardization and to avoid the probability of induced error, the advisors have recommended that our guidance require teflon or stainless steel sample-contact surfaces. The use of other materials may be proposed by owners and operators in consideration of site

specific factors and monitoring objectives. However, the use of well materials which require glue or solvents during installation should be expressly prohibited in all sampling wells. Bentonite pellets were recommended for sealing the annulous.

Detection monitoring requires information about the concentrations of specific constituent in the ground water as it exists in situ. As the ground water leaves the porous medium, flows through the filter pack, and the screen, and enters the well, it may be subjected to influences affecting those concentrations. Stagnant waters standing in the well column can be expected to have differences in concentrations of key indicators. The guidance is drafted in attempt to control such influence. Free flowing aquifers should be prebailed by an amount equal to three times the casing volume. While standard practice permits a general range from 1-10 volumes, this amount of variance can have measurable effects on concentrations.

Free flowing aquifers must be sampled immediately upon removal of the third volume of prebailing. In tighter formations, well recovery may be too restricted to allow discarding the three volumes. This presents additional problems. In these situations, the recharging water trickles down over the screen in a manner which allows air stripping of volatiles. To minimize this effect, the enforcement official should require that the wells which go dry before purging three volumes be sampled within three hours of recovery of a sufficient volume for analysis. While this approach will minimize variance, a bias remains which must be addressed by new technology development.

Sample taking procedures are specified to reduce the trauma involved in handling sampling equipment and in equipment/sample interface. Commonly, field crews are observed dropping the bailer down the well casing where it splashes into the water to be sampled. The enforcement official must forbid this practice, as well as the use of stranded cord, nylon, or other potentially contaminating line for retrieving the bailer.

To reduce sampling bias, bailers and pumps for use in sampling may not have neoprene fittings, PVC, tygon tubing, silicon rubber, neoprene impellers, polyethylene, or vitron in contact with samples. If they are not dedicated to an individual well, sampling devices must be steam cleaned between wells. Pumps may not operate at greater than 100 ml per minute extraction rate for the sample; the extraction rate under which the sample was taken must be recorded. Samples must be preserved in accordance with SW-846; they must be placed in a sample container with no head space. They should not be composited for subsequent division in the laboratory. Quality assurance programs must specify the use of field blanks, standards, and spikes. Calibration of lab equipment must be required. Standard detection limits must be agreed upon (such as, the ACS, 1980 approach).

These are but a sample of the types of standards needed in order to reduce the controllable sources of variance before the statistician can be expected to identify the influence of a facility. The ranges

of error we have associated with these sampling irregularities is indeed large. Field tests have attributed 10-15% error to even the better sampling devices. Operator error in some devices has been shown to result in a 50% loss of some volatiles. Studies at the Illinois Geologic Survey have identified 80% losses of some volatiles to silicon rubber tubing. Suction type sampling pumps can routinely be expected to lose 25-30% volatiles.

INTERIM STATISTICAL GUIDANCE

The use of Cochran's Approximation to the Behrens-Fisher solution has raised concerns about false positives. This is intuitively obvious when we stop to consider the assumptions on which that test was based. Fortunately, by good sense or good luck, the wording in paragraph 264.96 (h) (1) (ii), the alternate statistical test, does not require the use of replicates. Permit writers should take advantage of this flexibility by requiring replicates for quality control but averaging replicates into a single value.

This flexibility supports fertile cooperation between statisticians and hydrogeologists in designing a sampling protocol well tailored to the objectives. Trade-offs between the numbers of wells, the frequency, and the number of parameters should be judiciously made. Some randomization is appropriate, but the intuition of the hydrogeologist is also important.

We are now drafting advice to our permit writers based on the existing regulations (S264.97(h)(2)(ii). The draft is in keeping with the old adage, KISS (keep it simple, stupid), recognizing that no one statistical comparison technique will ever work for all sites, and further recognizing the difficulties in determining the comparison technique before sufficient data is amassed. The draft guidance advises a relatively simple technique to be used with lots of intuition and visual displays. Graphs and control charts should be used in conjunction with any specified simple comparison technique in order to establish confidence that the technique gives sensible answers.

The alternative statistical test is only available for sites whose data exhibit a coefficient of variation less than one. With its freedom from the replicate requirement, the alternative test should take full advantage and maximize independence of the upgradient values. To this regard, no fewer than four upgradient wells are suggested. Four quarters at four wells will yield 16 independent values avoiding the problem of falsely inflated degrees of freedom. The power of the statistical package should be viewed as a whole. A basic understanding of statistics and the requirements for consistent procedures for sampling should enable the permit writer to balance the possiblity of false positives and false negatives.

The permit writer's agreement to allow an alternative statistical test should be based on the owner or operator's commitment to bias-free sampling procedures. He/she should agree to consistently use a single

laboratory, or to split at least three routine sample periods between new and old labs prior to changing labs. The ACS detection limit package should be used. The owner or operator should agree to safeguard against missing values, such as preservation of additional or redundant sample volumes. He/she should use site-specific frequency-spacing selection criteria, not necessarily uniformly requiring the same frequency for all parameters and all wells. And finally, the owner or operator should insist on the best available QA/QC.

In recognition of the increase in system capability to detect contaminants, the permit writer can offer a fixed degree of freedom which will achieve more statistical power with less sensitive "hair trigger" upset values. This is the nature of the Bond-Ferranti test which adjusts the overall alpha by adjusting for individual comparisons.

CONCLUSIONS

In summary, the Agency now has a two-pronged initiative aimed at reducing the "noise-to-signal ratio" in ground water monitoring programs. It involves reducing the controllable variances which are due to sampling error and accounting for the real seasonal spacial and temporal variances by practical, simple statistical procedures. A simple comparison technique backup by visual and intuitive tests should result in heightened efficiency, useful until sufficient information is obtained on data variability and constituent behavior is available for more rigorous statistical evaluations.

Owners and operators should become familiar with the concepts presented in the draft regulatory interpretation guidance documents. While these concepts are presented in draft for comment, each addresses a potential source of error which could reduce the effectiveness of a monitoring system. After close of the comment period, the Agency will prepare final guidance containing those concepts most positively identified with the larger components of variance. Combining these controls on variance with a simple and reasonable alternative statistical test, should result in a marked improvement in detection house capability.

SOURCES AND MEANS OF OBTAINING COMPOUNDS FOR THE QUALITY ASSURANCE MATERIALS BANK

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ABSTRACT

"The quality of all analytical measurements rests utlimately upon the quality of reference materials employed." This statement is especially appropriate in the determination of trace toxic organic residues in environmental matrices. To support the need for a certified, quality-controlled, common data base for the analysis of hazardous waste residues in a variety of substrates, the U.S. Environmental Protection Agency maintains a repository of analytical grade reference standards. Known officially as the U.S. EPA quality assurance materials bank, the program is located at research Triangle Park, North Carolina, and is both funded and technically directed by the agency's environmental monitoring systems laboratory in Las Vegas, NV (EMSL-LV). Although originally established by the U.S. public Health Service in 1965, the program, under the auspices of EMSL-LV, has continued to expand its inventory of toxoc organic and hazardous waste standards in support of the requirements of the federal insecticide, fungicide, and rodenticide act (FIFRA), The resource conservation and Recovery Act (RCRA, 40 cfr, Part 261, Appendix VIII - hazardous constituents) and the comprehensive environmental response, Compensation and Liability Act (CERCLA) 40 cfr, Park 302, Appendix A - List of Hazardous Substances.

The repository replenishes its supply of standards by direct purchase from chemical supply houses, from other government repository programs, and by direct request of chemical and pesticide manufacturers worldwide. This last source supplies the majority of chemical standards used by the repository. Letters are sent to chemical and pesticide manufactureres requesting small quantities of pesticide chemicals for use as standards. Because the chemicals are provided free, requests for individual compounds are made to numerous manufacturers in hope that sufficient quantities of each compound can be maintained in the repository.

The response to these requests has been very positive. Standards are currently being provided free by 181 chemical manufacturers; 71 of these companies are either foreign or foreign-owned U.S. subsidiaries. Foreign companies provide approximately one-third of the standards that are ultimately distributed by the repository.

After the compounds are received (gratis or purchased), they are analyzed to verify their identity and purity. When necessary, these compounds are purified to meet minimum acceptance criteria as standards for instrument calibration. Once verified, high purity organic standards are developed (standard solution or "neat") and distributed for use by laboratories for the calibration of instruments and for quality control in sample analysis. The purity, concentration, stability, and applicability of each standard are evaluated by the QAMB and by its support contractor.