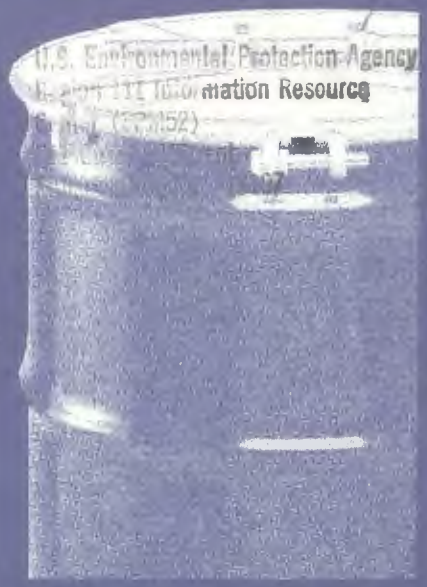


U.S. Environmental Protection Agency
Region III Information Resource

PROCEEDINGS

8TH ANNUAL WASTE TESTING & QUALITY ASSURANCE SYMPOSIUM

JULY 13—17, 1992
HYATT REGENCY CRYSTAL CITY
ARLINGTON, VA

THE SYMPOSIUM IS MANAGED BY THE AMERICAN CHEMICAL SOCIETY

printed on recycled paper

TABLE OF CONTENTS

Paper Number		Page Number
SAMPLING AND FIELD		
1.	Field QA and Representative Sampling: Findings of a National Workshop. **L. R. Williams**	1
2.	Quantitative In-Situ Soil Gas Sampling. **G.E. Robitaille,** K.T. Lang, K.P. Lucero	2
3.	Field and Laboratory Methods for a Superfund Ecological Risk Assessment at Milltown Reservoir Wetlands. **G. Linder,** M. Bollman, C. Gillett, J. Nwosu, S. Ott, D. Wilborn, G. Henderson, C. Callahan	15
4.	Use of HgI2 Spectrometers in Detection of Lead in Paint. **J.S. Iwanczyk,** Y.J. Wang, W.R. Graham	28
5.	Immunoassay Methods for Environmental Field Screening. **S.B. Friedman**	43
6.	Cost Effective PCB Investigation Utilizing Immunoassay. **J.S. Smith,** E. Brozowski, J.E. Rhodes	58
7.	Current Status of Lipid Containing Semipermeable Membrane Devices as Environmental Dosimeters. **J.D. Petty,** J.N. Huckins, J.A. Lebo, J.L. Zajicek	74
8.	Development of a Monoclonal Antibody Immunoassay for the Detection of Polyaromatic Hydrocarbons In Soil. **R.L. Allen,** T.M. Stewart, T.A. Withers, W.B. Manning, S.B. Friedman	86
9.	The Field Screening of a Large Site for Pentachlorophenol Contamination Using an Immunoassay-Based Analytical Method. **K.R. Carter**	87
10.	The Application of Immunoassay-Based Field Analytical Methods. **K.R. Carter**	90
11.	The Assessment of a Site for PCB Contamination Using an Immunoassay-Based Field Analytical Method. **K.R. Carter**	98
12.	A Mixed Waste Methods Compendium: DOE Analytical Methods for Environmental and Waste Management Samples. **S.C. Goheen,** M. McCulloch, S.K. Fadeff, R.M. Bean, R.G. Riley	105
13.	Analysis of PCB's by Enzyme Immunoassay. **R.O. Harrison,** R.E. Carlson	120
14.	Quantification of 2,4-D and Related Chlorophenoxyacetic Acid Herbicides by a Magnetic Particle-Based Solid-Phase ELISA. **F.M Rubio,** T.S. Lawruk, C.S. Hottenstein, D.P. Herzog, J.R. Fleeker	129
QUALITY ASSURANCE		
15.	Automating Analytical Quality Control on a Local Area Network Based Lims System. **R.D. Beaty,** M.R. Schoen	140
16.	Performance Evaluation of Analytical Methods for RCRA Regulatory Programs for the Petroleum Industry. **G. Walters,** D. Kocurek	154
17.	The Importance of Selecting Representative Samples in the Development of a Successful Treatability Study. **L.A. Hines,** S.E. Morrissette	175

18. Method Modificiation ...Or Deviation? Addressing Data Comparability. **R.C. Mealy** 190

19. Laboratory Auditing as a Quality Control Procedure to Evaluate Achievement of Data Quality Objectives. **I.A. Phillips** 197

20. Total Quality Management in the Environmental Laboratory. **F.J. Unangst** 203

21. Designing and Implementing a Representative Sampling and Analysis Plan for PCBs in Non Homogeneous Industrial Scrap. **D.N. Speis,** M.P. Hoyt 214

22. Advances in Data Quality Objectives Guidance for Superfund Remedial Investigation. **D. Neptune** 229

23. Performance Evaluation Samples—What Do They Tell Us?. **G.L. Robertson,** J. Lee 230

24. Database Trends in Problems Observed in Contract Laboratory Program (CLP) Inorganic Data Reviews. **K.A. Aleckson** 231

25. Use of Organic Tape and Data Reviews in Technical and Quality Assurance Oversight of Superfund Contract Laboratories. **J. Armour,** V. Dandge, D. Hewetson 232

26. Data Validation Procedures for Dioxin/Furan Data. **L. J. Dupes** 233

27. Cost Effectiveness of Data Quality Objectives in Environmental Monitoring Performance-Based Methodology. **M.Dymerski** 243

28. ENSR's Automated Data Validation System. **M. Fencl**, M. Hoyt, J. Karnofsky 244

29. Using Handheld Computers to Improve The Quality of Field Data Documentation and Transmittal. **B. Hill,** J. Holley 245

30. Laboratory Automation System for Standard and Reagent Preparation. **M. Hummel,** L. Lindquist, R. Doyi, F. Dias, B. Warden 251

31. Cost-Effective Monitoring Program—A Success Story. **K. Johnson** 260

32. Waste Minimization Program at Environmental Laboratories. **H.C. Mehra** 262

33. Laboratory Compliance Through Self-Audit. **G. L. Poling,** R.A. Thompson 263

34. Data Validation Guidance for EPA Organic and Inorganic Analytical Methods. **A. Rosecrance** 268

35. Use of Performance Evaluation Samples in Assessing Environmental Data Quality. **D. Sims Dwight,** P. Zawodny 283

36. Quality Assurance Practices for Data Entry and Electronic Data Transfer. **L.M. Tomczak** 287

37. The Impact of the GC/MS Raw Data Audit in the Monitoring of the USEPA Contract Laboratories. **M.K. Wolf,** D.J. Elkins 303

ORGANICS

39. Status of the RCRA Organic Program. **B. Lesnik** 304

40. Determining TCLP Volatiles in Waste Oil at Regulatory Levels. P. Marsden, B.W. Colby, **C.L. Helms** 305

41. Volatiles in Soils. **P. Kester** 320

42. Vacuum Distillation: An Alternative to the Analysis of Volatile Analytes of Conventional Purge and Trap. D.R. Youngman, **M.H. Hiatt** 321

43. Open Tubular Solid Phase Extraction. **P. Del Mar** 322

44. Accelerated Liquid/Liquid Extraction with Reduced Solvent Volume. **M.L. Bruce,** M.W. Stephens, J. Carl, B. Killough, T. Zine, D. Burkitt 335

45. A Rugged and Cost-Effective Method for the Determination of Explosive Residues in Environmental Water Samples. **M.G. Winslow,** B.A. Weichert, R. Baker 341

46. A Solid Phase Extraction Disk Method for the Extraction of Explosives from Water. **G. Le Brun,** P. Rethwill, J. Matteson 351

47. Analysis of Environmental Samples for Methylmercury Using Gas Chromatography with Electron Capture Detection. **D.K. Root,** W.W. Li 352

48. A Practical Means of Measurement of Purgeable Organic Halides at Low Concentrations by Oxidative Pyrolysis/ Coulometric Titration. **J.R. Simon,** Jr., J. Lowry, C. Ramsey 365

49. Ion Trap Mass Spectrometry for Pesticide Analysis and Other Applications. **M. Zimmerman** 376

50. Extending the Detection Limits of Quadrupole GC/MS Systems in Environmental Analysis: Common Problems and Novel Solutions. **L.C. Doherty** 385

51. Environmental Applications of Particle Beam LC/MS. **D.R. Doerge** 397

52. The Determination of Semi-Volatile Organic Compounds in Analytical Extracts Using Split Injection Technique with an Ion Trap GC/MS. **R. Brittain,** N. Kirshen, E. Almasi 412

53. Analysis of Pesticides in Groudwater Using Atmospheric Pressure Chemical. **D.R. Doerge** 413

54. The Use of Supercritical Fluid Extraction/GC-MS for the Quantitative Determination of PAHs in Soil. **J.M. Levy** 426

55. Supercritical Fluid Extraction (SFE) of Total Petroleum Hydrocarbons (TPHS) with Analysis by Infrared Spectroscopy. **M.L. Bruce,** M.W. Stephens 427

56. Using a Vacuum Centrifuge as an Alternative to Kuderna-Danish Distillation, Rotary Evaporators and Nitrogen Blowdown. **B.N. Colby,** C.S. Parsons 437

57. An Interlaboratory Evaluation of a Method To Extract Total Petroleum Hydrocarbons from Solid Samples Using Supercritical Carbon Dioxide. **W.F. Beckert** 442

58. Concentration of Water Soluble Volatile Organic Compounds from Solidsamples by Azeotropic Microdistillation. **M.L. Bruce,** R. Tomayko, M.W. Stephens 443

59. GC/MS Identification of Artifacts Formed During Sample Preparation Using EPA Methods 625 and 8270. **P.H. Chen,** W.A. VanAusdale, W.S.Keeran, D.F. Roberts 447

60. Analyses of 2,4-D,2,4,5-T, and Silvex in Hazardous Wastes and TCLP Extracts Using HPLC. **C.R. Hecht,** F. Thomas, J.W. Kolopanis 457

61. An Interlaboratory Calibration Study of a Thermospray-Liquid Chromatography/Mass Spectrometry Method for the Detection of Carbamates in Environmental Matrices. **T.L. Jones,** V. Lopez-Avila 471

62. The Determination of Sub Part Per Billion Levels of Volatile Organic Compounds in Air by Pre-Concentration From Small Sample Volumes. **N. Kirshen,** E. Almasi 472

63. Supercritical Fluid Extraction of Chlorophenoxy Acid Herbicides from Soil Samples. **V. Lopez-Avila,** J. Benedicto, N.S. Dodhiwala, W.F. Beckert 483

64. Molecular Profiling Oily Wastes by Thermal Extraction—Gas Chromatography-Mass Spectrometry: Use in Treatability Studies. **C. Sutton** 498

65. Isolation of PCDD/PCDF from Complex Sample Extracts With an Automated Modular Liquid Chromatographic System Using Disposable Prepacked Chromatographic Columns. T.O. Tiernan, **H. Shirkhan,** D.J. Wagel, G.F. VanNess, J.G. Solch, J.H. Garrett 499

INORGANICS

66. The Efficacy of Microwave Hot Acid Leaching for Determination of Metals. **L. Jassie,** E. Hasty, R. Revesz, H.M. Kingston 500

67. A New Device for High Pressure Microwave Digestion. **R. Kramer** 509

68. Microwave Digestion of Incinerator Samples. **Z. Yang** 510

69. Capillary Ion Analysis: A New Method for Determining Ions in Water and Solid Waste Leachates. **J.P. Romano** 519

70. Use of Capillary Electrophoresis for the Determination of Organic and Inorganic Anions in Ground Water at a Superfund Site. **L.W. Strattan**, M. Siao 520

71. The Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis. **L. Robinson,** F.F. Dyer, D.W. Combs, J.W. Wade, N.A. Teasley, J.E. Carlton, A.L. Ondracek, J.R. Stokely 532

72. Use of Transportable X-Ray Fluorescence for Determination of Selected Aqueous Trace Contaminants. **R.E. Phillips,** R.J. Bath, P.D. Greenlaw, J. Hudek, R.D. Spear 533

73. Comparative Evaluation of Sample Preparation Methods for the Determination of Metal Analytes in High Concentration Environmental Samples. **C. Jones,** W.R. Newberry, X. Suarez 534

74. Ion-Exchange Solid Phase Extraction: Factors Influencing Retention and Elution And Their Application In Method Development. **A.J. Spilkin** 535

75. Applications of X-Ray Fluorescence Spectroscopy to Hazardous Waste Analyses. **D. Kendall** 539

AIR AND GROUNDWATER

76. Handbook and Database of RCRA Ground-Water Monitoring Constituents: Chemical and Physical Properties. **A.E. Johnson,** R. Carlston, J.R. Brown, V.B. Myers 540

77. Rationale for the Design of Cost-Effective Groundwater Monitoring Systems in Limestone and Dolomite Terranes: Cost-Effective as Conceived is Not Cost-Effective as Built if the System Design and Sampling Frequency Inadequately Consider Site Hydrogeology. **J.F. Quinlan,** G.J. Davies 552

78. Releasable Cyanide and Sulfide; Dysfunctional Regulation. **J. Lowry,** J. Fowler, C. Ramsey, M. Siao 571

79. Design Considerations for an Automated On-Line Air Sampling System. **J. Ryan,** I. Seeley 576

80. Review of Army Research on Well Casings Used in Groundwater Monitoring. **L.V. Parker,** A.D. Hewitt 582

SAMPLING/FIELD

1 FIELD QA AND REPRESENTATIVE SAMPLING: Findings of a national workshop

Quality Assurance

Llewellyn R. Williams, PhD, Senior Science Advisor, U.S. Environmental Protection Agency, EMSL-Las Vegas, Nevada 89193

ABSTRACT

In recognition of an urgent need to share information on controlling in-field sources of data variability (often the largest components of variability in environmental measurements), a workshop was convened April 29-May 1, 1992, in Las Vegas, Nevada. The purpose of the workshop was to identify practical approaches to, and gaps in our knowledge of sampling, sampling design, and field quality assurance for environmental studies, particularly as applied to waste sites, heterogeneous waste streams, and contaminated soils or sediments. Scientists, engineers, and quality professionals from various agencies in the Federal, State and private sectors gathered. This paper reports consensus findings and workgroup recommendations for issues related to: (1) the design and implementation of statistically valid sampling approaches; (2) the application of the "Data Quality Objectives" process to field operations; (3) training and educational needs for field personnel; (4) quality control and quality assurance techniques and sample types applicable to field operations; (5) "best estimator" parameters for total measurement error; and (6) the complex problems posed by highly heterogeneous environmental media or atypical distributions of toxicants or other hazardous constituents.

2

Quantitative In Situ Soil Gas Sampling

George E. Robitaille, U.S. Army Toxic and Hazardous Materials Agency, Technical Support Division, CETHA-TS-C, Aberdeen Proving Ground, Maryland 21010-5401 and D.P. Lucero, Lucero Associates, 18421 Cedar Drive, Triangle, Virginia 22172

ABSTRACT

In conjunction with a triservice (Army, Navy, and Air Force) program to develop a cone penetrometer with associated sensors and detectors, a prototype soil gas sampling system has been fabricated and functionally tested. The system, referred to as TerraTrog, quantitatively samples hazardous soil gases and vapors. TerraTrog can be deployed by a cone penetrometer to depths of 100 ft far less expensively than drilling monitoring wells. The device may be permanently implanted or may be retrieved and deployed at multiple locations using the cone penetrometer.

TerraTrog comprises two modules: an implant of small dimensions containing a gas-permeable membrane of high diffusion impedance (located at subsurface levels) and a sampling and calibration interface with a pneumatic manifold (located at ground level). Unlike conventional non-quantitative soil gas sampling techniques requiring vacuum to operate, TerraTrog relies only on soil gas diffusion for subsurface soil gas collection and a carrier gas stream flowing at a slight positive pressure for lifting the sample to the surface. Because the sampling is diffusion-limited by a membrane of known impedance, the sampling rate and sample size are independent of soil permeability. Sampling does not deplete the local soil gas or vapor, guaranteeing the accuracy of measurements made with the device even after long periods of continuous sampling. The system has a 15 min. maximum time-rate-of-response.

Functional and performance testing has been performed with trichloroethylene in soil, water, and air, using a Photovac 10S70 portable gas chromatograph. The implant has been demonstrated to operate as designed, i.e., is diffusion-limited with implant response directly proportional to external soil gas partial pressure.

INTRODUCTION

A major problem in the cleanup process or assessment of sites contaminated by hazardous waste and toxic chemicals stems from the lack of information or misinformation regarding site subsurface characteristics, composition, and aerial and volumetric extent. Performing a general prospecting survey of the site hazardous fluids and their mobility or stability is of significant value in developing preliminary overall containment

and treatment plans (1). A network of relatively low-cost implanted gas samplers deployed throughout the site's vadose and peripheral zones as well as adjacent aquifers and high permeability strata can be utilized effectively for site prospecting and characterization. The notion of an implanted sampler network is a viable concept only if waste characterization data can be provided quickly and inexpensively and if the sampler can provide samples of all hazardous soil fluids and contaminants and can interface at the dump site with a variety of analyzers or monitors and secondary samplers.

This gas sampler system, called TerraTrog (2) for easy reference, is described below and addresses the above requirements satisfactorily, offering features that promote simple, low cost sampler deployment; minimal soil disturbance during deployment; minimal sample extraction during each sampling episode, providing a correspondingly more representative sample of soil gases; minimal hardware; and small dimensions. The TerraTrog implant has a 1-in. lateral dimension and can be deployed by cone penetrometers available commercially (3). In addition, sampler operation is independent of the soil permeability over a range of 0.1 to 1000 mD, and therefore, quantitative data are obtained for sandy as well as clay soil types. These operational features also render the sample obtained independent of sampling chamber volume, line length, sampling pump head, and corresponding pressure losses.

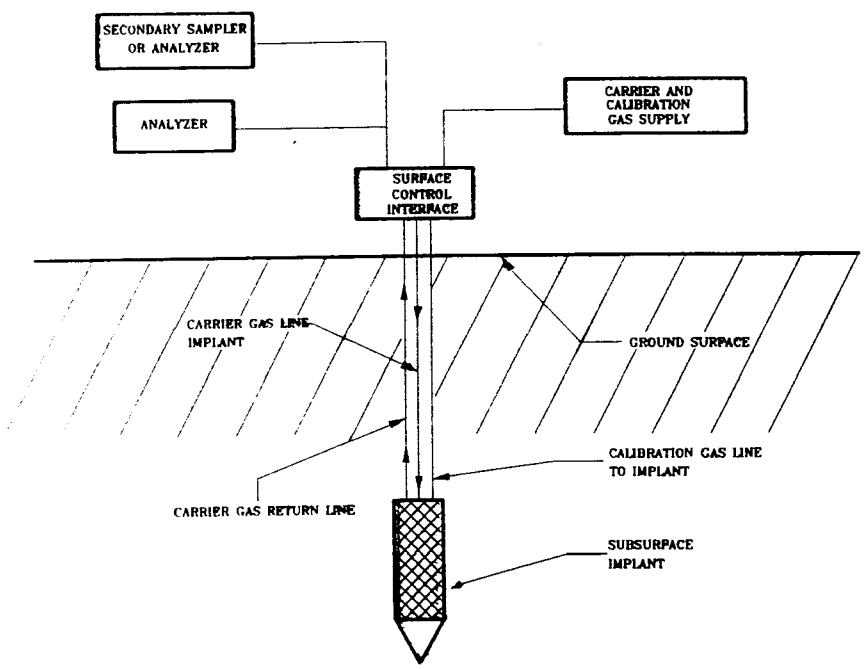


Figure 1 TERRATROG SOIL GAS SAMPLER SYSTEM

THE SAMPLER IMPLANT SYSTEM

TerraTrog comprises two modules: the subsurface implant and the surface control interface. Figure 1 illustrates the system deployed in the soil; deployment in groundwater is analogous exactly. Gases enter the implant at flow rates proportional to the individual gas partial pressures and the partial and vapor pressures of dissolved and pure liquids, respectively, regardless of the soil permeability. The soil gases are lifted to the surface by the carrier gas stream, which enters the surface module and flows at a controlled and measured flow rate to and through the implant and returning to the surface as shown. Soil gas analysis and monitoring is accomplished by the analyzer attached to the carrier gas stream return line at the interface. The analyzer/monitor and carrier gas used are compatible with all aspects of TerraTrog and the data quality requirements of the application. In addition, a secondary sampling device (adsortion tubes, bubbler, etc.) may be attached to the interface, and soil gas may be collected in batches for subsequent laboratory analysis. With a sufficiently large carrier gas stream flow rate, one or more analyzers/monitors and/or one or more secondary samplers can be attached to the carrier gas outlet of the interface and can be operated concurrently.

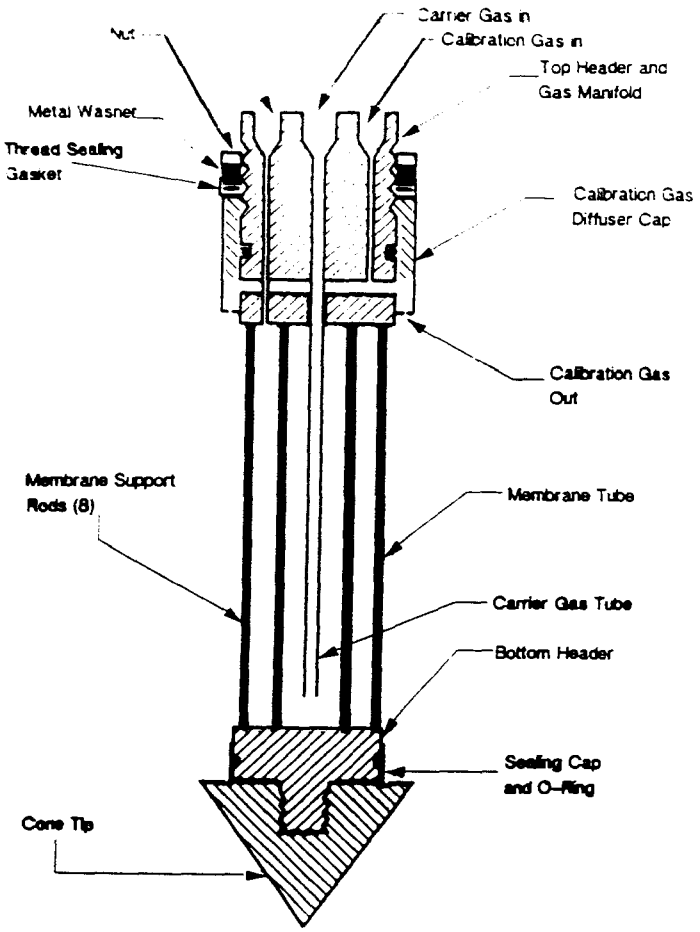


Figure 2 Sampler Implant

The cross-sectional illustration of the implant (Figure 2) depicts a cylindrical array of eight metal rods approximately 6 in. long, contained within a 1-in. diameter envelope. These are surrounded externally by a 1-in. diameter, 0.002-in. thick Teflon tubular membrane. The rods provide mechanical support for the tubular membrane.

The surface control interface module provides the means to accurately control the flow of the inert carrier gas. In addition, there are fittings for the carrier and calibration gas supply lines and the respective pneumatic lines to the implant. The carrier gas return line connects to a manifold which can be connected to an analyzer(s) and/or secondary sampling devices.

PRINCIPLE OF OPERATION

Implant operation is based on a flow of soil gases by diffusion through the semi-permeable tubular membrane of Figure 2 . In addition, the soil gas flow rate is diffusion limited by the membrane and consequently independent of the soil permeability. As carrier gas flows through the implant, the concentration of the soil gas species at the surface is a ratio of the two gas flow rates:

$$[G] = (Q_s/Q_c)\ 10^9 \qquad (1)$$

where

- $[G]$ = soil gas species concentration in the carrier gas stream at the interface module, parts per billion (ppb, v/v);
- Q_s = soil gas species flow rate into the implant, std ml/min; and
- Q_c = carrier gas flow rate, std ml/min.

The carrier gas flow rate is measured at the surface interface module. The soil gas species flow rate is the product of the soil gas species membrane conductance and partial pressure in the surrounding soil. By lumping the membrane and carrier gas parameters into the term, y, the soil gas partial pressure is related to [G] as follows (7,8):

$$P_{sg} = y\ [G] \qquad (2)$$

where

P_{sg} = soil gas species partial pressure in the soil, torr.

The system response time is approximately 100-300 s. For terratrog operating with a 50-std ml/min carrier gas flow rate stream, 0.0625-in inside diameter pneumatic lines, and an implant 50 feet below the surface, the lag time of the system is approximately 73 seconds.

Equations 1 and 2 describe the soil gas species concentration at the surface interface for TerraTrog operating in the dynamic sampling mode, i.e., the operating mode in which the carrier gas flows continuously through the implant. The implant can also be used in the static sampling mode, i.e., the operating mode in which the carrier gas does not flow ($Q_c = 0$) for a prescribed period of time preceding dynamic sampling but flows only after the equilibrium condition described below is attained. Note that soil gas flow into the implant will continue, regardless, until the soil gas partial pressure difference across the tubular membrane is zero. At this point, the net flow of soil gas into the implant is zero, and an equilibrium soil gas concentration internally and externally of the tubular membrane is obtained. After this equilibrium is attained, the carrier is used to lift the soil gas accumulated in the implant.

For the initial condition, where the soil gas partial pressure, P_{sg}, measured at the surface interface is zero (P_{ig}, the sampler implant intergral soil gas partial pressure is zero), the time required to obtain the static equilibrium condition with the soil gas pressure, i.e., $P_{sg} = P_{ig}$, is 7 days (7,8) for the implant dimensions listed above and a soil gas permeability coefficient of 8×10^{-10} std ml/min-cm^2-torr/cm (2).

DESIGN AND OPERATIONAL CONSIDERATIONS

Aside from fundamental system analytical and monitoring performance requirements, the system design constraints are established by reliability and service life requirements and deployment flexibility. TerraTrog reliability corresponds generally and most importantly with the exigencies of maintaining the relationship of soil gas species partial pressure, P_{sg}, and the measured soil gas species concentration, [G], described by equation 2. Adherence to this relationship is predicated on the design and operational integrity of the tubular membrane and the pneumatic lines leading to the surface. It is essential that the soil gas flow into the implant by a diffusion process only, therefore, the tubular membrane must be free of tears, punctures, and holes and other pneumatic leaks. Thus, pre- and post-assembly inspection of the tubular membrane as well as an implant leak check is required. The tubular membrane must not be damaged during the deployment and operational processes.

The maximum typical soil gas sample flow rate into the implant is approximately 0.01 std μl/min for arbitrary but realistic conditions. This estimate is based on a membrane material with $P_m = 2 \times 10^{-9}$ ml/min-cm^2-torr/cm at 20°C (9). In a relative sense, it is a very small sample, yet large enough to produce a [G] for many soil gas species within the response range of many gas phase analyzers/monitors that may be attached to the interface.

There are three important aspects to the relatively small sample size or flow rate: First, the disturbance to the soil is minimized; consequently, a more representative sample is obtained independent of soil fluid conditions. Second, for soil strata in and around dump sites, the soil gas flow rate into the implant is diffusion limited by the tubular membrane and is independent of the gas permeability of the surrounding soil. Thirdly and most importantly, these conditions lead to a quantitative measurement of the soil gas partial pressure.

The soil gas flow rate is proportional to the soil gas species pressure only, without regard to the form of the sample, i.e., gas phase, liquid phase, or dissolved gas/liquid phase. For example, the implant can obtain information regarding dissolved trichloroethylene (TCE) in water or TCE saturated in water, and insoluble gases contained in the water. Furthermore, the implant also functions as described immersed completely in an aquifer or other body of water or liquid.

GAS ANALYSIS AND MONITORING

In a relative sense, the actual analysis of the transport gas output stream from the interface panel is the most simple and direct procedure of the entire system. A variety of analyzers, monitors, and secondary sampling devices can be used singularly or simultaneously. The user, however, must establish preliminary requirements for the target species and the lower detection limits of the analytical devices contemplated, i.e., it is essential to consider the analyzer performance specifications to specify and adjust the operating conditions of TerraTrog accordingly.

TERRATROG PERFORMANCE

Laboratory Performance

Representative data for the TerraTrog time-rate-of-response in static sampling mode to dissolved phase TCE in water is shown in Figure 3. The internal concentration reaches equilibrium with the external TCE concentration in 7 days (168 hr.).

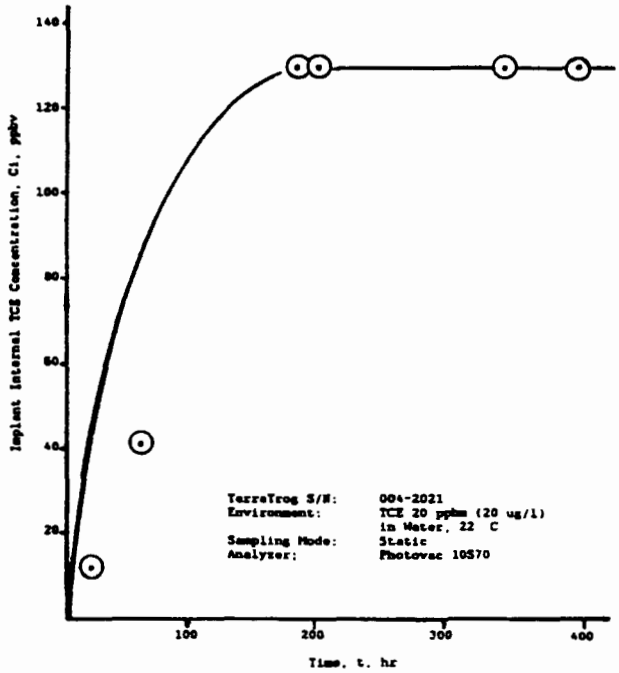


Figure 3 Implant Time-Rate-of-Response to TCE in Water

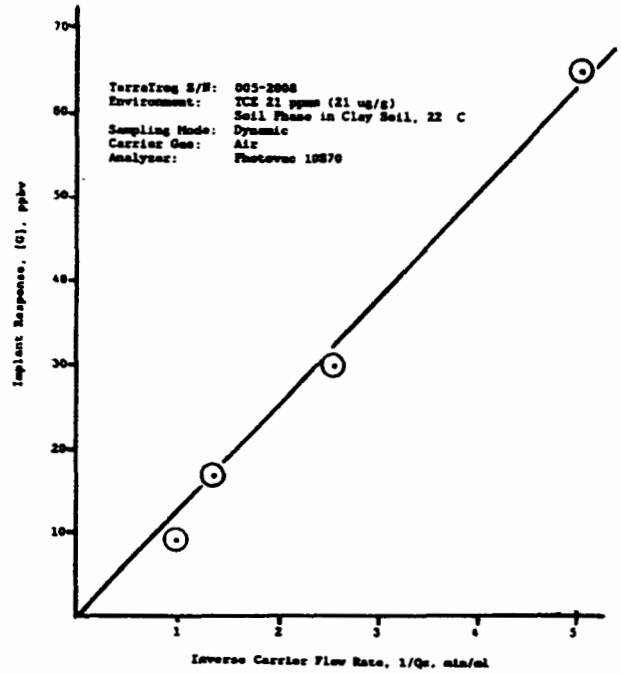


Figure 4 Implant Response to TCE in Soil

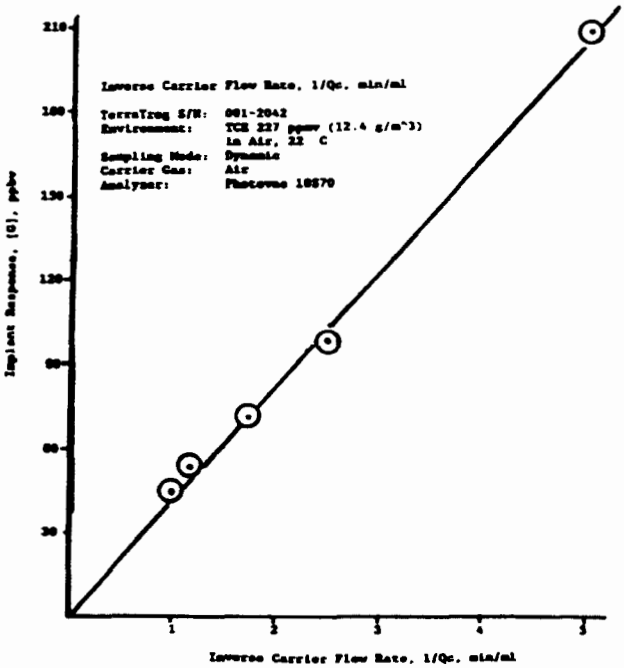


Figure 5 Implant Response to TCE in Air

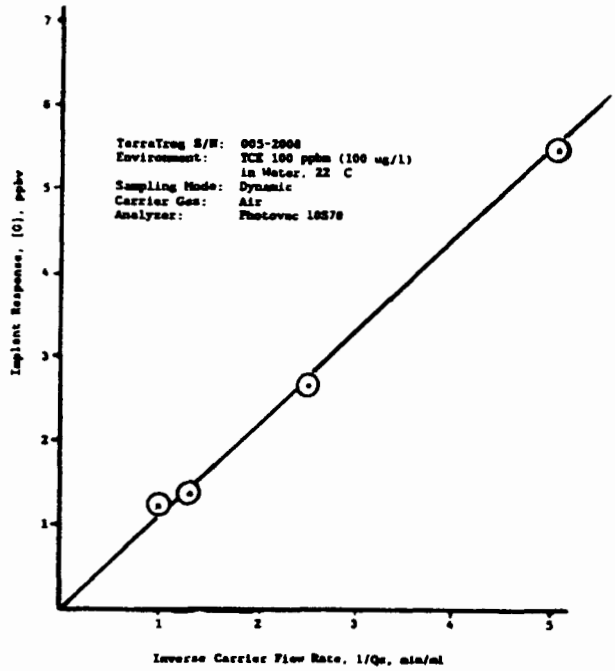


Figure 6 Implant Response to TCE in Water

Representative dynamic sampling mode data for the implant response, [G], to TCE as a function of inverse carrier flow rate, $1/Q_c$, is shown in Figures 4, 5, and 6. A multipoint calibration curve, Figure 7, shows the relationship between implant response, [G], and external dissolved phase TCE concentration in water. Figures 6, 7, and 8 show the implant response is linear regardless of whether the implant is deployed in soil, water, or air. Additionally, the flow rate of TCE into the implant, Q_s, is constant when the implant is sampled in dynamic mode in an environment of constant external TCE concentration. The sample flow rate, Q_s, is relatively small, ranging from 9.2×10^{-5} std. μl/min for dissolved phase TCE at 100 ppbm external concentration in water, to 3.7×10^{-3} std. μl/min for gas phase TCE at 227 ppmv external concentration in air. Figure 7 shows that the implant response, and hence Q_s, varies linearly with the external TCE concentration and therefore with the external TCE partial pressure. The data demonstrate that Q_s is dependent only on the permeability, P_m, of the implant gas permeable membrane, and the external TCE partial pressure, or concentration (6,7). Therefore, the implant operation is diffusion-limited by the implant gas permeable membrane and the implant response is directly proportional to the external TCE partial pressure in soil, water, or air, exactly as described by equations 1 and 2.

The multipoint calibration curve, Figure 7, can be used with the implant to directly measure the TCE concentration in contaminated groundwater in the field. For example, a user would deploy the implant to the desired depth in a monitoring well or other body of water and establish a carrier flow rate of 40 ml/min. The implant response would be measured using a conventional gas-phase TCE analyzer, such as the Photovac 10S70. The implant response would then be located on the vertical axis of the calibration curve, and the corresponding TCE concentration in the groundwater read off the horizontal axis of the curve.Since the implant response is shown to be linear in the multipoint calibration curve of Figure 7, it may be replaced with a single point calibration which yields a linear calibration factor, K:

$$K = [C_e] / [G]$$

where

K = implant linear calibration factor, ppbm/ppbv
$[C_e]$ = external TCE concentration, ppbm
$[G]$ = implant response, ppbv

The linear calibration factor may be used exactly as the multipoint calibration curve to make direct field measurements.

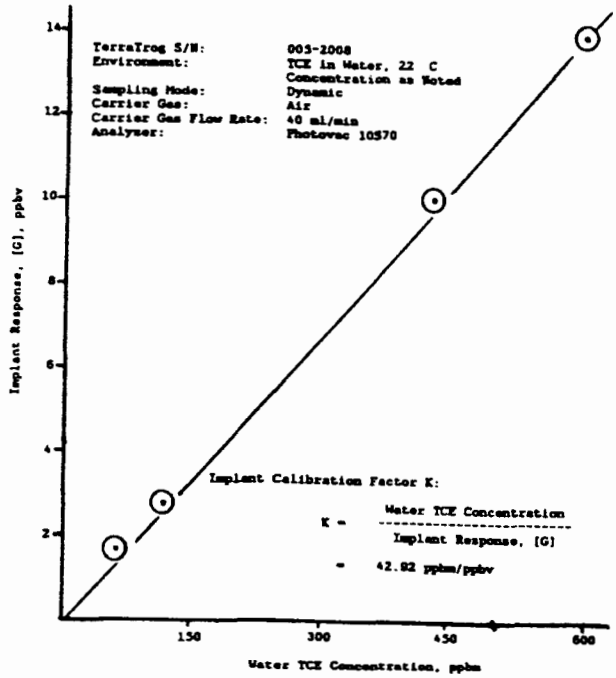


Figure 7 Calibration Curve for Implant Response to TCE in Water versus TCE Concentration

FIELD PERFORMANCE

Preliminary field charterization work was performed with TerraTrog deployed in groundwater wells at the U.S. Army Phoenix Nike Site, Baltimore, County, Maryland and in compacted soil at the Department of Energy (DOE) Savannah River Site (SRS). TerraTrog was used at both sites to sample primarily for trichloroethylene (TCE).

Groundwater Wells

Two terraTrog implant modules were deployed in groundwater wells. Each implant module was suspended approximately 40 ft in the well 2 to 3 ft below the water level over periods of several months. One unit developed leaks through punctures in the membrane and was repaired on several occasions. The implant modules were all leak checked prior to deployment and it was surmised that the membrane was damaged during deployment. After several attempts the implant module was deployed successfully.

The learning process continued in analytical attempts to analyze the groundwater for TCE with a portable GC (Photovac model 10S70+ with a CPSi5CB-10m by 0.53mm column) and with sorbent sampling tubes. Analytical success was finally achieved with the portable GC in that dynamic and static measurements were obtained and the results of both measurements correlated well. TerrTrog used a Helium carrier gas at 15 ml/min. The GC used an Ultra Zero Air Carrier at 5 ml/min with the oven temperature at 40C and was calibrated at 92 and 900 ppb. A 500ul syringe was used to obtain the discrete samples with the TerraTrog surface module and inject it into the GC. The Helium flow was shutoff after each sample as taken and started again to obtain the discrete samples from the

TerraTrog surface module and inject it into the GC. The Helium flow was shutoff after each sample was taken and started again to obtain the next sample. The TCE retention time was 142s. Nine separate samples were taken over a 40 minute period as shown below and in figure 8.

TIME (min)	1.5	3.0	4.5	8.0	9.0	15	25	34	40
CONO (ppb)	256	982	1280	1080	1040	497	145	91	119

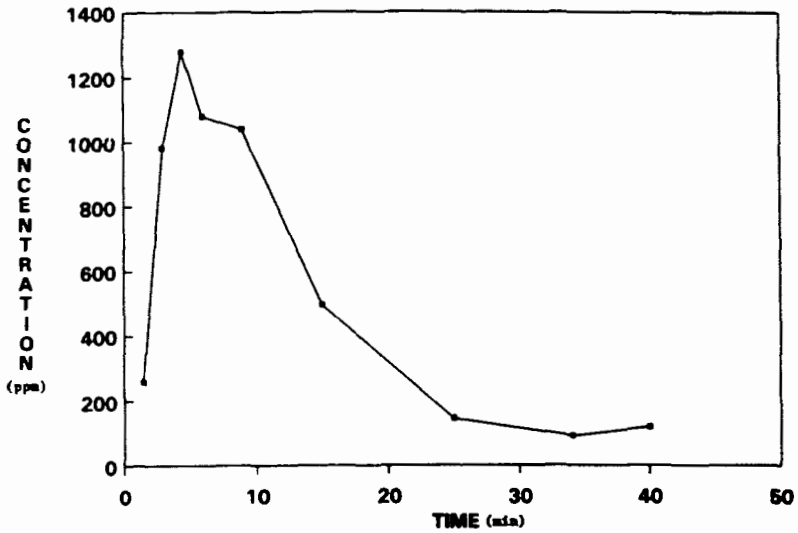


Figure 8 TCE Concentration versus Time

The total volume of the implant module and the return line to the surface module is approximately 100 ml. Approximately 6.7 minutes are required for one TerraTrog volume exchange. Thus, the static sample "peak" should appear between 2-6 minutes as determined by TerraTrog volume and the carrier gas flow rate. The data above shows a broad peak at 4.5 minutes tailing off slowly for about 15 minutes and attains a steady state level near 100ppb.

From the static data considerations, it is determined that the groundwater headspace TCE partial pressure is at least 1260ppb. A simple plot of the data and an extrapolation to the peak yields a concentration near 1380ppb.

From the dynamic data considerations and the calibration curve of Figure 3 corrected for the reduced TerraTrog carrier gas flow rate, i.e., 15 ml/min and K = 16.) it is determined that the groundwater TCE concentration is 1.46ppmm. At this stage of the field testing the dynamic and static measurements correlate well.

Compacted Soil

Deployment and retrieval experiments were performed to assess the implant field worthiness and to obtain TCE samples for on site analysis by a portable GC (Photovac Model 10S70 with a CPSi5CB-10m by 0.5mm column) operating with 10 ml/min of Ultra Zero Air and an oven temperature of 25C.

The implant was deployed in sandy-gravely soil to a 3ft depth and retrieved 20 hr later. Inspection of the implant-tool assembly showed accumulation of dense compacted soil containing gravel on the conetip shoulder. Small rocks (0.1 to 0.05 in. average diameter) with sharp edges were lodged adjacent to the membrane. A post-deployment leak check of the implant-tool assembly showed a small leak at the base of the TerraTrog implant. Upon removal of the implant from the tool, a small rock (0.05 in. diameter) was found to have punctured a small hole in the membrane.

The implant was deployed in grassy clay-like soil to a 4 ft depth and retrieved 14 hr later. No leaks in the membrane were detected and the implant was fully functional. A TCE response was obtained with 40 ml/min TerraTrog carrier gas flow rate. Inspection of the implant-tool assembly showed an accumulation of moderately dense, compacted sandy-clay soil that was visibly moist on the shoulder of the penetrometer tip.

The implant was deployed a third time in highly compacted sandy soil to a 14 ft depth and implanted permanently. Twelve hours after deployment the GC was connected to the TerraTrog surface module and 0.05ppm TCE level responses were obtained from the carrier gas. From these data it was estimated the TCE headspace partial pressure was 10 to 20ppm.

A second set of field experiments were performed 22 weeks later. The sample analysis was performed in real time with an ion trap mass spectrometer supplied and operated by the Oak Ridge National Laboratory (ORNL). In addition, discrete samples were taken by in-line sorption tubes developed by ORNL. Static samples were not obtained because of an operational error made in connecting the TerraTrog sample return line to the real-time monitor sample inlet fitting. However, soil gas dynamic samples of TCE, Benzene, Toulene and Xylene were obtained and analyzed with the real time monitor as were discrete results correlated with 10% for each species. However, it was possible to estimate the soil headspace concentration for only TCE and Benzene because the implant gas conductance for the remaining species has not been determined. It was estimated that the TCE and Benzene soil headspace partial pressures are 62.8 and 13.2ppmv respectively.

CONCLUSION

The development of the TerraTrog is viewed as having potential for future use in the evaluation of hazardous waste sites. The potential utility of the device includes not only initial site assessment, but possibly of more importance, its use in the routine monitoring that is essential to the long term assessment of a site before, during and after remedial activities are accomplished. Although initially designed to be used in a cone penetrometer, the utility of the device for routine groundwater monitoring is also recognized due to its small diameter and ability to descend down standard well casings.

ACKNOWLEDGEMENTS: Mark Wise, Ceril Thompson and Roger Jenkins from Oak Ridge National Laboratories for their assistance in collecting data at the Savannah River Site. Mark Kluger and Steve Kane from Viking Instruments for their assistance with data collection at the Phoenix Nike site.

REFERENCES

(1) S.C. Golian, E.E. Dodge, and B. Bixler, "Conducting Remedial Investigations on Feasibility Studies Under CERCLA," Superfund '88 Proceedings of the 9th National Conference, Hazardous Materials Control Research Institute, Silver Spring, MD, p. 1, 1988.

(2) K.T. Lang, D.T. Scarborough, M.E. Glover, and D.P. Lucero, "Quantitative Soil Gas Sampler Implant for Monitoring Dump Site Subsurface Hazardous Fluids," "Proceedings of the Second International Symposium for Hazardous Waste and Toxic Chemicals," Las Vegas, NV, 12-14, February 1991, p. 423.

(3) L.R. Taylor and N. Berzins, "Subsurface Contamination Screening by Combined Soil Gas/Groundwater Survey Procedure," Superfund '88 Proceedings of the 9th National Conference, Hazardous Materials Control Research Institute, Silver Spring, MD, p. 158, 1988.

(4) R.M. Barrer, Diffusion In and Through Solids, Cambridge University Press, London, Chapter 1, 1981.

(5) D.P. Lucero, "Performance Characteristics of Permeation Tubes," Analytical Chemistry 43, p. 1744, 1971.

(6) D.P. Lucero, "Ultra Low-level Calibration Gas Generation by Multi-Stage Dilution Techniques," Calibration in Air Monitoring, ASTM STP 598, American Society for Testing Materials, Philadelphia, PA, pp. 301-319, 1976.

(7) D.P. Lucero, "Soil Gas Sampler Implant for Monitoring Dump Site Subsurface Hazardous Fluids," Proceedings of the 6th National Conference on Hazardous Wastes and Hazardous Materials, New Orleans, Louisiana, April 12-14, 1989.

(8) D.P. Lucero, "A Soil Gas Sampler Implant for Monitoring Dump Site Subsurface Hazardous Fluids," Hazardous Materials Control 3, 5, p. 36, 1990.

(9) A.D. Little, Development of a Vapor Phase Calibrator for the APIMS-1 Analyzer, AMXTH-TE-TR-84305, U.S. Army Materiel Command, Aberdeen Proving Ground, MD, September 1984.

3

FIELD AND LABORATORY METHODS FOR A SUPERFUND ECOLOGICAL RISK ASSESSMENT AT MILLTOWN RESERVOIR WETLANDS

Greg Linder, **Mike Bollman, Chris Gillett, Julius Nwosu, Suean Ott, David Wilborn**, ManTech Environmental Technology; **Gray Henderson**, University of Missouri; and **Clarence Callahan**, US Environmental Protection Agency, Environmental Research Laboratory, 200 S.W. 35th Street, Corvallis OR.

ABSTRACT: Within ecological contexts, biological evaluations in the field and laboratory should be considered critical components in the ecological risk assessment process for Superfund, since integrated approaches to hazard evaluation consider contaminant bioavailability and subtle expressions of adverse biological effects associated with chronic exposures. Depending upon habitat type, field and laboratory methods have been developed for hazard evaluation which lend themselves directly to the Superfund ecological risk assessment process. For example, wetlands in mining districts in the western U.S are frequently impacted by heavy metal-laden sediments. The present study summarizes a baseline ecological risk assessment completed by U.S. EPA Region 8 for a Superfund site located at Milltown Reservoir wetlands (MRW) in western Montana. As part of the ecological risk assessment, a variety of biological test methods [e.g., terrestrial and aquatic tests] were critical to the wetland evaluation. For evaluating heavy metal effects at MRW, various field and laboratory methods were included as part of the ecological assessment. These included:

- Preliminary food-web contamination survey
- Vegetation tests in emergent and upland habitats
- Heavy metal uptake studies using plants
- Soil macroinvertebrate tests
- Sediment macroinvertebrate studies
- Studies using amphibians
- Studies using bacterial tests
- Soil and chemical analysis

In conjunction with chemical analyses, these biological and ecological evaluations yielded an integrated evaluation of ecological effects and exposure at MRW. The data gathered from laboratory and field work at MRW has reduced the uncertainty associated with the

baseline ecological risk assessment, and suggested that biological and ecological effects were subtle in their expression in the wetland.

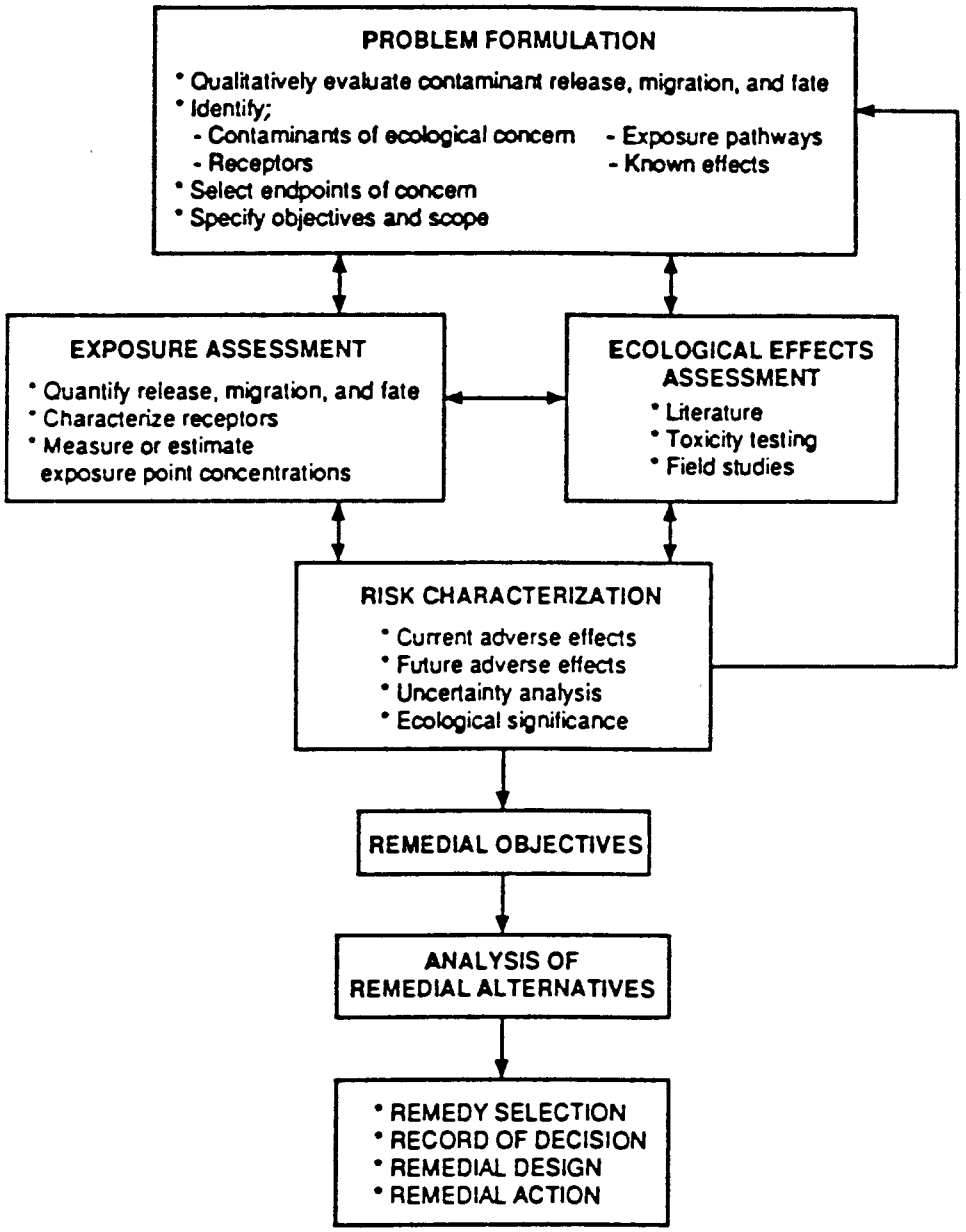
INTRODUCTION

Milltown Reservoir and its associated wetlands are located on the Clark Fork River in western Montana, six miles east of Missoula, Montana. The reservoir was formed in 1907 following the construction of a hydroelectric facility located on the Clark Fork River immediately downstream from its confluence with the Blackfoot River. Since construction of the dam, a wetland habitat has been created. Because of the upstream mining activities on the Clark Fork River, however, Milltown Reservoir has accumulated a large volume of heavy metal-laden sediment. The Milltown Reservoir wetland was initially identified under CERCLA [Comprehensive Environmental Response, Compensation, and Liability Act] in 1981 after community well-water samples were found to have arsenic levels that ranged from 0.22 to 0.51 mg/L; the EPA recommendation for potable water supplies suggested that arsenic not exceed 0.05 mg/L. Within an ecological context, however, the impact of the contaminated sediments on the wetlands was unclear; the laboratory and field investigations evaluated the extent of contaminant and its impact on the indigenous wildlife and vegetation characteristic of the site. For the wetlands evaluation, heavy metals appear the most critical contaminant which must be considered in the ecological assessment at Milltown; those of primary interest include arsenic, cadmium, copper, lead and zinc (Woessner, et al. 1984).

Assessment strategy. In general, an ecological assessment may be considered an integrated evaluation of biological effects derived through measurements of ecological effects and exposure (U.S. EPA 1988; 1989), and an overview of the assessment strategy used at MRW during field and laboratory operations is summarized in Figure 1. Within the context of Superfund ecological risk assessment, chemical and biological interactions associated with contaminant exposures in soil or sediment may be evaluated according to various assessment strategies. For example, both chemically-based and toxicity-based approaches have made significant contributions to ecological assessments for hazardous waste sites (Parkhurst, et al. 1989). From an ecotoxicological perspective, ecological effects and exposure assessments are complex interrelated functions which yield estimates of hazard associated with environmental contaminants in various matrices sampled at a site. Ecological assessments at Superfund sites reflect the site-specific demands required by waste sites, and represent integrated evaluations of ecological effects, including toxicity, and exposure. Depending upon the site, both laboratory tests and field methods will be required for an ecological assessment.

Toxicity assessments are derived from acute tests as well as subacute and chronic tests which measure biological endpoints other than death, and are generally completed as part of the ecological effects assessment. These toxicity assessments are usually derived from laboratory-generated data, but in situ toxicity assessments, while not as well developed

Figure 1. Ecological effects and exposure assessments as components of the ecological assessment process for hazardous waste sites (US EPA 1991).



as laboratory toxicity tests, are becoming more prominent in the ecological assessment process (Warren-Hicks, et al. 1989). In situ methods more closely infer a linkage between toxicity and exposure functions, and reduce the problems associated with lab-to-field extrapolations of toxicity data. Ecological effects assessments also rely upon field methods which measure ecological endpoints, either on-site or at reference sites, and yield survey data relevant to estimates of adverse ecological effects associated with a waste site.

Depending upon the environmental matrix being tested, site-specific toxicity assessments may be derived using various tests(e.g., Horning and Weber 1985; Peltier and Weber 1985; Weber, et al. 1988; Greene, et al. 1988), and may include invertebrate and vertebrate, algal, plant, and microbial test systems. These toxicity assessment tools potentially yield information regarding acute biological responses elicited by site-samples or their derivatives, and may suggest longer-term biological effects (e.g., genotoxicity or teratogenicity) potentially associated with subacute and chronic exposures to complex chemical mixtures characteristic of hazardous waste sites. Linkages among chemical contaminants, adverse ecological effects, and ecological toxicity (Parkhurst, et al. 1989; Stevens, et al 1989) may subsequently be evaluated during the site-assessment process using quantitative or statistical methods (Figure 2). When toxicity assessments are combined with (1) chemical analyses which evaluate pertinent site samples and (2) field surveys which measure ecological endpoints, higher level biological organization (e.g., populations and communities) ecological risk assessments may be derived with less uncertainty to assure that sound ecological management practices are implemented during the remedial investigation/feasibility study process.

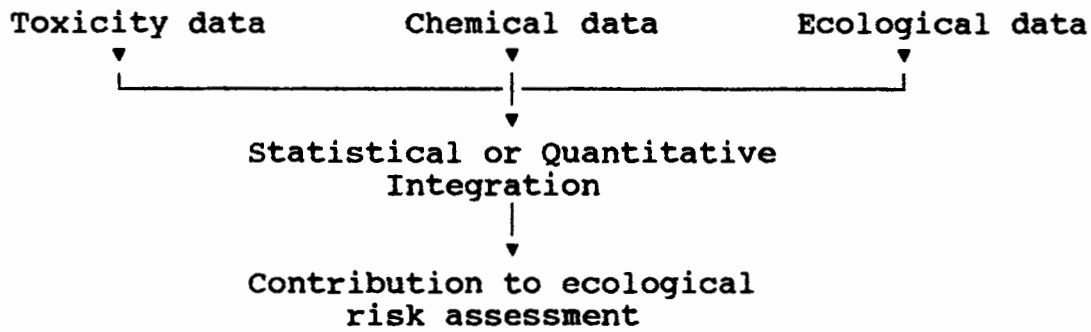
MRW assessment methods. For an ecological assessment at MRW, various tasks were completed during the preliminary (ETI 1990c) and definitive year's work. These tasks included:

- Preliminary food-web contamination survey [field and laboratory methods]
- Vegetation evaluations [laboratory root elongation tests on groundwater; emergent and upland vegetation tests in field and laboratory]
- Earthworm evaluations [field and laboratory methods]
- Preliminary and scoping year studies using amphibians [field and laboratory methods]
- Preliminary and scoping year studies using bacterial tests [laboratory tests]
- Plant uptake studies [field/greenhouse methods]
- Plant fluorescence evaluations [field and laboratory methods]

- Soil characterization and chemical analysis [soils, sediments, and biota; laboratory methods]

Whether completed during the preliminary or definitive year's studies, the data gathered from laboratory and field work at MRW has been summarized as a contribution to the baseline ecological risk assessment.

Figure 2. Sources of information (toxicity, chemical, and ecological) that contribute to an ecological assessment.



Preliminary Food-Web Contamination Survey [field and laboratory methods]. In preliminary food-web analyses for small mammals at MRW, there appears to be no overt indication of metal biomagnification in the small mammal community at Milltown. Additionally, in support of screening level risk calculations, the comparative literature suggests that no overt problem is indicated by tissue metal residues in either carcass or selected organs of the herbivores collected at Milltown during the preliminary field season. Observations regarding health and status of resident small mammal populations was also considered in the evaluation of small mammal risks associated with metal exposures. Upon gross examination, external features were generally unremarkable in all animals collected at MRW.

From a similar food-web contamination evaluation for fur-bearers (beaver and muskrat) the comparative data for metal loading in terrestrial and semi-aquatic mammals suggests that no adult muskrat or beaver would approach critical whole-carcass burdens, although no empirical site-specific data were collected at MRW to support this position. As with herbivorous small mammals, no target organ metal loads were considered quantitatively in these screening calculations. If target organs were considered (e.g., kidney), metal residues could be relatively greater than in carcass. But, small mammal data collected at MRW do not suggest that target organ toxicity or biomagnification are being expressed. Again, calculated metal concentrations in muscle tissue are relatively low which may suggest that the metal bioavailability in plant tissue (e.g., cattail tuber) is relatively limited, or that exposure is minimized due to selective feeding.

Vegetation Evaluations [laboratory root elongation tests on groundwater; emergent and upland vegetation tests in field and laboratory]. During the scoping year's field and laboratory efforts, seed germination testing was completed using site-soils. Both on-site and laboratory methods were employed in these preliminary soil contamination evaluations, and no overt expressions of phytotoxicity were observed. During the definitive year's studies, rather than continue work with these two phytotoxicity test methods, alternative test methods were used in evaluating MRW. One, groundwater samples were collected at selected sites across the wetland and were tested using the root elongation procedure. Two, emergent zones in the wetlands were evaluated using laboratory and field methods that tested native marsh plants as well as a standard submerged aquatic vascular plant (Potamogeton pectinatus and a standard test species Hydrilla verticillata).

The root elongation tests that were completed on groundwater samples collected at MRW were consistently not acutely toxic, suggesting that groundwater coincident with the rhizosphere would generally not be overtly phytotoxic. These groundwater samples were collected from deposition zones in the braided stretches of the Clark Fork River, and while generally not acutely toxic, some statistically significant biological activity was noted with respect to root elongation inhibition, however, at some sampling locations at MRW. These groundwater samples were clearly inhibitory to root elongation as measured using the standard test species. Field surveys completed in conjunction with the sampling and laboratory testing, however, did not suggest that these biological effects were currently being expressed at these sampling locations.

In addition to root elongation testing for groundwater evaluations, field and laboratory testing was completed with an indigenous emergent vascular plant, sago pondweed (Potamogeton pectinatus), as well as a standard test species Hydrilla verticillata during the definitive year's operations. In general, emergent vegetation testing in laboratory and field suggested that effects, when expressed, were not acute but sublethal in expression. The in situ testing with sago pondweed (P. pectinatus) indicated no adverse effects for growth endpoints (root and shoot length), and physiological markers (peroxidase activity [POD]) indicative of plant stress were similarly unremarkable. Indigenous plant samples (Elodea sp.) were also collected concurrent with in situ testing and were analyzed for POD activity. Statistically significant differences among sites were noted across MRW sampling locations which may be indicative of general plant stress. In parallel laboratory exposures, no consistent pattern was noted with respect to growth endpoints (root and shoot lengths and chlorophyll a) for either test species (P. pectinatus and H. verticillata) when tested with bulk sediments collected from MRW sites. While morphologic endpoints related to growth (e.g., shoot and root length) suggested no acute toxicity in laboratory or field exposures with MRW sediments, differences in POD activity across MRW may reflect the spatial variability in metals that are differentially bioavailable.

Root elongation tests on soil eluates. Eluates prepared from site soil samples were tested using root elongation as the toxicity endpoint. While qualitative differences were observed with respect to the inhibition of root growth, no soil-derived eluate expressed statistically significant results following 120-hr incubation.

Earthworm evaluations [field and laboratory methods]. Earthworm tests -- both on-site and laboratory -- expressed no acute toxicity. Subtle biological response data (e.g., morphologic and dermatopathologic effects) from laboratory and field tests were frequently expressed in soils with elevated total metals, however. For example, on-site testing with earthworms suggested that soil from some sampling locations was associated with sublethal effects in exposed earthworms. These sampling locations had also been identified in the root elongation tests completed with groundwater samples collected via hand-driven well points. Again, no acute toxicity was expressed, and differential bioavailability of metals may be considered a possible source of these spatially variable expressions of subacute and chronic effects.

Preliminary and scoping year studies using amphibians [field and laboratory methods]. Laboratory tests completed on Milltown surface water grab samples collected during the preliminary year expressed spatially variable, but sampling-location consistent results as summarized by ETI (1991c). No overt toxicity was expressed by 96-hour tadpoles when exposed to site samples in the laboratory, and in conjunction with laboratory work using defined metal mixtures and single-metal exposures, chemical analysis of these site-samples had also suggested that metal concentrations were not sufficient to mediate acute effects. Subacute and chronic effects measured on Milltown surface water grab samples were generally expressed in altered growth, though only a limited number of embryos appeared to present those growth effects in a statistically significant manner. These subacute, or teratogenic, endpoints were frequently subtle (e.g., mild abdominal edema, hyperpigmentation) though gross malformations were occasionally expressed. No contaminant-specific malformations were noted in these exposures. Amphibian testing was suspended during the definitive year's operations and replaced in the site assessment by the emergent vegetation evaluations.

Preliminary and scoping year studies using bacterial tests. As with the amphibian evaluations, Microtox® afforded an opportunity to characterize potential short-term effects associated with water soluble constituents derived from site soils and surface water grab samples during the preliminary year's work. None of the surface water samples expressed adverse biological effects on screening, and only soil sample eluates yielded responses in screening tests [undiluted samples at highest dilution possible] that required definitive tests being completed. Four soil eluates presented sufficient biological effects to warrant additional testing and calculation of EC_{50}s. While Microtox® indicated that some biological activity was associated with either surface water grab samples or soil eluates, those limited number of responsive samples were consistent with other biological tests completed during the preliminary field and laboratory season. The relative

agreement among the various test methods used during preliminary studies in FY 90 suggested that Microtox[R] become a secondary evaluation method during the definitive year's studies, and consequently more ecologically relevant methods were applied during FY 91 field and laboratory operations.

Plant uptake studies [field/greenhouse methods]. The preliminary data collection for plant uptake studies established baseline information regarding soil fertility; the definitive year's work involved two interrelated greenhouse exposures using field-collected soil or exposed sediment samples. The greenhouse studies considered [1] qualitative screening tests which addressed age-related changes in metal disposition in plant tissue and [2] quantitative studies which addressed metal uptake by representative garden species following growth typical of a domestic garden.

The qualitative study regarding normal plant growth from germination through seedling and mature plant to senescence suggested that, if germination and early seedling survival were not impaired, and a typical plant life cycle could be completed under ideal garden conditions. However, the quantitative early seedling growth and plant vigor test which was completed in conjunction with the metal uptake studies suggested that soils collected from some depositional areas may exert biological effects that would not be detected in seed germination and root elongation tests. For example, companion work completed on MRW samples with these routine plant toxicity tests suggested no overt adverse effects associated with soils collected from old "ox bow" reaches along the river, but in historic depositional areas growth reduction was indicated. It should be noted, however, these samples were few in number, and while reductions in biomass in both species tested (lettuce and radish) were consistent, additional samples would have to be evaluated to determine the spatial pattern of these effects. Root elongation tests completed on sample splits also indicated some statistically significant reductions in growth. Contrasted to these controlled greenhouse and laboratory exposures with commercial garden varieties, field surveys failed to indicate widespread vegetation response in the sampled area. In part, the physicochemical characteristics of the soils across MRW may explain the variation expressed in growth reduction, particularly in those depositional areas occasionally associated with reduced plant vigor in laboratory tests. The geochemical heterogeneity of soils across MRW was apparent, even in sampling units that were similar with respect to texture, for example. While all MRW soils are xerofluvents, the soils ranged in texture from loams to sandy loams and presented cation exchange capacities (CECs) that could, in part, contribute to the differential bioavailability of metals. Generally, soils with higher CECs ($\geq$ 30mEq/100gram soil) were more likely to be associated with subacute effects, and frequently expressed adverse effects in plant tests. Variability at relatively lower CECs could be associated, in part, by subtle differences in soil texture, as well as organic content and geochemistry.

These interacting soil matrix characteristics undoubtedly contribute to the apparent heterogeneity in metal uptake in plants -- both native emergents, for example, and the

garden species tests under greenhouse conditions. In plant uptake studies, metals did accumulate in plant tissues with the trend, not surprisingly, clearly suggesting that roots would accumulate metals to a greater extent than leaves. The pattern of metal accumulation in roots differed, in part, as a function of soil type. For example, root crops grown in a relatively high clay soil did not have as much metal associated with its epidermis as did plants grown in a lighter, loam soil. Nonetheless, these roots did accumulate metal in the parenchyma tissue of the root core. To fully characterize the biological disposition of metals in garden crops, additional time course work would be required, and in order to adequately address human health risks, metal bioavailability in plant tissues should be address. The human health implications of this differential plant uptake were not considered in this work.

Plant fluorescence evaluations [field and laboratory method]. Definitive year's studies with indigenous flora were variable in expression, and the preliminary year's work undoubtedly captures a similar variability with respect to soil matrix and metal interactions. When considered as a qualitative measure of plant health and as a supplement to the emergent vegetation and root elongation evaluations completed at MRW, plant fluorescence data suggests that no overt phytotoxicity is being expressed, but subtle indications of plant stress may be indicated at various depositional areas at MRW.

Soil and chemical analysis [soils, sediments, and biota; laboratory methods]. Within an ecological assessment for MRW, biological effects measured in toxicity tests must consider interactions, or potential interactions between the soil matrix and metals in the soil, particularly with respect to bioavailability of metals in soils. Soil pH, percent total nitrogen [TN] and percent organic material [OM] were measured on soil samples collected at MRW during the definitive year's work. Soil texture analysis was also completed, as was DTPA [diethylenetriaminepentaacetic acid, 0.025M] metals as a physicochemical analog of bioavailable metals. With these soil matrix characteristics available, potential confounding effects associated with soil physicochemical properties could be identified, and metal toxicity interpretations were more adequately developed.

Soils at MRW were, not surprisingly, heterogeneous across the site, but within sampling unit variability was relatively limited though subtle soil geochemical differences were indicated when plant testing was considered. Soils throughout MRW were xerofluvents and ranged from loams to silty loams to occasional silty clay loams. Organic material was variable across MRW but was relatively invariant within defined sampling strata. Total nitrogen, soil pH, and cation exchange capacity were similarly variable but relatively similar within strata. Overall, these physical characteristics were invaluable to interpretations of the biological effects associated with soil metal burdens.

PROJECT SUMMARY

The ecological assessment at MRW suggests that no overt toxicity or adverse biological effects are being expressed at the current time. Consistently, and regardless the field or laboratory test methods used, biological assessments at MRW were unable to characterize acute toxicity. With the exception of subtle biological effects noted in samples collected from depositional areas, future remediation plans should consider the potential biological and ecological impacts associated with remediation efforts in light of the current impacts associated with elevated metals in soils and sediments. While the current subtle effects and potential future effects should not be understated, currently any widespread physical alteration of wetland habitats may not be justified. Future site monitoring should address potential problems associated with remediation both at MRW and at upstream operable units, and in particular should consider the long-term effects associated with vegetation exposures in the depositional areas. Also, indirect effects, e.g., habitat alteration associated with reduced vegetative growth, associated with future management plans (e.g., "walk away" or sediment dredging) should be considered as a potential consequence of the in situ metals that presently occur in the soils and sediments at MRW.

For those biological and, by inference, ecological effects that were considered during the course of the work at MRW, uncertainty within the risk assessment process must be given high regard. For example, whether "sentinel species" (Lower and Kendall 1990) are appropriate to an ecological assessment, and whether adequate surrogate test species (in either laboratory or field) were used in the biological assessment have been and will continue to be, the proximate sources of uncertainty in the ecological risk assessment process; the work at MRW is no exception and the uncertainty associated with those tools used during the ecological assessment must be considered. At MRW specifically:

- the preliminary food-web contamination survey suggested that bioaccumulation of metals was evident in emergent vegetation in some reaches of the deposition zones within MRW, but biomagnification or trophic level transfer of metals to herbivores did not appear to be a problem for the endpoints considered. Field surveys at MRW did not contradict these assessments, but the sparse comparative toxicity data base, particularly for chronic endpoints must be considered as part of the uncertainty in this regard.

- Vegetation tests, particularly in evaluating water collected from the rhizosphere, suggested that no acute effects were associated with groundwater or surface water, but subtle growth-related effects were not infrequent in samples collected from deposition zones at MRW. These subtle indications were noted in both laboratory tests using emergent vegetation and in standard root elongation tests. Again, field surveys found no overt expression of altered vegetation patterns and reduced cover,

for example, was evident only in those areas that had been previously physically manipulated.

- Provided earthworms are good "sentinel species" to assess soil health, earthworm evaluations in both field and laboratory were consistently negative, suggesting that soil macroinvertebrates may not be at great risk as long as the current soil conditions exist. Soil microbial communities, however, were not adequately described and should be evaluated when methods are available.

- Preliminary and scoping year studies using amphibians suggested that subtle biological effects may potentially be expressed at MRW, but field surveys did not support any conclusions that those effects would be prominent nor potentially adverse.

- Preliminary and scoping year studies using bacterial tests were consistent with the balance of biological test methods used at MRW, but may not be representative of the soil community that occurs at MRW. Biological and ecological assessments for soils are currently characterized with relatively high uncertainty.

- Plant uptake studies suggest that garden crops, like those native plants collected as part of the food-web contaminant evaluation, accumulate metals differently, depending upon the plant species and anatomical feature considered (e.g., root versus leaf). While empirical data illustrate the accumulation of metal in plants growing in MRW soil, the relationship between metal loads in plant tissue and consumer (e.g., small mammals or humans) are quite heterogeneous and potentially a source of much uncertainty.

- Plant fluorescence evaluations were primarily supportive of more definitive plant tests and at present should be considered as less sensitive than "whole-plant" test endpoints that integrate biological responses over longer periods of time.

- Characterization and metal analysis of MRW soils, sediments, and biota clearly indicated that metals have accumulated in various environmental matrices, and that MRW is spatially quite heterogeneous with respect to metal deposition. Within sample unit variation was relatively less than across MRW variation. Soils within sample units were relatively homogeneous, although sufficient variation was evident that accounted for, in part, the variability noted in biological samples (e.g., emergent plants and terrestrial invertebrates) collected at stations within the sample units.

REFERENCES.

Environmental Toxicology International, Inc. (ETI). 1991a. Milltown Reservoir sediments site baseline risk assessment: Ecological risk assessment work plan. TZ4-C08012-WP-H1416. Prepared for U.S Environmental Protection Agency, Region 8. Helena, MT under U.S. EPA Technical Enforcement Support Contract.

Environmental Toxicology International, Inc. (ETI). 1991b. Milltown Reservoir sediments site baseline risk assessment: Sampling and analysis plan. TZ4-C08012-WP-H1417. Prepared for U.S Environmental Protection Agency, Region 8. Helena, MT under U.S. EPA Technical Enforcement Support Contract.

Environmental Toxicology International, Inc. (ETI). 1991c. Preliminary field survey and laboratory evaluations at Milltown Reservoir. TZ4-C08012-FO-H1287. Prepared for U.S Environmental Protection Agency, Region 8. Helena, MT under U.S. EPA Technical Enforcement Support Contract.

Greene, J.C., C. Bartels, W. Warren-Hicks, B. Parkhurst, G. Linder, S. Peterson, and W. Miller. 1989. Protocols for Short Term Toxicity Screening of Hazardous Waste Sites. EPA/600/3-88/029. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Horning, W.B., II, and C.I. Weber. 1985. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. EPA/600/4-85/014. Environmental monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.

Lower, W.R. and R.J. Kendall. 1990. Sentinel species and sentinel bioassays. In Biomarkers of environmental contamination. McCarthy, J.F. and L.R. Shugart (eds.). 1990. Lewis Publishers, Inc. Chelsea, Michigan. pp. 309-331.

Parkhurst, B, G. Linder, K. McBee, G. Bitton, B. Dutka, and C. Hendricks. 1989. Toxicity tests. In W. Warren-Hicks, B. Parkhurst, and S. Baker, Jr. (eds.). Ecological assessment of hazardous waste sites. EPA/600/3-89/013. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Peltier, W. and C.I. Weber. 1985. Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms. Third Edition. EPA/600/4-85/013. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.

Stevens, D. 1989. Field sampling design. In W. Warren-Hicks, B. Parkhurst, and S. Baker, Jr. (eds.). Ecological assessment of hazardous waste sites. EPA/600/3-89/013.

U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Stevens, D., G. Linder, and W. Warren-Hicks. 1989. Data interpretation. In W. Warren-Hicks, B. Parkhurst, and S. Baker, Jr. (eds.). Ecological assessment of hazardous waste sites. EPA/600/3-89/013. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Suter, G.W. 1990. Endpoints for regional ecological risk assessments. Environ. Manage. 14:9-23.

Suter, G.W. and J.M. Loar. 1992. Weighing the ecological risk of hazardous waste sites. Environ. Sci. Tech. 26:432-438.

U.S. EPA. 1991. Ecological assessment of Superfund sites: An overview. In ECO Update, Vol. 1, Number 2. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Office of Emergency and Remedial Response, Hazardous Site Evaluation Division (OS-230), Washington, D.C. Publication 9345.0-05I.

Warren-Hicks, W., B. Parkhurst, and S. Baker, Jr. (eds.). 1989. Ecological assessment of hazardous waste sites. EPA/600/3-89/013. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Weber, C.I., W.H. Peltier, T.J. Norberg-King, W.B. Horning II, F.A. Kessler, J.R. Menkedick, T.W. Neiheisel, P.A. Lewis, D.J. Klemm, Q.H. Pickering, E.L. Robinson, J.M. Lazorchak, L.J. Wymer, and R.W. Freyberg. 1989. Short-term methods for estimating the chronic toxicity of effluents and surface waters to freshwater organisms. Second Edition. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH. 600/4-89/001.

4

USE OF HGI_2 X-RAY SPECTROMETERS FOR THE DETECTION OF LEAD IN PAINT

J.S. Iwanczyk, Y.J. Wang and W.R. Graham
Xsirius, Inc., 4640 Admiralty Way, Suite 214, Marina del Rey, CA 90292

Abstract: A laboratory study of HgI_2 spectrometers for use in the in-situ determination of lead on painted surfaces has been conducted. The energy resolution attainable with HgI_2 detectors in the energy region corresponding to lead K x-rays has been measured. Sources of ^{241}Am, ^{109}Cd and ^{57}Co have been used for this purpose. Energy resolutions of 880 eV (FWHM), 1370 eV (FWHM) and 1940 eV (FWHM) were obtained at energies of 60 keV, 88 keV and 122 keV, respectively. Measurements on pure lead and thin film standards, ranging from 0.5 mg Pb/cm^2 to 2 mg Pb/cm^2, have been conducted. Spectra from these samples, excited by ^{109}Cd and ^{57}Co sources, are illustrated in the paper. Well separated $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, $K_{\beta 2}$ and L_l, L_α, L_β, L_γ lines compare very favorable to those measured with a cryogenically cooled Ge detector. Future plans for the development of a portable HgI_2 XRF lead analyzer are also discussed.

INTRODUCTION

There is a growing awareness about the health hazards related to lead-based paint poisoning that can occur in many old houses. Recent legislation required the U.S. Department of Housing and Urban Development (HUD) to establish procedures to remove, as far as practicable, such poisoning hazards. In response to this legislation, HUD promulgated a regulation which requires abatement to eliminate paint poisoning hazards in housing in which the concentration of lead in paint equals or exceeds 1 mg/cm^2 [1]. In addition, the legislation requires HUD to periodically review and reduce the level below 1 mg/cm^2, to the extent that reliable technology makes feasible the detection of a lower level, and medical evidence supports the imposition of a lower level.

Because of the large number of homes that may be involved in testing, it is very important to develop instruments and testing methods which will provide for the reliable, rapid, and inexpensive measurement of lead in lead-based paints,

and that also could be transferable for the measurement of lead in household dust and urban soil. There are basically two general types of instrumentation and techniques that are presently in use: 1) analytical laboratory methods, 2) in-situ field methods.

Analytical Laboratory Methods

This group include Flame Atomic Absorption Spectroscopy [2,3], Inductively Coupled Plasma [4], Voltammetry [5], Laboratory X-Ray Fluorescence [6], Neutron Activation Analysis [7], Mass Spectrometry [4], and Ion Selective Electrodes [4]. All the above techniques, alone or in combination, can provide the required sensitivity and accuracy. The major drawback with all these laboratory methods is in the problem of collecting representative samples. For example, it is necessary to ensure that all layers making up the paint film are collected in proper and relative amounts. Additionally, all lab methods require the destruction of part of the painted surface in the sample collection process. The time and labor involved in sample collection, transportation and preparation (many techniques require dissolution of the lead) makes the laboratory techniques very expensive and slow, which practically eliminates them as methods of choice for the application described above.

In-situ Field Methods

Field methods, by contrast, potentially offer lower costs and shorter times to complete the analyses. There are two general types of screening tests, a) chemical spot tests [8,9] and b) tests carried out with portable testing equipment, e.g., portable x-ray fluorescence spectrometry (XRF). Although some of the spot tests were reported to have adequate detection limits, the tests were designed for lead ions in solution. The process of producing a solution of lead ions, starting from a dried paint film, normally involves the use of concentrated acids, and hence would not be readily performed in the field. There have been certain successes reported with another method using sodium sulfide and scratching the paint film [8]. This method is capable of detecting lead in new paint films for concentrations greater than 0.5%, however it is limited to use on white, or light colored, films and by its susceptibility to interference by other metal ions, e.g., mercury. In addition, the effects of a non-homogeneous distribution of lead throughout the film, the composition, age, and exposure history of the paint, and the possible overcoating of many layers of new paints, will all increase the error and lower the precision and accuracy of any spot test method.

The only type of portable instrument for non-destructive detection of lead in paint films reported in the literature is an x-ray fluorescence (XRF) spectrometer [10,11]. The XRF technique can potentially satisfy all the requirements for the measurement of the lead content in paints. This non-destructive technique can provide very quickly (in seconds) information about lead concentrations without any sample preparation. In addition, using information from the characteristic L and K x-ray lines of lead simultaneously, it is possible to determine whether lead is present on the surface or it is buried under layers of paint.

Laboratory XRF units employing cryogenically cooled detectors are broadly used and provide high accuracy and precision. Currently, however, there are no truly portable, battery operated, hand held XRF units available on the market that can offer similar parameters. It was shown in the literature [12] that it is mandatory to use the lead K x-rays in the determination of lead concentrations. The lead L x-rays can serve only as supplementary additional information due to their strong attenuation by paint overlays. The high energy of Pb K x-rays (about 75 keV) requires detectors built from high atomic number materials in order to assure a good detection efficiency, which in turn additionally narrows the choice of a detector. Presently available field instrumentation can be divided into the following categories: a) poor detection efficiency and poor energy resolution (this include systems using gas filled proportional counters and room temperature silicon detectors) [13,14], b) good efficiency but poor energy resolution (this includes systems employing NaI(Tl) and other scintillating detectors) [15,16,17,18] and finally c) good efficiency and resolution, but a serious lack of portability (this include systems utilizing cryogenically cooled Ge[Li] and High-Purity Ge detectors) [12,18,19,20].

Without the need for cryogenics, HgI_2-based XRF spectrometers are extremely attractive, due to their high energy resolution, small size, low power requirements and the possibility of constructing truly portable instruments for lead paint detection. HgI_2 detectors, due to the very high atomic numbers of its constituents, strongly absorb x-rays, assuring almost 100% detection efficiency for both the K and L characteristic x-rays of lead. Mercuric iodide portable XRF units seem to be ideally suited for detecting lead concentrations in urban housing, offering very convenient, non-destructive and reliable field methods suitable for use by non-technical personnel. Such an

instrument has a significant potential to improve the precision and accuracy over the existing field portable instrumentation, particularly at critical decision points such as the 1.0 mg/cm^2 level of lead in paint. Also, it may substantially reduce the time and cost of the analysis. With small modifications, the instrument also can be transferable for the measurement of lead in household dust and urban soil, with the addition of inexpensive sample preparation techniques and target holders.

GENERAL DESCRIPTION OF XRF

X-ray secondary-emission spectrometry, or x-ray fluorescence spectrometry, is a non-destructive instrumental method of qualitative and quantitative elemental analysis. In XRF, a collection of atoms, the sample, is excited by an external source (e.g., x-rays, electrons, etc.). This primary radiation is incident on the sample, where it interacts to excite inner shell electrons, which then de-excite to produce fluorescent x-rays, whose energies are uniquely characteristic of the elemental identity of the atom emitting them. Therefore, if these emitted fluorescent x-rays are collected, one may use them as an indication of the composition of the sample. Primary excitation photons incident on the sample interact either by the photoelectric effect to produce the desired characteristic x-rays, or by scattering - mainly from the atoms in the low-atomic-number substrate. These scattered x-rays constitute an unwanted background that sets the detection limit for the fluorescence measurement. Thus, excitation, detection, and spectrum analysis are the three major steps in energy dispersive XRF analysis. The selection of the excitation source, sample-fluorescer-detector geometry, and proper software for the calibration and analysis of the results are very important. The analysis method is basically driven, and often limited, by the types of x-ray detectors available to sense the fluorescence radiation from the test sample. The detection efficiency and energy resolution of the detector used determines whether it is possible to achieve the required detection limits, precision and accuracy. As noted, the ratio of the signal to the unwanted scattered background must be higher for better energy resolution. Better energy resolution helps also to separate signals from neighboring chemical elements, whose atomic numbers are close to that of lead.

THE EXCITATION SOURCE

The function of the excitation source is to excite the characteristic x-rays in the spectrum via the x-ray fluorescence process. Several types of sources have been used, including nuclear sources, Bremsstrahlung radiation, secondary fluorescence, charged particles, and synchrotron sources. The latter three will not be further considered here, since they are not practical for in-situ applications. For the best portability, isotope excitation sources are preferable due to their relatively small size. Monoenergetic excitation energies of isotope sources produce the unmodified (Rayleigh) and modified (Compton) scattering peaks just at and below the incident energy. For good sensitivity, the fluorescence x-rays of the elements must not overlap the scatter peaks. This effect favors the use of monoenergetic x-ray excitation sources, rather than broadband excitation, which would distribute the scattered radiation over the entire range of energies. Disadvantages of isotope sources include a lack of ability to adjust their energies, and special requirements on their handling, shielding and accountability. Also, many of them have relatively short half lives, requiring periodic replacement of the source and continuous software adjustment for changing intensities.

Recently, significant progress has been made in the area of miniature x-ray generators. The advantages of an x-ray tube source include its higher intensity and controllable output, and its higher safety factor. In order to efficiently excite the characteristic K lines of lead, the x-ray tube would need to operate at bias voltages well in excess of 100 kV. There are such x-ray generators operating from batteries (e.g. Kevex Model PXS6; size 18" x 7.3" x 7.3"; weight 30lbs; bias voltage up to 130kV), but they do not satisfy the criteria of small size and weight.

As a result of the above analysis a conclusion can be drawn that for the construction of a truly portable instrument, isotope excitation sources represent the best choice. For the excitation of K and L lines of lead there are two practical sources available: ^{57}Co and ^{109}Cd. Major gamma and x-ray lines of these sources, with respect to the absorption edges of lead, are described in Table I.

TABLE I

	^{57}Co				^{109}Cd				
	Major gamma radiations				Major gamma, x-radiations				
Energy (keV)	14.4	122.1	136.5	692.0	22.0	22.2	24.9	25.6	88.03
Intensity (%)*	9.5	85.5	10.7	0.16	28.9	54.5	13.7	2.7	3.6
Half-life time:days	270				453				

Lead Absorption Edges				
	L_{IIIab}	L_{IIab}	L_{Iab}	K_{ab}
Energy (keV)	13.044	15.207	15.870	88.001

*See the definition in "Table of Radioactive Isotopes", Edgardo Browne and Richard B. Firestone, John Wiley & Sons. 1986.

The ^{109}Cd source offers several advantages over the ^{57}Co source. First, a ^{109}Cd source has a longer half-life time than a ^{57}Co source (453 days vs. 270 days). Therefore, longer periods between source replacement and system recalibration are possible with the ^{109}Cd isotope source. Second, the radiation energy of ^{109}Cd is lower than that of ^{57}Co (88 keV vs. 122 keV), allowing easier shielding for personnel protection and beam confinement. The third advantage is related to certain properties of paint and its substrates. In general, there are mainly low-Z elements in the paint and substrate materials. In contrast to heavy metals, these low Z elements cause a strong Compton scattering interaction with the incident primary gamma-ray photon. The background from such scattered photons may seriously limit the lower detection limit of the system. While the 122 keV photons of ^{57}Co are well above the K-shell binding energy of lead and provide a good source for Pb x-ray excitation, the scattered energy from this source is in the range 83 keV to 122 keV (corresponding to the scattering angle of 180° to 0°). In order to separate the scattered radiation from the Pb K x-rays in the energy region (73 keV-87 keV), the system excitation geometry has to be modified to produce a scattering angle of close to 0°, i.e., a grazing angle scattering. Hence, the scattering peak can be

shifted to a higher energy region. However, this is an inefficient excitation geometry, and the low energy tail of the direct radiation from the source will overlap the Pb K x-ray region. For a ^{109}Cd source (88 keV gamma line), on the other hand, the majority of the scattered energy is in the range 65 keV to 75 keV, corresponding to scattering angles of 180° to 90°. In this case, the 180° backscatter angle yields the best system geometry, and the Compton scattering peak from this angle can be shifted to the lowest possible energy region.

THE HGI_2 X-RAY DETECTOR

The broad band gap of HgI_2 (2.2 eV) results in a low detector leakage at room temperature (typically below 1 pA), and with a construction designed to keep detector capacitance in the vicinity of 1 pF, the electronic noise from such detectors is very low. In a working model of an HgI_2 spectrometer built for NASA's Comet Rendezvous Asteroid Flyby Mission, a total energy resolution of 198 eV (FWHM) has been obtained for the 5.9 keV K_α line of Manganese. The noise contribution for this system was about 152 eV (FWHM) [21]. Also, because of the high atomic numbers of its constituents, HgI_2 strongly absorbs x-rays and so exhibits almost 100 % detection efficiency up to energies of characteristic x-rays of lead (75 keV).

A field-portable XRF system, based upon the use of mercuric iodide x-ray detectors, has several critical advantages, foremost of which is its ability to operate without a supply of liquid nitrogen cryogens (as would be the case for a Ge x-ray detector), and with much better energy resolution than scintillator-based detectors, or room-temperature-operable Si[Li] detectors and proportional counters. HgI_2 XRF spectrometers have the advantages of small size and low power needs, with obtainable energy resolution approaching those of cryogenically cooled Ge systems, making possible truly portable, hand held, automated instruments.

EXPERIMENTAL RESULTS

The energy resolution attainable with HgI_2 detectors in the energy region corresponding to lead K x-rays has been measured. For this purpose, sources of ^{241}Am, ^{109}Cd and ^{57}Co have been used. Energy resolutions of 880 eV (FWHM), 1370 eV (FWHM) and 1940 eV (FWHM) were obtained at energies of 60 keV, 88 keV and 122 keV respectively. Figure 1 presents a

gamma-ray spectrum obtained with an ^{241}Am source. Figure 2 is the spectrum obtained with a ^{109}Cd source.

A series of XRF measurements have been performed recently to verify the feasibility of HgI_2 detectors for use in XRF analyzer application for lead detection. Experiments were performed with two isotope sources: ^{109}Cd and ^{57}Co. The ^{109}Cd annular shaped source was 9 years old with an activity of about 0.15 mCi. The activity of the decayed Mossbauer ^{57}Co source was about 3.6 mCi. The setup for using the annular ^{109}Cd source is illustrated in figure 3. The setup for the ^{57}Co excitation is illustrated in figure 4. A Tennelec TC244 spectroscopy amplifier with a shaping time of 12 μs has been used for the experiments. The spectra were collected using multichannel analyzer consisting of a Nucleus Personal Computer Analyzer (PCA) card installed in an IBM PC-type computer.

Figure 5 shows a spectrum of a lead sample excited by the ^{109}Cd source. Figure 6 presents a spectrum from the same sample, but excited with the ^{57}Co source. In both cases one can see the clearly separated $K\alpha_1$, $K_{\alpha 2}$, $K_{\beta 1}$, and $K_{\beta 1}$ lines of lead. Figure 5 shows much more pronounced L lines than can be seen in Fig. 6, due to the very intense 22 keV excitation energy present in the ^{109}Cd source.

In addition to measurements on the pure Pb sample, tests were also made on thin film samples with low lead concentrations. Thin lead coating standards made on Mylar films and backed with plastic substrates, ranging from 0.5 mg Pb/cm^2 to 2 mg Pb/cm^2, were obtained from the National Institute of Standards and Technology. The annular shaped ^{109}Cd source discussed earlier was used for these thin film measurements. The backscatter peak of ^{109}Cd falls at approximately 66 keV, with a sharp high energy edge which is below the K peaks of Pb. Figures 7 and 8 show spectra taken from a standard sample with a 1.025 mg/cm^2 concentration of lead, which is at the detection level required by HUD. Lead K lines are shown in Figure 7, while Figure 8 presents the Pb L x-ray lines region. Besides lead $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, $K_{\beta 2}$ and L_l, L_α, L_β, L_τ lines, one also observes counts from Compton and Rayleigh scattering. Note that the lead K characteristic line spectra measured with an HgI_2 detector (presented in figures 5, 6 and 7) compare very favorable to those measured with a cryogenically cooled Ge detector and presented in References 13,19, and 20.

CONCLUSIONS

The preliminary experimental results show the great promise of HgI_2 detectors for use in XRF analyzer applications for lead detection. A truly portable instrument for lead paint detection can be implemented by the use of such HgI_2 detectors. Such an instrument can easily meet the requirement for a critical detection limit of 1.0 mg Pb/cm^2, which is the regulatory (HUD) limit for the lead concentration in paints. In addition to being a qualitative screening device, the HgI_2 XRF lead analyzer can also be used to determine the lead concentration quantitatively by using the information obtained from the spectra. To do so, specialized software can be used in the data analysis which will convert the measured Pb x-ray intensities directly to lead concentrations in the paint. This software should meet the following requirements: a) Minimize influence of matrix effects of paints and different substrates by utilizing information from the entire energy spectra b) Best use of the information from both the L and K characteristic x-rays to obtain the highest precision and to determine the relative location of the lead in the depth of the film. Further experiments related to quantitative analysis, geometry optimization for the detector-sample-excitation source, and the miniaturization of the whole system are planned as future tasks. In particular, the measured detection limits, accuracy and precision will be studied and compared with those obtained for existing portable XRF lead analyzers in order to show clear advantages of HgI_2 based systems.

ACKNOWLEDGMENTS

The research work described in this paper was supported by the National Aeronautics and Space Administration, Contracts NASW-4432 and NAS5-33045; NIH Grant No. 5R01 GM37161. In addition the authors wish to acknowledge the support and helpful assistance of Mr. Bart Dancy in the construction of the HgI_2 spectrometer probes, Ms. Fanny Riquelme for the fabrication of the HgI_2 detectors, and Mr. Wayne Schnepple for assistance in preparation of this paper.

REFERENCES:

1. Federal Register, 53, No. 108, June 6, 1988, 20791

2. K. A. Hausknecht, E. A. Ryan, L. P. Leonard, "Determination of Lead in Paint Chips Using a Modified Ashing Procedure and Atomic Absorption Spectrophotometry", Atomic Spectroscopy 3(2), 1982, 53-55.

3. "Standard Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy", ASTM D 3335-85a, Annual Book of ASTM Standards, 6.01, American Society for Testing and Materials, Philadelphia, PA, 19103, 1988, 507-509.

4. D. A. Skoog, Principles of Instrumental Analysis, Third Edition, CBS College Publishing, 383 Madison Ave., New York, NY, 1985.

5. P.C. Lai, K. W. Fung, "Determination of Lead in Paint by Differential-Pulse Anodic-Stripping Voltammetry", Analyst, 103, 1978, 1244-1248.

6. G. S. Kuntz, R. L. R. Towns, "Determination of Lead in Paint by Energy Dispersive X-Ray Fluorescence Spectrometry", Journal of Coatings Technology, 54(687), 1982, 63-69.

7. G. J. Lutz, "Determination of Lead in Paint with Fast Neutrons from a Californium-252 Source", Analytical Chemistry, 46, 1974, 618-620.

8. H. P. Vind, C. W. Mathews, "Field Test for Detecting Lead-Based Paints", Technical Note N-1455, Civil Engineering Laboratory, Port Hueneme, CA, 1976.

9. F. Feigl, V. Anger, R. E. Oesper, Spot Tests in Inorganic Analysis, Elsevier Publishing Company, London, 1972, 285-286.

10. W. E. Byrd, M. E. McKnight, "Potential Methods for Measuring and Detecting Lead in Existing Paint Films: A Literature Review", NISTIR 89-4205, National Institute of Standards and Technology, Gaithersburg, MD 20899, Jan 1990.

11. M. E. McKnight, W. E. Byrd, "Screening Procedures for Detecting Lead in Existing Paint Films: A Literature Review", NISTIR 89-4044, National Institute of Standards and Technology, Gaithersburg, MD 20899, Jan 1990.

12. J. L. Campbell, L. A. Crosse, "Portable Instrumentation for the Determination of Lead in Painted Surfaces", Bulletin of Environmental Contamination and Toxicology, 16(4), 1976, 469-473.

13. G. R. Laurer, T. J. Kneip, R. E. Albert, F. S. Kent, "Insitu Determination of Lead on Painted Surfaces for the Prevention of Childhood Lead Poisoning", Applications of Low Energy X and Gamma Rays, C. A. Ziegler, ed., Gordon and Breach, New York, NY, 1971, 289-301.

14. M. E. McKnight, W. E. Byrd, W. E. Roberts, E. S. Lagergren, "Methods for Measuring Lead Concentrations in Paint Films", NISTIR 89-4209, National Institute of Standards and Technology, Gaithersburg, MD 20899, Dec. 1989.

15. J. C. Spurgeon, "Response Characteristics of a Portable X-Ray Fluorescence Lead Detector: Detection of Lead in Paint", NBSIR 73-231, June 1973, National Institute of Standards and Technology (formerly The National Bureau of Standards), Gaithersburg, MD 20899.

16. A. P. Cramp, H. W. Berger, "Evaluation of New Portable X-Ray Fluorescent Lead Analyzers for Measuring Lead in Paint", NBSIR 78-1466, May 1978, National Institute of Standards and Technology (formerly The National Bureau of Standards), Gaithersburg, MD 20899.

17. D. Barltrop, C. L. Harford, N. J. P. Killala, "The Determination of Lead in Paint Films with a Portable Isotope Fluorescence Analyzer", Bulletin of Environmental Contamination and Toxicology, 6(6), 1971, 502-508.

18. S. D. Rasberry, "Investigation of Portable X-Ray Fluorescence Analyzers for Determining Lead on Paints Surfaces", Applied Spectroscopy, 27(2), 1973, 102-108.

19. G. R. Laurer, T. J. Kneip, M. Eisenbud, R. E. Albert, N. Nelson, "New York City Health Research Council X-Ray Fluorescence Analyzer for Lead", Isotopes and Radiation Technology, 9(3), 1972, 275-277.

20. G. R. Laurer, T. J. Kneip, R. E. Albert, F. S. Kent, "X-Ray Fluorescence: Detection of Lead in Wall Paint", Scince, 172(3982), 1971, 466-468.

21. J. S. Iwanczyk, Y. J. Wang, J. G. Bradley, J. M. Conley, A. L. Albee, and T. E. Economou, "Performance and Durability of HgI_2 X-Ray Detectors for Space Missions", IEEE Trans. Nuclear Science 36, No. 1, 841-845 (1989)

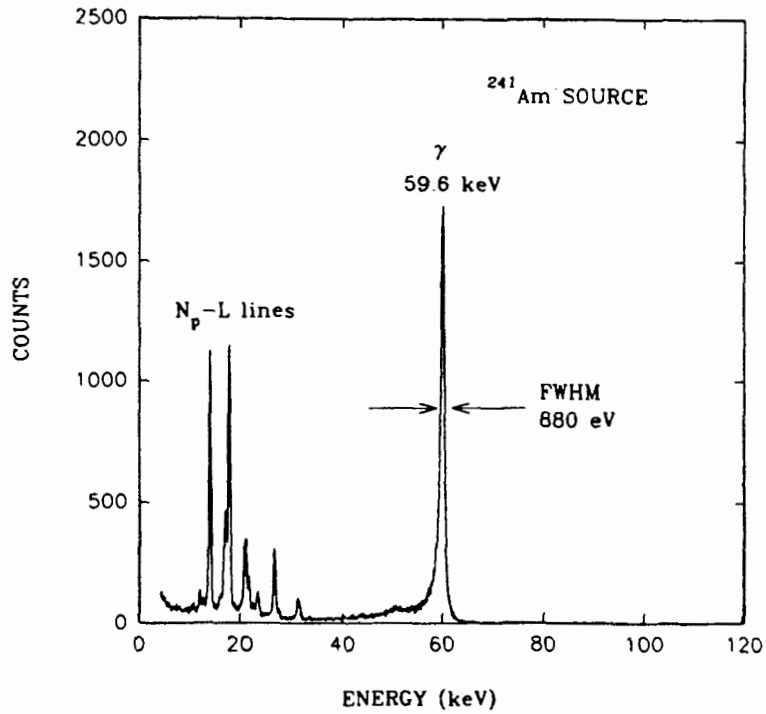


Figure 1. The spectrum from an ^{241}Am source.

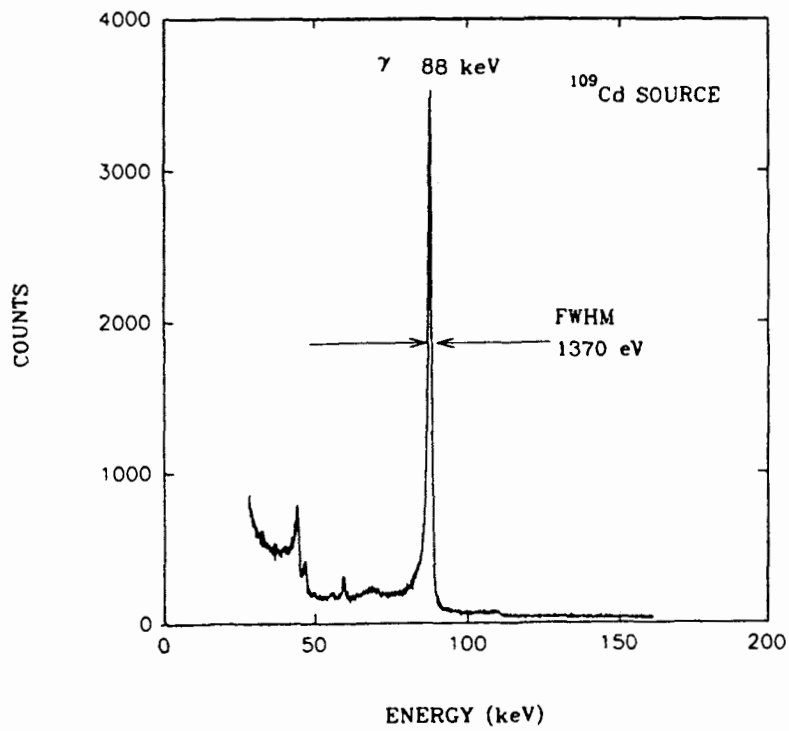


Figure 2. The spectrum from a ^{109}Cd source.

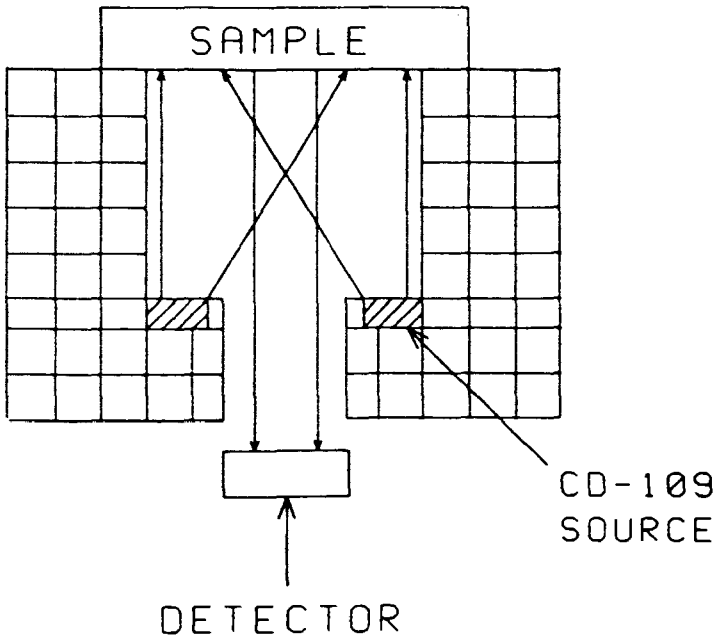


Figure 3. Geometry of detection system with the ^{109}Cd source.

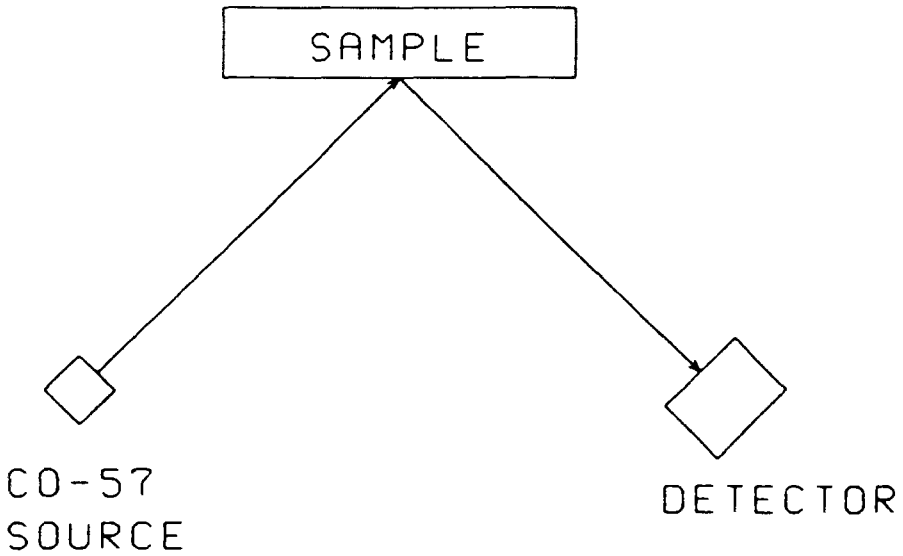


Figure 4. Geometry of detection system with the ^{57}Co source.

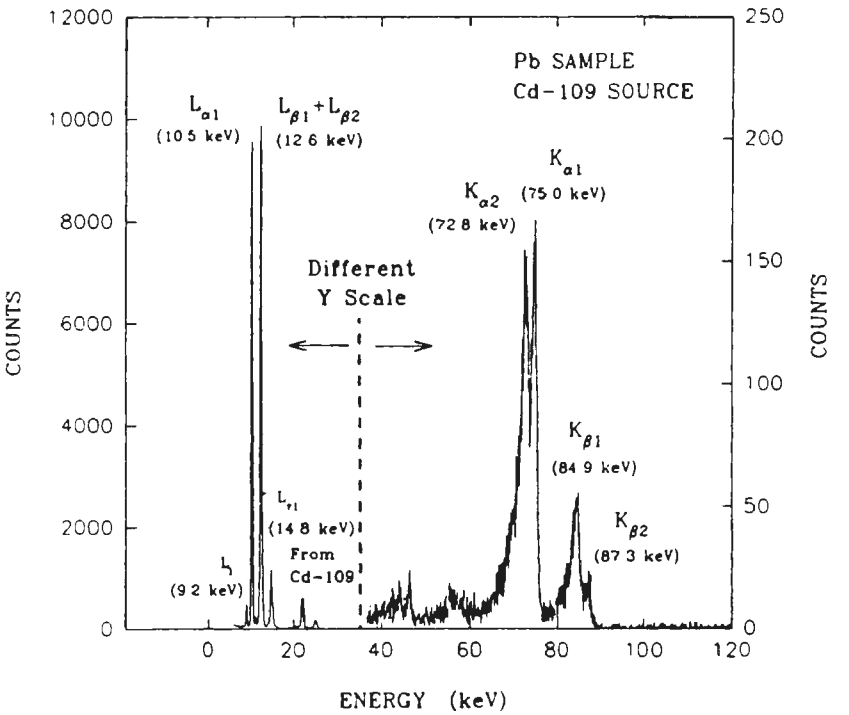


Figure 5. The spectrum of a lead sample excited by a ^{109}Cd source.

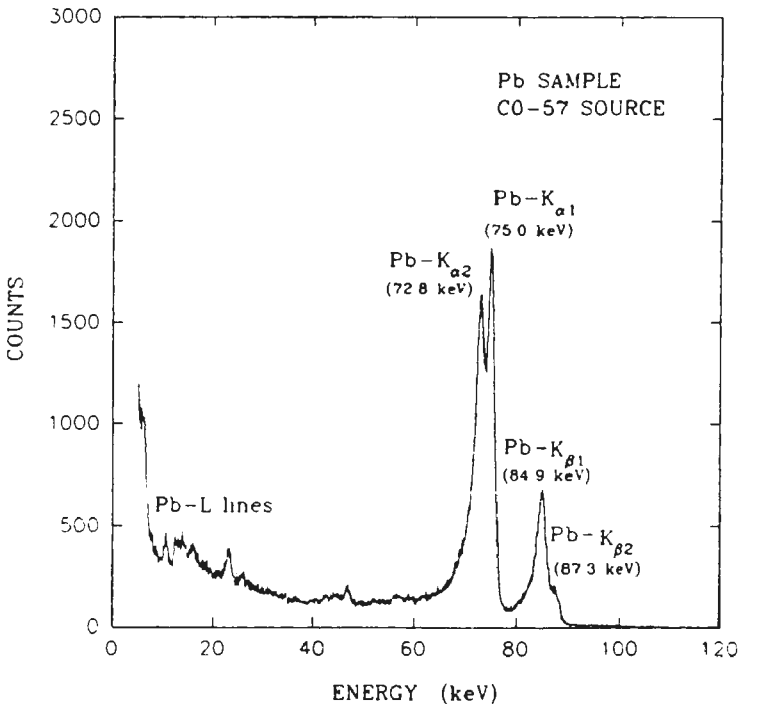


Figure 6. The spectrum of a lead sample excited by a ^{57}Co source.

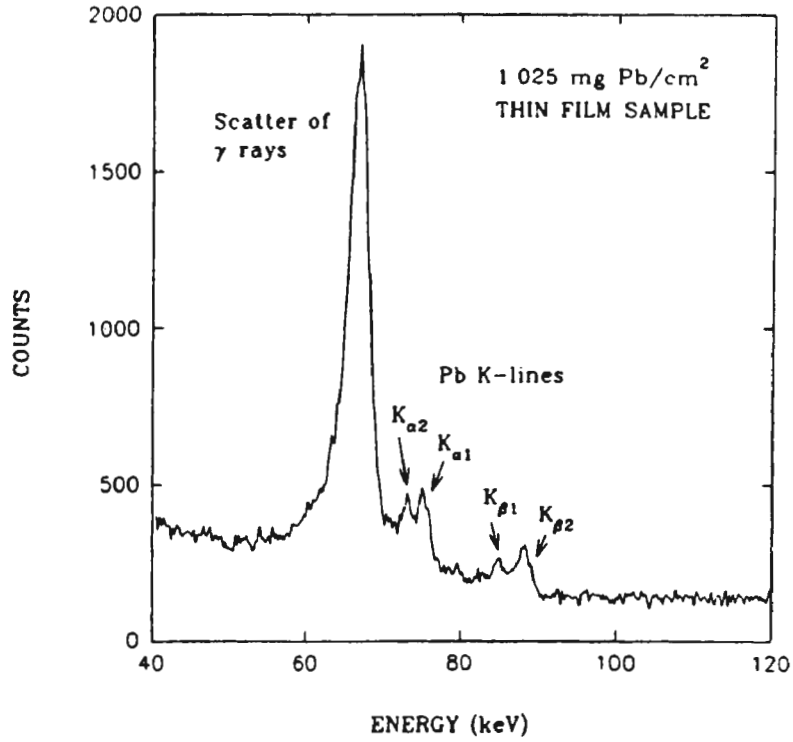


Figure 7. The Pb-K line spectrum of a 1.025 mg Pb/cm^2 thin film sample excited by a ^{109}Cd source.

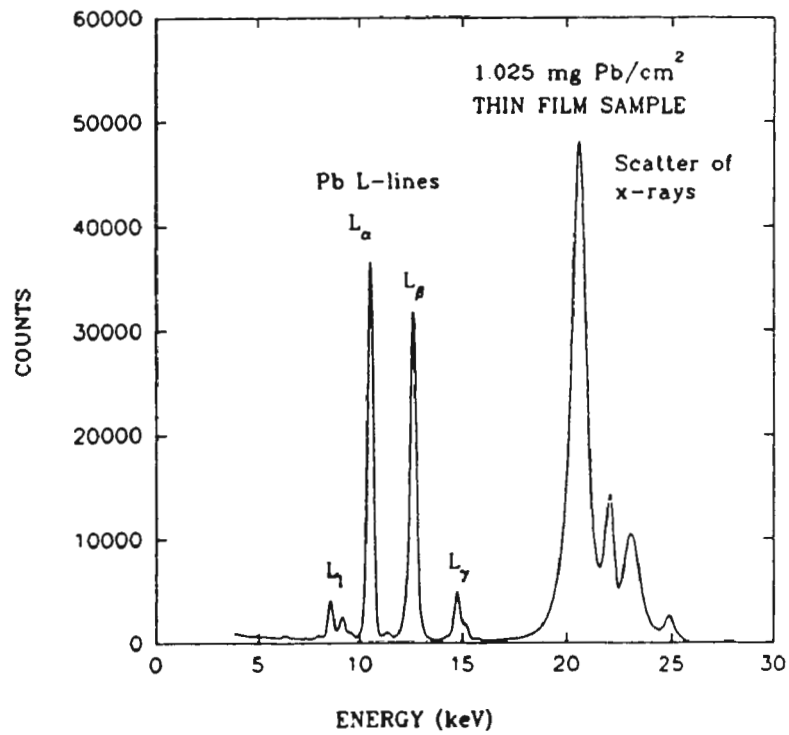


Figure 8. The Pb-L line spectrum of a 1.025 mg Pb/cm^2 thin film sample excited by a ^{109}Cd source.

5 IMMUNOASSAY METHODS FOR ENVIRONMENTAL FIELD SCREENING

Stephen B. Friedman, Ph.D.
Vice President, Research and Development

EnSys Inc.
P.O. Box 14063
Research Triangle Park, North Carolina, 27709

Abstract

Effective field screening methods can increase the efficiency of site management and improve overall data quality when used to supplement the services of regional laboratories. The development of these methods, however, begins with the selection of a technology that will be compatible with numerous compounds and matrixes and yet be simple, effective and rugged enough to be incorporated into a protocol for use in the field.

We have developed several immunoassay-based field screening methods for the detection of pentachlorophenol, PCB's, and petroleum contamination, in solid and liquid waste samples. Performance and stability evaluations of these methods have been evaluated within our own laboratories and in numerous external field studies. These studies have demonstrated the effectiveness of these methods when used in field screening applications. The immunochemistry underlying these methods, and the preparation of the reagents, will be reviewed. A description of the protocol and the characteristics that minimize the incidence of false negative results will be presented. Their general performance characteristics and application to site characterization will be discussed.

Introduction

Testing is an essential, and integral, component of all environmental protection and restoration activities. It is the rate limiting element that influences the time, cost and overall efficiency of project management.

The management of toxic waste sites usually involves a progression through the phases of identification, characterization, remediation and monitoring, with testing being performed during each phase. Reference laboratory methods can effectively identify and quantify unknown compounds in a sample, but become relatively inefficient when used to rapidly locate contamination (i.e. mapping), and assist in remediation and monitoring activities. The complexity of laboratory protocols, and the laboratories proximity to the test site, delays the availability of information and increases the cost of data. The ultimate cost is in the time required by the field crews. Effective field screening methods can increase the efficiency of the clean-up process by providing an on-site, high-throughput, and cost-effective way to locate contamination and manage its remediation.

The EPA has long promoted and supported the concept of screening methods to supplement laboratory analysis and increase overall efficiency. The need for more effective methods has been recognized in the Superfund Amendments and Reauthorization Act of 1986 which specifies the development and evaluation of alternative time and cost-saving methods that will assist in the eventual remediation of the nations Superfund sites.

We have developed several field screening methods that are being used to detect Pentachlorophenol, PCB's, Petroleum Products, and PAH's in both soil and water matrixes, and on solid surfaces. Our objective has been to develop reliable and cost effective methods for obtaining the data needed for site investigation, remediation and monitoring activities, waste screening, process control, and monitoring activities to maintain regulatory compliance. Our approach was to develop methods that were consistent with a list of essential screening characteristics.

Essential Field Screening Characteristics

Screening methods need to provide fast, simple, cost-effective and reliable information when operated under field conditions. The reagents and equipment should be portable and stable at ambient conditions, and the claims relating to performance should accurately reflect anticipated field use. The methods should be able to rapidly provide an ample quantity of data, and the protocol should be simple to

perform and safe to use. Performance characteristics relative to sensitivity, freedom from matrix interferences and cross-reacting compounds, and correlation to an acceptable reference method should be carefully evaluated. Developers must maintain high, and consistent, quality standards relative to the consistency of their manufacturing protocols, the adequacy of in-process and pre-release quality control methods, and the reliability of their product claims. A characteristic of particular significance for screening methods is that they exhibit a very low frequency of false negative results.

Screening methods detect contamination at specified concentrations. The concentration may relate to a hazardous threshold, a clean-up target, or a process-control parameter. The potential implications of false negative data far outweigh those of false positive results. The consequence of a false positive, while a costly problem that needs to be minimized, results in additional testing or treatment. False negative data, however, provides the erroneous perception of a clean site, and may have serious environmental and legal consequences. Safeguards that minimize the incidence of false negative results are imperative. Appropriate control over the frequency of false positive data needs to be established and maintained.

Immunoassay Applications

The field of immunochemistry, and the development of immunoassay technology, has been evolving since the late 19th century. However, the majority of these methods have been developed for use by the medical community. These methods have achieved a reputation for reliability and cost-effectiveness. Literally hundreds of immunoassay's have been developed for Drugs of Abuse testing, Therapeutic Drug Monitoring (e.g. digitalis derivatives, anti-asthma formulations, anti-epileptic reagents, antibiotics), pregnancy testing, hormone testing (e.g. thyroxine, thyroid stimulating hormone), tests for pathological markers (e.g. lactic dehydrogenase isozymes, creatine kinase isozymes), tests for acute phase proteins (e.g. carcinoembryonic antigen, alpha fetoprotein) and tests for of tumor marker proteins.

Environmental applications have been explored for the better part of a decade and a number of immunoassay methods have been developed[1,2,3]. Most have been used for the detection of herbicides and pesticides in

aqueous matrixes. The application of immunoassay technology to the testing of solid waste, complex matrixes, and highly lipophilic compounds, has provided unique challenges for the chemistry.[4] The feasibility of developing such methods, however, has been demonstrated with immunoassay's for Dioxin[5,6] and in the screening methods developed by EnSys.

Historical Prospective

The history of immunoassay technology can be traced to 1900 when Karl Landsteiner described the A, B and Zero (O) blood types after observing the agglutination reaction (i.e. aggregation) that resulted when he mixed the erythrocytes and serum from several of his co-workers on a slide[7]. His observation became the basis for present day blood typing methods. Landsteiner remained a dominant figure in immunology for the next 40 years performing numerous experiments that demonstrated the extraordinary specificity of the antibody binding reaction. He introduced the term hapten to define compounds that are unable to directly stimulate antibody production when injected into an animal, but are capable of binding to an antibody if they are produced by an alternate means. Most environmental chemicals are haptens, and although potentially toxic, will not stimulate the immune system to respond[8].

For 50 years following Landsteiner's discovery, immunoassay technology continued to rely upon the binding and cross-linking ability of an antibody to cause agglutination, cell lysis, and protein flocculation reactions. These methods were relatively insensitive when compared to the immunoassay methods of today, and better suited to the analysis of larger compounds and organisms (e.g. bacteria, proteins).[9] A major advance occurred in the 1950's when Drs. Berson and Yalow, while investigating the metabolism of radiolabelled insulin administered to diabetic patients, observed the production of anti-insulin antibodies in the serum of insulin-treated diabetics. They described a radioimmunoassay (i.e. RIA) method in 1959 that used anti-insulin antibody molecules, and radiolabelled insulin, in a highly sensitive procedure to quantify insulin in the serum of patients. The method used a competitive antibody binding reaction, where radiolabelled insulin and sample insulin compete for a limited number of antibody binding sites.[10] In 1977, Rosalyn Yalow was awarded the

Nobel Prize in Medicine for her work on the development of the radioimmunoassay method for peptide hormones [11]. RIA rapidly became a universally accepted method that demonstrated exceptional specificity, sensitivity, and simplicity.

A simpler, safer, and more convenient immunoassay was reported in 1971, when two independent research teams, Engvall and Perlmann,[12] and Van Weeman and Shuurs,[13] simultaneously disclosed a competitive immunoassay method that used an enzyme-labelled conjugate instead of a radiolabelled-conjugate, to produce a test that generated a visible end-point signal. The new ELISA (i.e. enzyme linked immunosorbent assay) method eliminated the problems associated with the safety, disposal and detection of radioactive reagents. The method offered long term stability, the opportunity to generate quantifiable data using instruments commonly available in most laboratories, and a mechanism to develop separation-free (i.e. homogeneous) procedures and simple qualitative screening tests.

Current immunoassay technology benefits from the diversity of detection systems that have been developed that use enzyme-catalyzed chromogenic reactions, radionuclides, chemiluminescence, fluorescence, fluorescence polarization and a variety of potentiometric and optical biosensor techniques. Improvements in the sensitivity achieved by these methods has necessitated the generation of new descriptive nomenclature for methods that can detect ligands at "zeptomolar" (10^{-21}, 600 molecules) concentrations.[14]

Enzyme Immunoassay Chemistry and Protocol

Immunoassay methods combines the specific binding characteristics of an antibody molecule with a read-out system that is used to detect and quantify compounds. Antibodies are binding proteins that are produced by the immune system of vertebrates in response to substances that are perceived as foreign. The immunoassay methods we have developed use antibody reagents, and a chromogenic detection system, that specifically bind and detect hazardous chemicals in both solid and liquid waste samples.

The EnSys chemistry uses two basic reagents, namely, an antibody, for example anti-pentachlorophenol, and an enzyme conjugate reagent

composed of, for example, PCP molecules covalently bound to the enzyme horseradish peroxidase.

The Antibody Molecule

The physiological role of antibody, or immunoglobulin, molecules is to bind, and thereby label for destruction, a foreign substance within an organism. Antibody molecules are synthesized by a subset of lymphocytes, termed B lymphocytes, that become activated to produce antibody after exposure to substances having prerequisite size, complexity and "foreignness" to the host organism. They are large, polymeric proteins (i.e. $\geq 1.5 \times 10^5$ d), that can be classified into sub-populations on the basis of their sequence, size and number of sub-units. Five major populations, or isotypes, exist that carry the designations of IgM, IgA, IgD, IgG and IgE, with immunoglobulin G (IgG) usually found in the highest concentration.[15]

Binding affinity and specificity is influenced by the chemistry and conformation of a binding cleft at the N terminal end of the molecule, that exists between juxtaposed, and convoluted, portions of "heavy" and "light" polypeptide chains. The amino acid sequence, and therefore the conformation at the N terminus, is highly variable and influences the binding specificity of the molecule.[16] Studies have demonstrated that binding is a function of the conformational complimentarity that exists between the target ligand and the antibody binding site[17], and that the "goodness" of fit relates to the interaction between the electron cloud within the binding site and the bound ligand. Antibody binding is not covalent, and the affinity or strength of binding, is a function of cooperative hydrophobic, Van der Waals, electrostatic and hydrogen bonding interactions[18] In general, equilibrium constants for the most avid antibody binding reactions do not exceed 10^{12} L/M.[19]

To induce the formation of antibodies that can be used to detect, for example, pentachlorophenol, molecules of PCP must first be derivatized and coupled to large carrier molecules such as albumin, hemocyanin or thyroglobulin. The increased size and complexity of this "immunogen", once injected, is sufficient to stimulate the immune system to produce an antibody response. The effectiveness of the immunogen is influenced by the surface density of the chemical on the carrier (i.e.

epitope density), the nature of the bridge chemistry used, the immunization protocol, immunogen concentration, incorporated adjuvants (i.e. immune response stimulants), and the species of the host animal. Significant progress has been made in deciphering the mechanisms of the humoral immune response, but a great deal is still not understood. Experience and good fortune continues to play a significant role in the production of effective antibody reagents for test kit development.

The Enzyme Conjugate Reagent

The enzyme-conjugate reagent for the EnSys PCP detection method is synthesized by derivatizing PCP and coupling it to the enzyme horseradish peroxidase. Numerous functional groups on enzyme molecules (e.g. amino, sulfhydryl, carboxyl, carboxamide, tyrosyl, sugars) offer convenient points for the attachment of ligand molecules. Enzymes enhance the sensitivity of the method by the catalytic amplification of the detection signal. A single molecule of the enzymes commonly used in immunoassay methods will convert approximately 10^6 molecules of a substrate into a product within one minute at ambient temperatures.[20] Catalysis is a function of the conformation at the enzymes catalytic site, and it is this conformation, and the alignment of certain amino acid residues at spatially significant positions, that influences its rate and selectivity. The catalytic site is maintained by both non-covalent (i.e. hydrophobic, hydrogen bonding, ionic and Vander waals interactions) and covalent (i.e. disulfide) forces, and can be influenced by temperature, the binding of ions, chaotropic agents, detergents, lipids, etc.. It is therefore important to normalize and correct for anticipated variations in the reaction environment.

An effective enzyme conjugate reagent must retain the ability to both bind antibody, and hydrolyze a substrate reagent into a detectable signal. Some of the more commonly used enzymes include horseradish peroxidase (i.e. HRP), alkaline phosphatase, and b-galactosidase. Each is compatible with a wide variety of different substrates offering unique choices in kinetics and hydrolysis products. The EnSys methods use a hydrogen peroxide substrate solution with a tetramethylbenzidine chromogen that produces a blue chromophore in the presence of horseradish peroxidase enzyme.

Analysis of Solid Waste

Immunoassay methods have predominantly been used to test liquid matrixes such as blood, urine, and water. The testing of solid waste requires that the issues of sample collection, dispersion, extraction and clarification be addressed and integrated with the immunoassay component. A reproducible, particulate-free, leachate must first be produced. The extraction and recovery of a compound from soil requires the selection of an appropriate solvent system, adequate sample dispersion, sufficient time for partitioning, non-invasive clarification and compatibility with the subsequent immunochemistry. For polar compounds, buffers, detergents (e.g. Tweens, Tritons, etc.) or solvents, used together, or in combination, have proven to be effective for extraction. Analytical methods for the analysis of solid waste rely upon gravimetrically collected samples, and results are reported in gravimetric units. Volumetric sampling for solid waste should be avoided because of the potential bias that may be caused by the specific gravity of the sample.

Solid waste analysis using the EnSys system involves the gravimetric collection of a 10 g sample using a small battery-operated balance. The sample is transferred into a dispersion vial containing a solvent and dispersing pellets, and is subjected to a one minute manual agitation for adequate dispersion and partitioning of the ligand. Filtration of the sample suspension to produce a particulate-free leachate is accomplished using a fingertip-operated filter unit fitted with non-adsorbing filters. The clarified leachate is next analyzed using the immunoassay component.

Immunoassay Component

The EnSys immunoassay chemistry is explained using the following pentachlorophenol model. Anti-PCP antibody is immobilized to the bottom of polystyrene tubes at a pre-defined concentration (see figure). The concentration and affinity of the antibody for the sample molecules and enzyme conjugate molecules directly influences the overall sensitivity of the final method. High and equivalent affinity, and minimal non-specific signal generation, will usually produce assays having superior sensitivity.

For this illustration we will simultaneously test a negative PCP sample, a sample containing >5 ppb PCP, and a standard solution containing the equivalent of 5 ppb PCP. We begin by adding the samples, and standard to separate, and identical, anti-PCP antibody-coated test tubes. To each tubes we also add an equal volume of HRP-PCP enzyme conjugate solution. The three tubes are then allowed to incubate at ambient conditions for ten minutes.

During the incubation period sample PCP molecules and PCP-HRP conjugate molecules compete for the limited number of antibody binding sites that are available on the bottom of each of the tubes. The antibody concentration present is insufficient to permit the binding of all of the sample PCP and PCP-enzyme conjugate molecules simultaneously, and a situation somewhat analogous to the game of musical chairs exists, with the limited antibody binding capacity serving as the chairs in this example. The concentration of enzyme conjugate immobilized in each tube is inversely proportional to the concentration of PCP in the sample or standard. The PCP in the "standard" tube, limits the binding of enzyme conjugate, the "negative" sample permits more conjugate to bind (i.e. relative to the standard), and the "positive" sample limits the binding of the conjugate (i.e. relative to the standard). At the end of the 10 minute incubation period, the tubes are washed leaving only the enzyme conjugate that was retained by the antibody on the bottom of each tube.

The enzyme-conjugate remaining is next used to produce a detectable signal. Upon addition of the substrate/chromogen reagents (i.e. H_2O_2 and tetramethylbenzidine), the enzyme molecules catalyze the formation of a blue product. The color that is generated is directly proportional to the concentration of enzyme in each tube.

Therefore, the negative sample tube containing < 5 ppb of PCP (i.e. tube 2) rapidly produces a solution that is visibly darker (i.e. greater absorbance) than the standard tube. The positive test sample in tube #3, that contains > 5 ppb of PCP, produces a solution having less color (i.e. lower absorbance) than the standard tube. By comparing the absorbance of the sample tubes to the absorbance of the standard tube that contained 5 ppb of PCP using the battery-operated comparative photometer offered with the system, sample contamination can

empirically be determined. In competitive ELISA methods, the final absorbance produced is inversely proportional, and logarithmically related, to the ligand concentration present in the initial test sample.

Screening Method Characteristics

We have developed six screening methods that share several common performance characteristics (see figure). Each of the methods can process multiple samples in less than 30 minutes. A single individual has been able to analyze fifty samples within one day of testing. The methods are self-contained, field-compatible, do not require refrigeration or use hazardous components. The detection level for each can be set at the users discretion, with the maximum obtainable sensitivity consistent with significant regulatory levels. The PCB-RISc methods will detect PCB contamination in soil at a concentration of 5 ppm, and at 10 ug/100 cm^2 when using the "wipe" method for solid surfaces. The Penta-RISc method screens for PCP in water to a concentrations of 5 ppb, and to 500 ppb when using the soil analysis method. The Petro-RISc method will detect petroleum product contamination in soil at, or above, a concentration of 100 ppm, and the PAH-RISc method detects contamination in soil at, or above, 10 ppm. Each method is configured to permit multilevel analysis of samples in order to facilitate the construction of concentration profile maps.

Screening Applications

Numerous applications for these screening methods have been demonstrated during field trial and site investigational activities. In general, these methods have been used to facilitate site characterization and remediation activities, and assist in a variety of monitoring programs.

The EnSys immunoassay screening methods have been used to locate contamination. Their relatively low cost has amplified the quantity of data generated and has provided the information needed to produce high-resolution site maps quickly. The information, provided in real time, has increased the efficiency of field operating crews, and has provided a mechanism for the selective screening of samples destined for subsequent laboratory analysis. The costly analysis of uncontaminated samples, and the time required to complete site

investigational activities, has been significantly decreased. The methods have accelerated the progress of remediation activities. Field crews have used them to follow contamination plumes and indicate when excavation can be discontinued. They have been used to assist in the design of effective remediation protocols.

In support of monitoring programs, these methods have helped to maintain compliance with appropriate discharge levels, and screen waste prior to acceptance for treatment, storage, transport or disposal.

Summary

The advantages of immunoassay technology can be attributed to the underlying lock and key binding principle and its compatibility with aqueous matrixes. The method does not involve, nor require, the chromatographic separation of sample components, nor does it require that compounds absorb light of a specific wavelength for detection. Interferences from other compounds are considerably less of a problem because of the conformational nature of the antibody binding process. Sample processing time is significantly reduced, and the direct testing of aqueous samples, or water-soluble leachates of soil, can be performed. The technology offers a unique, and conservative, approach to field screening. The incidence of false negative data is exceptionally low. Aspects that tend to interfere with immunoassay methods tends to cause an overestimation of contamination, or false positive result.

The advantages of these methods relates to their specificity and compatibility with aqueous matrixes. Their disadvantages relate to these same characteristics. As a screening method for specific compounds these methods excel, but become less efficient when multiresidue analysis of samples is required. The development of tests for highly lipophilic ligands, and matrixes, offer unique challenges because of the phase disparity issues that exist.

As a technical platform immunoassay technology offers significant versatility and performance advantages. These methods offer a convenient and effective new tool that can enhance the efficiency of site management activities and the utilization of our national laboratory system.

[1] Hammock, B.D.; Gee, S.J.; Showing, P.Y.K.; Miyamoto, T.; Goodrow, M.H.; Van Emon, J.; Seiber, J.N. Utility of Immunoassay in Pesticide Trace Analysis. In "Pesticide Science and Biotechnology; Greenhalgh, R., Roberts, T.R., Eds.; Blackwell Scientific: Ottawa, 1987; pp 309-316

[2] Hammock, B.D.; Mumma, R.O. Potential of Immunochemical Technology for Pesticide Analysis. In Pesticide Analytical Methodology; Harvey, J., Zweig, G., Eds.; ACS Symposium Series 136; American Chemical Society: Washington, DC, 1980; pp 321-352

[3] Mumma, R.O.; Brady, J.F.; Immunological Assays for Agrochemicals; In Pesticide Analytical Methodology; Harvey, J., Zweig, G., Eds.; ACS Symposium Series 136; American Chemical Society: Washington, DC, 1980; pp 341-348

[4] Albro, P.W.; Luster, M.I., Chae, K., Chaudhary, S.K., Clark, G., Lawson, L.D., Corbett, J.T., McKinney, J.D.; Toxicology and Applied Pharmacology; 50:137-146 (1979)

[5] Vanderlaan, M.; Stanker, L.H.; Watkins, B.E.; Improvement and Application of an Immunoassay for Screening Environmental Samples for Dioxin Contamination Environmental Toxicology and Chemistry, 7:859-870, 1988

[6] Stanker, L.H.; Watkins, B., Rogers, N.; Vanderlaan, M.; Monoclonal Antibodies for Dioxin: Antibody Characterization and Assay Development; Toxicology, 45:229-243, 1987

[7] Landsteiner, K. "Uber Aggluntinationserscheinungen Normalen Menschlichen Blutes." Wein. Klin. Wschr. 14:1132,1901

[8] Basic and Clinical Immunology, Stites, D.P.; Terr, A.I. eds.; Appleton and Lange, Connecticut, 7th Edition, 1991

[9] Ritzman, SE: Behring Diagnostic Manual on Proteinology and Immunoassays, 2nd Edition, Behring Diagnostics, 1977

[10] Principles of Competitive Protein Binding Assays, Second Edition; ODell, W.D., Franchimont, P (editors); Chapter 1, Introduction and General Principles; ODell, W.D.; John Wiley and Sons, New York (publishers);

[11] Basic and Clinical Immunology, Stites, D.P.; Terr, A.I. eds.; Appleton and Lange, Connecticut, 7th Edition, 1991

[12] Engvall, E. and Perlmann, P : Enzyme-Linked immunosorbent assay (ELISA). Quantitative assay of immunoglobulin G; Immunochem., 8:871-874, 1971

[13] Van Weemen, B.K. and Schuurs, A.H.W.N.: Immunoassay using antigen-enzyme conjugates; FEBS Letters, 15: 232-236, 1971

[14] Proceeding of the Twenty-Third Annual Oak Ridge Conference on Advanced Analytical Concepts for the Clinical Laboratory; April 11, 12, 1991; Clinical Chemistry; 37: 9, 1991

[15] Immunology; Roitt I.M., Brostoff J., Male D.K.; C.V. Mosby Co. and Gower Medical Publishing; St. Louis, Mo.; 1985

[16] Capra JD, Kehoe JM: Hypervariable regions, idiotypy, and the antibody-combining site. Adv. Immunolo., 1975:20:1

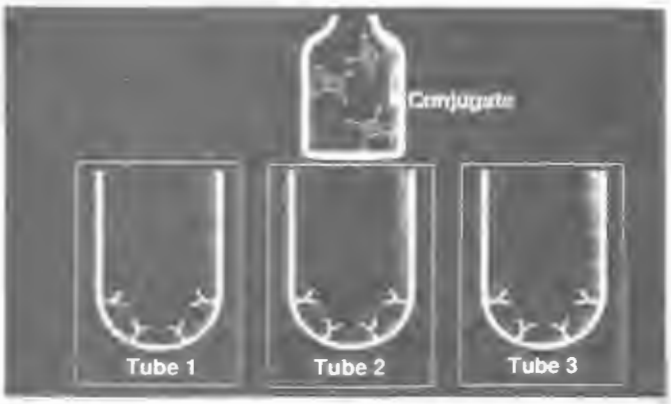
Wu TT, Kabat EA: An analysis of the variable regions of Bence Jones proteins and myeloma light chains and their implications for antibody complimentarity. J. Exp. Med. 1970; 132:211

[17] Basic and Clinical Immunology; Stites D.P., Terr A.I.; Seventh edition; Appleton and Lange(pub.), E. Norwalk, Conn.; 1991

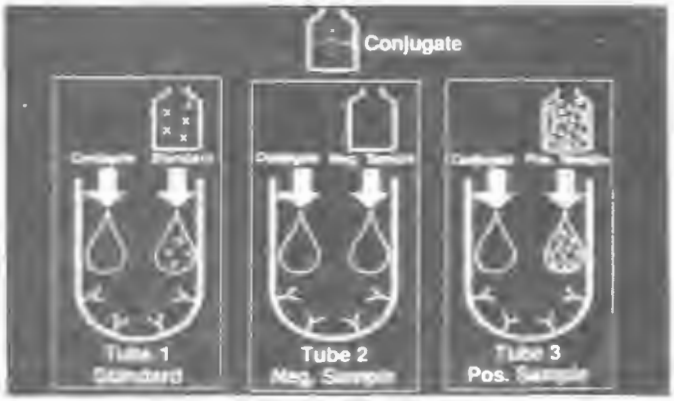
[18] Immunology; Roitt, I.M., Brostoff, J.; Male, D.K. eds.; C.V. Mosby Company, St. Louis, Missouri, 1990, pp 7.1

[19] Immunoassays for the 80's; Ekins, R., Chapter 2; Voller A., Bartlett A., Bidwell D. eds; University Park Press, Baltimore, Md., 1981

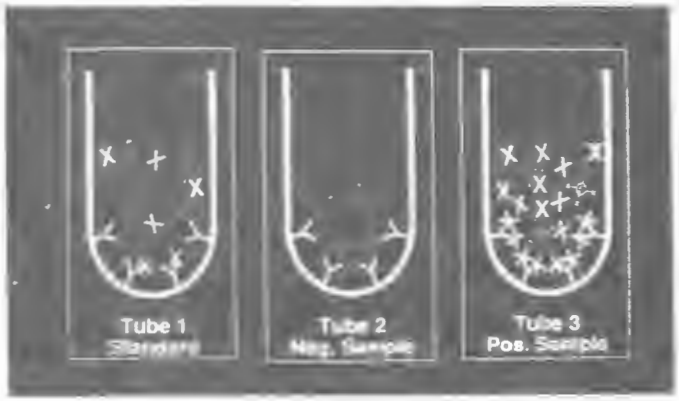
[20] Ngo T.T.; Enzyme Mediated Immunoassay: An Overview;



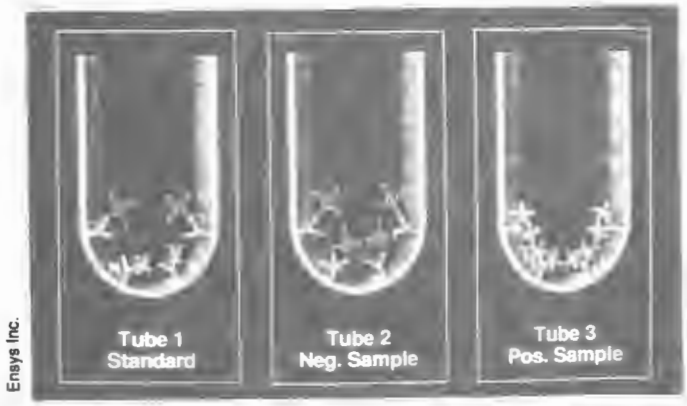
1. Components in ELISA chemistry



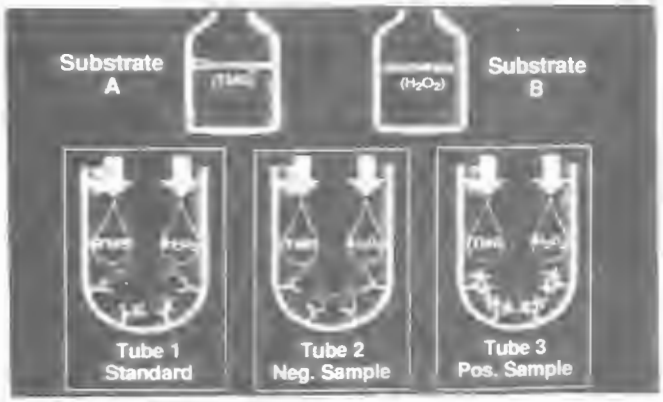
2. Enzyme addition

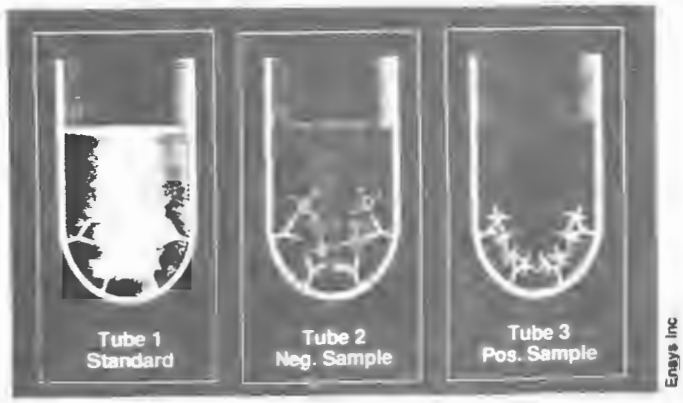


3. Incubation and competitive binding reaction



4. Wash





5 & 6. Color development

EnSys Enzyme Immunoassay Chemistry

EnSys Field Screening Test Kit

6 COST EFFECTIVE PCB INVESTIGATION UTILIZING IMMUNOASSAY

James Smith, Chemist and Eugene Brozowski, Analyst, Trillium, Inc. Coatesville, Pennsylvania 19320 (215) 383-7233 FAX (215) 383-7907, and John E. Rhodes, Environmental Engineer, Rhodes Engineering, 505 South Leola Road, Moorestown, New Jersey 08057, (609) 273-9517 FAX (609) 273-9518.

ABSTRACT

The discovery of PCBs at a site inevitably leads to the expenditure of a major amount of money on analytical measurements. The most cost effective approach to the site investigation and the PCB remediation is to accomplish the analyses at the site with a minimum turnaround time. This approach would limit the number of samples taken during the site investigation and focus sampling to the "hot spots" in an efficient manner. The same approach can facilitate the removal of contaminated soil as well as limit the amounts of soil remediated without costly delays waiting for analytical results. This approach has been used by many contractors in field laboratories.

Most field PCB analyses have been based on the gas chromatographic methods developed by Dr. Tom Spittler of U.S. EPA Region I laboratory.[1] We feel that the introduction of the immunoassay for PCBs has increased the efficiency of the field laboratory by decreasing the turnaround time of the analyses with consequent decreases in cost. A single field laboratory analyst can complete approximately 40 to 50 immunoassays in an 12-hour shift. A typical single analyst 12-hour shift using the Tom Spittler methods can extract, clean-up, and analyze approximately 10 to 20 % of the total number of samples that can be tested by the immunoassay method.

The immunoassay for PCBs is a colorimetric test and is utilized as a positive or as a negative measurement. It is highly specific for PCBs in that the test is usually free from false positives. The test can be conducted by anyone with minimal training with few false positives or false negatives when compared to acceptable and consensus field and laboratory methods.

In the case study to be described in this paper, we used the PCB immunoassay by EnSys for a "go/no go" at a 5 ppm (mg/Kg) concentration (as received basis). Utilizing a grid, the sampling team obtained surface soil samples at an efficient pace by defining the PCB contamination versus area using the

immunoassay results. Each sample delivery group consisted of a soil blank and a soil blank spike at 5 ppm (ug/Kg dry weight basis). The rapid immunoassay turnaround time of 20 minutes allowed better solution of the next group of samples. The field results were verified by analyzing 10-20% of the samples by subsequent field gas chromatographic analyses and/or laboratory analyses by approved methods.

Our results indicate the cost effectiveness of the immunoassay to both PCB site investigations and remediations. The cost of an immunoassay was $28.50 per test. We foresee numerous cost-effective uses for PCB immunoassays including the use of the 50 ppm assay for better definition of "hot spots."

INTRODUCTION

Immunoassay

The immunoassay technique is based on the specific binding of the analyte with an antibody. The first step in producing a test for an analyte involves the cultivating of the antibody that will bind with a high degree of affinity and specificity to the analyte when the analyte is present in very low concentrations. A reporter conjugate must be present. This is made up of a ligand attached to an enzyme molecule. Antibodies are specific binding proteins that are produced in response to a foreign substance, and that bind and label that substance - antibody for disposal by the immune system. It is believed that the antibody's binding is mainly a function of conformational complimentarily between the target analyte and the antibody's binding site. Antibodies are the key ingredient for an immunoassay. They are produced by vertabrate organisms. The immune systems of animals will only respond to bacteria, virus and pollen. These "invaders" are macromolecules or micro organisms compared to target analytes of environmental concern. The target environmental analytes are unable to directly stimulate the production of antibodies and large immunogen cojugates must be prepared in order to trigger an antibody response.

In order to produce antibodies that bind to the environmental target analyte, a derivative of the target analyte is made and chemically bonded to a macromolecule, usually a protein, called a carrier molecule. This synthesized immunogen is now effective in stimulating an animal's immune system and antibodies are generated and collected for use in the immunoassay.

The PCB immunoassay incorporates chromogenic reactions as a detection system. The chromogenic ELISA (enzyme-linked immunosorbent assay) chemistry uses two essential reagents, an

antibody and an enzyme conjugate reagent. The enzyme conjugate is a PCB molecule linked to horseradish peroxidase. This conjugate must be able to both bind to the antibody via its attached target analyte and convert a substrate into a detectable color. The horseradish peroxidase molecule catalyzes the conversion of a colorless chromogen tetramethylbenzidine to a blue derivative in the presence of the substrate, hydrogen peroxide.

The Test

Tubes are coated with the antibody. The sample extract, or known, standard is added with a predetermined amount of the conjugate containing the horseradish peroxidase (HRP). The sample PCBs and the conjugate - HRP compete for the available sites of the antibodies on the tube coating. After this competition or incubation is complete, the sample and conjugate - HRP are washed out of the tubes. The color reaction mixture is added and developed. The more PCB molecules present in the tube the fewer enzyme conjugate molecules that will bind and thus less blue color will develop. The more PCB molecules bound to the antibodys, the less blue color is developed. By utilizing a standard PCB concentration one can colorimatrically determine if the sample contained a concentration greater than or less than that of the standard.

This immunoassay system was used to carry out a site investigation for PCBs using a 5 ppm "go - no go" test kit developed by EnSys Inc. of Research Triangle Park, North Carolina.

Experimental

This work was not a test but a real project. The immunoassay was added to the site investigation in order to reduce the cost of the project. The site consisted of approximately an acre with three masonry buildings. In the most recent past, this site was a heating oil storage and transfer facility for a small local home distributor. In an economical move, the heating oil firm ceased the use of this facility and removed the large above ground storage tanks. To complete the site clean-up in preparation for sale or lease, several small gasoline underground storage tanks were removed. Testing that accompanied the tank removal did indicate some areas with high total petroleum hydrocarbons. In the negotiations with the state UST agency, there was a review of the data by an expert hired by the law firm representing the heating oil company. The tentatively identified compounds (TICs) that were previously ignored by everyone indicated approximately 1000 ppm of PCB in the semivolatile organic analyses. This

observation was quickly verified by a gas chromatographic pesticide - PCB analysis. The state agency was informed immediately and the planning for a PCB site assessment began.

The site assessment for PCBs was planned using a 20 foot square grid except for the gasoline underground storage tank area. This was considered to be the "hot spot" and the grid was reduced to 10 foot squares. Along the northern border a row of 10 foot squares were placed next to an electric substation because it might be a possible source of contamination.

The site assessment was planned for three days. It included the sampling of surficial soil in the center of each square from the surface to a depth of six inches. All of the soils collected from the 10 foot squares of the grid would be analyzed using the immunoassay tests. Twenty samples would be confirmed using the field gas chromatographic method developed by Dr. Spittler. At least twenty samples would be chosen for laboratory analysis. These laboratory analyses were performed by Envirotech Research of Edison, New Jersey, utilizing method 8080.

For the immunoassay, the quality control samples that were used to ensure that the tests were being run correctly were blank soils, blank spiked soils and replicates of field samples. Blank soil was prepared by air drying and sieving to homogenize the soil. The blank spike soil was a portion of this blank soil spiked with approximately 20 ppm (mg/Kg) of Aroclor 1242. This concentration was confirmed by gas chromatography.

RESULTS

In the three days of testing, a blank soil was run at the beginning and at the end of a 12 hour work day. Table 1 shows that all soil blanks gave satisfactory results.

The blank spikes were run at the same frequency as the blank soils. Table 2 shows that these blank spike results were satisfactory. However, we did learn that a single technician running 50 plus immunoassays and 7-8 gas chromatographic runs for twelve hours on three consecutive days leads to "burn out." Thus, there was an omission of a blank spike from our program!

However, there was an extra replicate as indicated on Table 3. These replicate analysis did show the necessity to check at least one sample, K-1, by gas chromatography.

The field gas chromatographic method was a great help in making us feel comfortable with the immunoassay results. Tables 4,5, and 6 give the field gas chromatographic results versus the immunoassay results. This comparison indicates that the immunoassay may give false positive results at or near its detection limit of 5 ppm (mg/Kg-wet weight).

The laboratory gas chromatographic method results are compared to the immunoassay results in Tables 7,8 and 9. This comparison gives the same conclusion concerning the effectiveness of the immunoassay test for PCBs in soil. There are approximately 20% false positives and all of these samples have PCB concentrations near the immunoassay detection limit.

CONCLUSIONS

There were a total of 151 field samples run by the immunoassay methodology for PCBs. Twenty one more tests were run on quality control samples. Mapping the results on the site grid and the comparison of the immunoassay results with verified laboratory gas chromatographic results gave adequate information for a remedial action work plan for the PCB contamination. It clearly shows that the source of PCBs is not the electric substation. The data indicates that the suspected "gasoline" underground storage tanks were used for the storage of PCBs.

Most importantly for the owner of this site was that the cost of this site assessment was less than 50% of the projected costs of a conventional assessment. The savings were realized in the cost of analyses as well as the time spent on the site. The added benefit was the ability to select new samples based on the results of previously run samples. The analytical costs are given in Table 10.

The false positives were not an important problem in this work. If there was a false negative, it was not a factor either. However, we believe that false negatives in this type of project are inclined to be due to a heterogeneous soil sample with a concentration near the detection limit.

This program was a success. The immunoassay will become an important methodology in environmental testing in the near future.

FOOTNOTES

[1]Spittler, Thomas M., Ph.D., Field Measurement of PCBs in Soil and Sediment Using a Portable Gas Chromatograph," U.S. Environmental Protection Agency, Region I, Lexington, Massachusetts

TABLE 1

BLANKS

All positive sample values indicate a "not detected" (ND) with a detection limit of 5 parts per million (ppm) PCBs.

Blank No.	*Value*
1	*+0.18*
2	*+0.14*
3	*+0.32*
4	*+0.30*
5	*+0.27*
6	*+0.05*

TABLE 2

BLANK SPIKES

20 mg/Kg (Air Dried) PCB 1242

All negative sample values indicate that the sample contains 5 mg/Kg or more of PCBs.

Blank Spike No.	*Value*
1	*-0.33*
2	*-0.16*
3	*-0.11*
4	*-0.10*
5	*-0.23*

TABLE 3

REPLICATES

(Co-located)

	Values				
Sample Location	*Run 1*	*Run 2*	*Run 3*	*Run 4*	*Run 5*
D-9	*+0.04*	*+0.22*			
G-10	*- 0.12*	*- 0.07*			
H-3	*+0.15*	*+0.22*			
H-14	*+0.24*	*+0.28*			
K-1	*- 0.01*	*- 0.01*	*+0.22*	*+0.09*	*+0.01*
K-5	*- 0.43*	*- 0.25*			
K-10	*+0.17*	*+0.21*			

Positive values: <5 mg/Kg (wet weight)
Negative values: >5 mg/Kg (wet weight)

TABLE 4

FIELD GC

"HITS" (Negative Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
D-6	*-0.47*	*>400*
F-9	*-0.09*	*16*
E-1	*-0.55*	*100*
J-5	*-0.39*	*18*
J-4	*-0.56*	*120*
I-7	*-0.23*	*24*
D-7	*-0.42*	*40*
D-4	*-0.51*	*400*
I-5	*-0.60*	*150*

TABLE 5

FIELD GC

"CLEAN" (Positive Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
D-10	*+0.06*	*ND*
B-6	*+0.36*	*ND*
C-8	*0.00*	*2*
B-10	*+0.07*	*ND*
B-8	*+0.38*	*2*
H-20	*+0.37*	*ND*
J-14	*+0.28*	*ND*

ND is not detected with a detection limit of 1 mg/Kg (wet weight).

TABLE 6

FIELD GC

"OOPS"

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (wet wt.)*
G-10	*-0.12 and -0.07*	*ND*
K-1	*-0.01 and -0.01 and +0.22 and +0.09 and +0.01*	*6 and 8*
K-9	*-0.01*	*1*
D-8	*-0.06*	*4*

3 False Positives
1 False Negative

ND is not detected with a detection limit of 1 mg/Kg (wet weight).

TABLE 7

LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"HITS" (Negative Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (dry wt.)*
B-1	*-0.51*	*730*
D-4	*-0.54*	*960*
D-6	*-0.47*	*700*
E-1	*-0.55*	*640*
H-6	*-0.45*	*210*
J-5	*-0.39*	*36*
S-4	*-0.22*	*5*

TABLE 8

LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"CLEAN" (Positive Values)

Sample Location	*Immuno Assay Value*	*GC Value mg/Kg (dry wt.)*
A-15	*+0.32*	*0.4*
A-16	*+0.33*	*0.8*
A-17	*+0.37*	*ND*
A-18	*+0.06*	*2.7*
A-26	*+0.34*	*0.5*
B-6	*+0.36*	*1.3*
B-10	*+0.07*	*0.6*
L-14	*+0.15*	*0.6*
O-24	*+0.67*	*ND*
V-12	*+0.63*	*ND*

ND is not detected with a detection limit of 0.1 mg/Kg (dry weight).

TABLE 9

LABORATORY RESULTS
(Sum of PCB 1248 and PCB 1260)

"OOPS"

Sample Location	Immuno Assay Value	GC Value mg/Kg (dry wt.)
G-10	-0.12 and -0.07	ND
K-1	-0.01 and -0.01 and +0.22 and +0.09 and +0.01	1.5
K-9	-0.01	1.4
P-2	-0.23	1.7

3 False Positive Values
1 False Negative Value

ND is not detected with a detection limit of 0.1 mg/Kg (dry weight).

TABLE 10

SUMMARY

SAMPLE COSTS

Immuno Assay	*$ 5,160*
Field GC Analyses (including technician for field GC)	*2,560*
*Laboratory GC Analyses**	*4,050*
Total Analytical Invoice:	*$11,770*

**Includes 2 duplicates, 2 matrix spike/matrix spike duplicates, and data package.*

7 CURRENT STATUS OF LIPID CONTAINING SEMIPERMEABLE MEMBRANE DEVICES AS ENVIRONMENTAL DOSIMETERS

ORGANIC

J.D. Petty, J.N. Huckins, J.A. Lebo, J.L. Zajicek, and J.C. Meadows, National Fisheries Contaminant Research Center, U.S. Fish and Wildlife Service, 4200 New Haven Road, Columbia, MO 65201 USA.

ABSTRACT

Layflat polyethylene and capillary silastic® tubes containing pure triolein (lipid) are shown to have considerable promise as passive in-situ samplers for nonpolar organic contaminants in water and potentially from the vapor phase. These semipermeable membrane devices (SPMDs) appear to simulate the bioconcentration of hydrophobic contaminants by aquatic organisms. Bioavailable organic contaminants in water passively diffuse through the thin membranes into the enclosed lipid. Contaminant molecules associated with particles and dissolved organic carbon are excluded because the transport corridors through these dense polymers are < 10 Å in cross- sectional diameter. Equilibrium SPMD-triolein-water partition coefficients (K_{tw}) of test chemicals as determined by static tests closely correspond to the octanol-water partition coefficients of the same chemicals, resulting in enriched analyte concentrations in triolein. Moreover, enrichment of hydrophobic organic contaminants (eg. PCBs) from airborne residues appears to be extremely facile. Thus, SPMDs with 1.0-g of triolein achieve sampling rates for PCB residues from water of $\simeq$ 5 L/day at 18°C and $\simeq$ 4,000 L/day from air at 26°C. Contaminants concentrated in the lipid are recovered from intact SPMDs (polyethylene) using organic solvent dialysis.

INTRODUCTION

Passive air monitors or dosimeters are widely accepted for determining occupational exposure of workers to ambient organic vapors (1,2). They use diffusion coefficients of vapors through a quiescent air gap or a permeable membrane to obtain a sampling rate that is proportional to exposure time and to the mean airborne concentrations. However, this integrative approach has seldom been applied to contaminants in aquatic environments. Huckins et.al. (3) developed a lipid-containing semipermeable membrane device (SPMD) for in-situ integrative monitoring of aquatic contaminants. The SPMD is

conceptually similar to passive air monitors and fills a gap in current analytical and biomonitoring techniques for organic contaminants.

The SPMD (3) is constructed from virgin (no additives) layflat tubing of low density polyethylene (PE), but other nonporous polymers such as polypropylene (PP), silastic, plasma-treated silicon or silicon-PP laminates (4) can be used. Polymeric films used in SPMDs are referred to as nonporous, although transient cavities with diameters up to ca. 10Å are formed by random thermal motions of polymer chains (5,6). Due to the extremely small and dynamic nature of cavities or transport corridors in most of these membranes, permeant molecules are considered to be "solubilized" by the polymer (7,8). Because the cross-sectional diameters of many environmental contaminants (9) approach the maximum size of membrane transport corridors, only dissolved organics should diffuse through the membrane and be concentrated.

SPMDs contain a thin film or small-diameter plug of a high molecular weight ($\geq$ 600 daltons) neutral lipid, such as triolein; purified lipid extracted from a representative organism, or lipid-like synthetic compounds. The capacity of triolein-containing SPMDs to concentrate an organic chemical is delineated by its K_{tw} (equilibrium triolein-water partition coefficient). Contaminant residues sequestered in triolein are readily recovered from intact PE SPMDs by dialysis in organic solvent (10).

Lipid-containing SPMDs have been used in several environmental settings (3,11-13), and their ability to sequester trace concentrations of both persistent (polychlorinated biphenyls (PCBs) etc.) and biodegradable (PAHs) organic contaminants has been demonstrated. Prest et al. (11) compared the devices to freshwater bivalves (Corbicula fluminea) for environmental contaminant monitoring in the Sacramento and San Joaquin Delta. He recommended further development of the SPMD approach based on ease of use, interpretability of data, and low concentrations of interfering substances in SPMD blanks relative to control bivalves. Also, Gray and Spacie (14) found that SPMD K_{tw}s of lindane and trifluralin were much closer to lindane's and trifluralin's fish bioconcentration factors than the concentration factors in hexane-filled dialysis (cellulose) tubes (15). They concluded that PE-SPMDs have greater promise for field application because of their durable construction and high contaminant concentration potential.

The use of SPMDs for monitoring and removal of organic vapors also holds considerable promise. The high surface area of the PE membrane relative to the low volume of enclosed triolein permits very high sampling rates of ambient vapors. In addition, the presence of a thin liquid phase on the exterior PE membrane surface, consisting of low molecular weight lipid impurities in 95% triolein, appears to enhance the uptake of organic vapors by SPMDs. Presented herein are the results of selected studies from our ongoing research designed to define the applicability of the SPMD technology for sampling both aqueous environments and air-borne hydrophobic pollutants.

EXPERIMENTAL

The experimental details of the preparation and exposures of SPMDs and subsequent analysis of SPMD sample dialysates have been published previously (3, 10, 12, 13, 16).

We choose an urban creek for the first field application of SPMDs that specifically targeted polycyclic aromatic hydrocarbons (PAH) residues. The creek runs through a local Midwestern city, and our primary criterion in choosing it for sampling sites was its proximity to our laboratory. During low water conditions, the depth of the creek ranges from about 5 to 80 cm. The creek bottom consists of rock, gravel, and sand.

For sampling the creek, we deployed the SPMDs in the protective shrouds of galvanized steel. Use of the shrouds enabled us to place SPMDs in the horizontal orientations necessary for sampling this shallow stream. The shrouds protected the SPMDs from abrasions and protected the sequestered PAHs from light. Exposures were conducted for 21 days.

RESULTS AND DISCUSSIONS

As part of our ongoing research designed to delineate the functional processes of contaminant uptake by the SPMDs and to define the kinetics of contaminant enrichment, SPMD membranes consisting of PE layflat tubing and silastic tubing were compared in flow through exposures to 2,2',5,5'-tetrachlorobiphenyl (TCB). In general silastic tubing has greater polymeric free volume than PE and even though the wall thickness of SPMD silastic tubing was 3.2.-fold greater than the PE tubing, it was expected to concentrate the 2,2',5,5'-TCB at approximately the same rate. This arises because the permeability coefficient of nonelectrolyte organics in silastic membranes are, generally much greater than the corresponding values for low density PE membranes of the same thickness.

Figure 1 and 2 illustrate the uptake of 2,2',5,5'-TCB by the silastic and PE SPMD configurations. Following seven days of exposure, the concentration factor of 2,2',5,5'-TCB in the triolein of silastic SPMDs was approximately 6,000 whereas the concentration factor in triolein of PE SPMDs for identical exposure conditions was approximately 20,000. These data indicate that for PCBs the permeability or sampling rate of silastic and PE SPMDs of the same membrane thickness, may be similar.

Huckins et al. (3) suggested that membrane permeation is the rate-limiting step, ie. highest resistance to mass transfer, in the uptake of several hydrophobic organic contaminants (log K_{ow}s $\simeq$ 5 to 8) by SPMD lipid. Membrane control of analyte sampling rate is required to accurately estimate average concentrations of contaminants in water or air (unless equilibrium is achieved during exposure interval), because the variance

associated with intrinsic properties of SPMDs (membrane and triolein) can be minimized, whereas the minimization of variance associated with systems controlled (extrinsically) by boundary layers (3,7), ect., is very difficult. The membrane control design also enables the use of less complex kinetic models to estimate analyte water concentrations from SPMD residue data.

Depending on the physicochemical properties of the contaminant and the components of the selected SPMD design, equilibrium or uptake kinetic modeling approaches may be needed (16) for the estimation of contaminant concentrations in water. Assuming the exposure time is sufficient to reach 0.9 of the K_{tw} of a particular contaminant (limitations of this approach are delineated by Huckins et al. [16]), then its water concentration can be estimated by the pseudo-equilibrium relationship

$$C_w = C_t/0.9\ K_{tw},$$

where C_w is contaminant concentration in water and C_t is its concentration in SPMD triolein. The PE membrane represents a major portion of the SPMD mass and it contains a significant amount of sequestered contaminant residues. Calculation of C_t from contaminant residues recovered in dialysates can be done by using the following equation:

$$C_t = A_{md}/\ (M_t + K_{mt}M_m),$$

where A_{md} is analyte mass in the SPMD dialysate M_t and M_m are the masses of the triolein and the membrane, and K_{mt} is the distribution coefficient of a contaminant in the membrane and triolein phases.

For contaminants with high K_{tw}'s ($\geq 2 \times 10^4$), kinetic modeling approaches are usually more appropriate. Based on the definition of solute transport in polymers, linear SPMD uptake can be described as

$$C_t = (PK_{mw}C_wA_s/Vl)\ (t - T_t),$$

where P is the analyte permeability coefficient, K_{mw} is the membrane-water partition coefficient, A_s and l are the membrane surface area and thickness, V is the volume of the triolein, and T_t is the lag time for contaminant transport through the membrane into the triolein.

If SPMD uptake kinetics are nonlinear then

$$C_t = (K_{mw}C_w/K_{mt})[l - \exp(K_{mt}PA_s/Vl\{T_x - t\})]$$

can be used, where T_x is the x-intercept of the model. This exponential model was

fitted to data from the flow-through exposures of SPMDs to C^{14}-2,2',5,5'-TCB and the model estimate of C_ws were within 50% of the measured values.

To determine the effectiveness of SPMDs for sampling pollutants in the environment, SPMDs were deployed in a small urban stream suspected to be contaminated with PAHs. The reproducibility of the SPMDs for monitoring aqueous PAH residues is exemplified by Figure 3. In Figure 3 we present mirror imaged chromatograms representing duplicate SPMDs deployed in the urban creek. The SPMDs were exposed for 21 days. Because of the intrinsic reproducibility of the SPMD uptake of PAHs these simple devices are extremely useful for determining the relative degree of PAH contamination in aquatic sites where conditions such as temperature and periphytic growth are similar. Research on the effects of temperature variation and the efficacy of antifouling agents is underway.

Another area of our current research is the use of the SPMD technology for concentrating hydrophobic organic contaminants from the atmosphere. It has long been recognized that areial transport of organic contaminants occurs on a global basis (18,19). Such materials exist in both the vapor phase and associated with particulate matter.

A variety of techniques have been employed to measure both wet and dry deposition of atmospheric contaminants (20,21). These techniques include glycerol-coated plates or pans, Teflon® sheets, containers of water, polyurethane foam plugs, carbon or other adsorbent traps. While great progress has been made in improving active air samplers, these devices suffer the consequences of complexity and mechanical operation. Passive air samplers, either diffusion or permeation type (e.g. personal monitors) are attractive due to their simplicity but generally have low sampling rates (total for device) because of the low surface area of the tube (air diffusion zone) or membrane sampler relative to the volume of trapping media. SPMDs have high surface area (membrane and their exterior lipid film) relative to the volume of trapping media, permitting membrane control of sampling rates, while achieving very high total sampling rates.

We exposed SPMDs to the laboratory air at the National Fisheries Contaminant Research Center (NFCRC). The SPMDs were exposed for a period of 14 days and subsequently analyzed by gas chromatography/electron capture detection. The chromatogram of an air sample and a control SPMD sample are presented in Figure 4. The major portion of the electron capture response from the air sample is associated with PCBs. Indeed, the PCBs sequested represent 7μg total residue.

In order to estimate the sampling rate of the SPMDs exposed to the laboratory air, we used a standard method for determining PCBs in air (23) as a benchmark. Thus, the NIOSH method resulted in a determination of 30 ng/m^3 in the laboratory atmosphere. Using the 7 μg total PCB residue sequestered in a sampler array consisting of 3

SPMDs ($\simeq$ 0.46 g triolein/SPMD) and the 30 ng/m^3 determined by the standard NIOSH method, it can easily be ascertained that each SPMD sampled approximately 4 m^3 of air per day. This is an extremely facile sampling rate for a passive sampler. We are currently exploring the kinetics of SPMD uptake of organic pollutants and will field test the technique in the near future.

SUMMARY

The SPMD technology has been demonstrated to be a simple and highly efficient method for sequestering hydrophobic organic contaminants from both water and air. The SPMDs provide a means of estimating the presence and relative amounts of a broad spectrum of bioavailable (assuming no food contribution) organic contaminants. The SPMD technique allows the determination of episodic contamination and pollutants (e.g. PAHs) rapidly metabolized by sentinel organisms.

The extension of the SPMD technology into the area of air sampling potentially provides an efficient method for determining non-particulate bound residues without the problems associated with filtration. The passive nature of the SPMD technology lends itself to a wide variety of sampling situations.

REFERENCES

1) Underhill, D.W.; Feigley, C.E. Anal. Chem. 1991, 63, 1011-1013.

2) Fowler, W.K. Am. Lab 1982, 14, 80-87.

3) Huckins, J.N.; Tubergen, N.W.; Manuweera, G.K. Chemosphere 1990, 20, 533-552.

4) Zander, A.K.; Chen, J.S. and Semmens, M.J. Wat. Res. 1992, 26, 129-237.

5) Lieb, W.R.; Stein, W.D. Nature 1969, 224, 240-243.

6) Flynn, G.L.; Yalkowsky, S.H. J. Pharm. Sci. 1972, 651, 838-852.

7) Comyn, J., Editor, "Polymer Permeability" 1985; Elsevier Applied Science Publishers LTD, New York, NY, p 383.

8) Hwang, S.T.; Kammermeyer, K., Editors, "Membranes in Separations" 1975; Robert E. Krieger Publishing Company, Inc. Malabar, FL, p 559.

9) Opperhuizen, A; Velde, E.W.; Gobas, F.A.P.C.; Liem, D.A.K.; Steen, J.M.D. Chemosphere 1985, 14, 1871-1896.

10) Huckins, J.N.; Tubergen, M.W.; Lebo, J.A.; Gale, R.W.; Schwartz, T.R. J. Assoc. Off. Anal. Chem. 1990, 73, 290-293.

11) Prest, H.F.; Burns, S.A.; Jarman, W.M. 12th Meeting of the Society of Environmental Toxicology and Chemistry, EMAP Session. 1991, Poster No. 323, p 219.

12) Huckins, J.N.; Meadows, J.C.; Manuweera, G.K.; Lebo, J.A. 12th Meeting of the Society of Environmental Toxicology and Chemistry, EMAP Session. 1991, Poster No. 315, p 217.

13) Lebo, J.A.; Zajicek, J.L.; Huckins, J.N.; Petty, J.D. "A Demonstration Method for the Application of Semipermeable Membrane Devices to In Situ Monitoring of Environmental Waters for Polycyclic Aromatic Hydrocarbons" Chemosphere. 1992, In Press.

14) Gray, M.A.; Spacie, A. 12th Meeting of the Society of Environmental Toxicology and Chemistry, EMAP Session. 1991, Poster No. 272, p 206.

15) Södergren, A. Environ. Sci. Techno. 1987, 21, 855-859.

16) Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Lebo, J.A.; Mackay, D. "Lipid Containing Semipermeable Devices for In-Situ Estimation of Time Weighted Aqueous Concentrations of Organic Contaminants; Background, Theory and Model Development" 1992, Submitted to ES&T.

17) Neff, J.M. 1985. G.M. Rand and S.R. Petrocelli, Editors. "Fundamentals of Aquatic Toxicology." Hemisphere Publishing Corp., Washington, D.C., USA, p 416-454.

18) Helmig, D., J. Müller and W. Klein. Chemosphere. 1989, 19, 1399-1412.

19) Bidleman, T.F. and C.E. Olney, Science. 1974, 183, 516-518.

20) Swackhamer, D.L., B.D. McVeety and R.A. Hites, Environ. Sci. Technol. 1988, 22, 664-672.

21) Broman, D., C. Näf, C. Rolff and Y. Zehühr, Environ. Sci. Technol. 1991, 25, 1841-1850.

22) Eller, P.M., NIOSH Manual of Analytical Methods. 3rd ed. Cincinnati: U.S. Department of Health and Human Services. Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1984. DHHS (NIOSH) publication No. 84-100: 5503-1-5503-5.

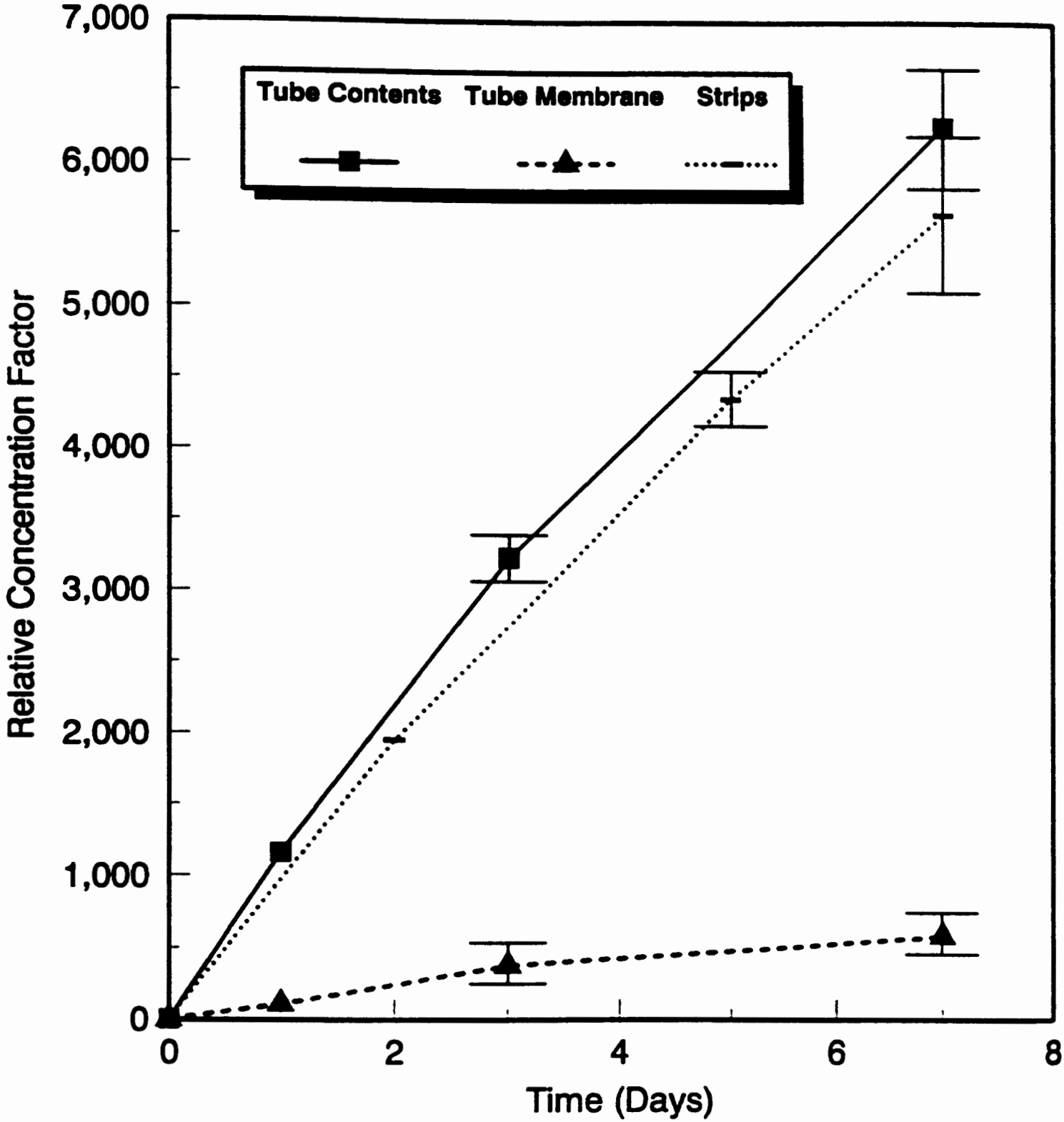


Figure 1: Relative concentration factors of 2,2',5,5'-TCB in triolein (tube contents), silastic tube containing triolein (tube membrane) and silastic strips.

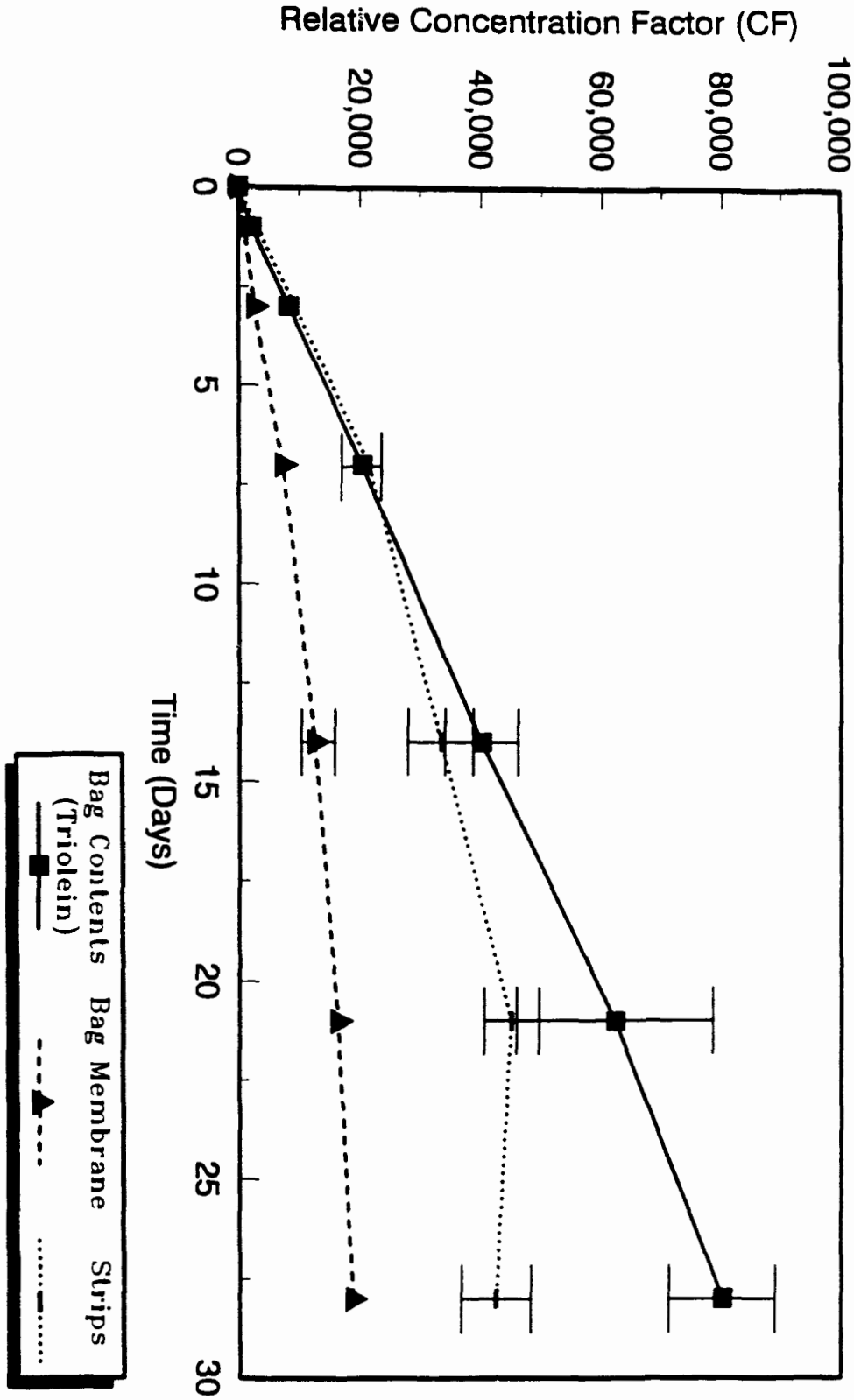


Figure 2: Relative concentration factors of 2,2',5,5'-TCB in triolein (Bag Contents), PE membrane containing the triolein (Bag Membrane) and PE layflat tubing (Strips).

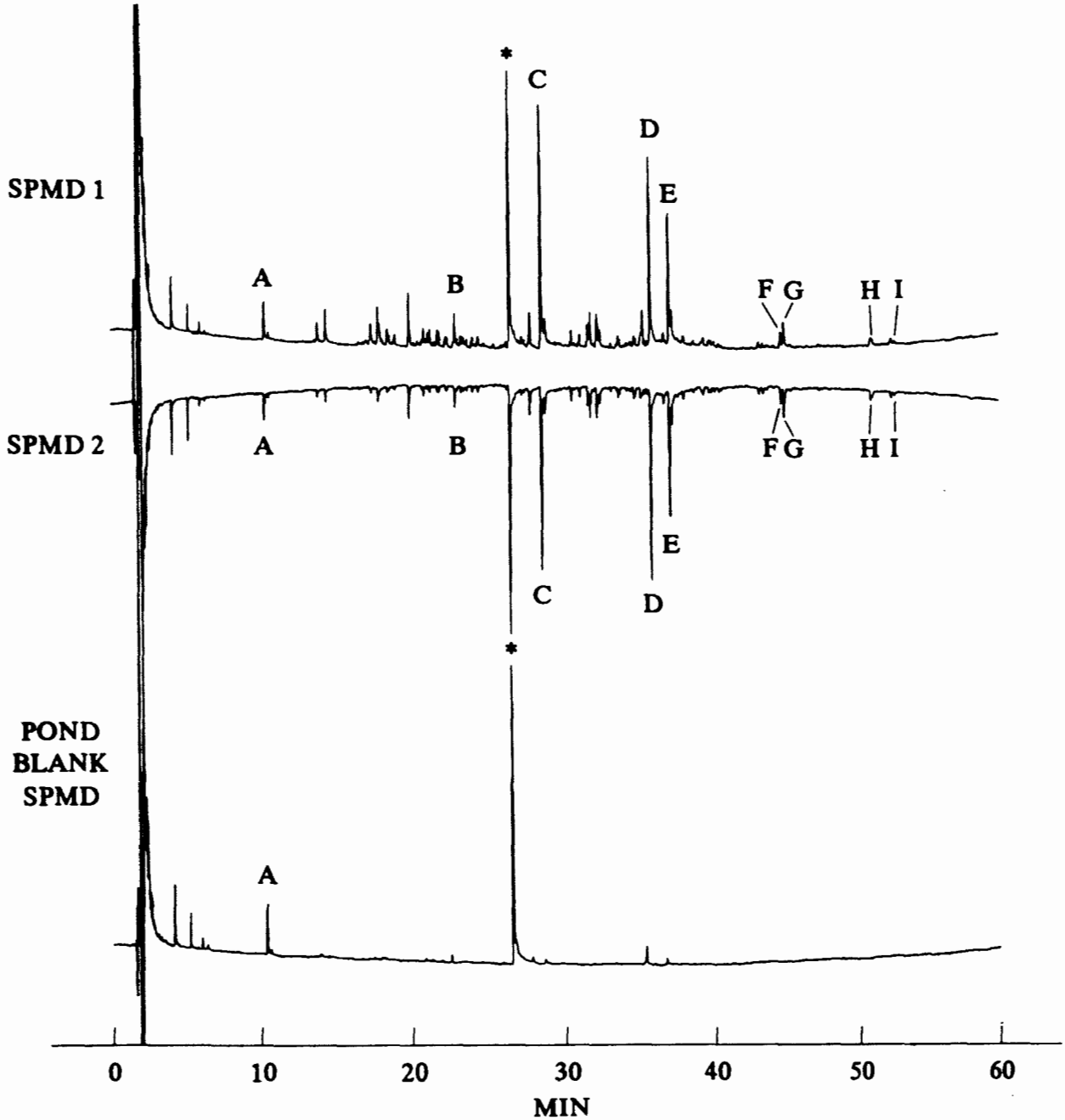


Figure 3: Chromatograms of dialysates from SPMDs exposed for 21 days in a small urban stream (top) and a control pond. **Mirror Image Traces:** two SPMDs deployed contiguously for 21 days. **Bottom Trace:** SPMD exposed in a control pond. **Labeled Peaks:** A) naphthalene; B) fluorene; *) 1-methylfluorene (internal standard); C) phenanthrene; D) fluoranthene; E) pyrene; F) benz(a)anthracene; G) chrysene; H) benzo(b)fluoranthene and benzo(k)fluoranthene; and I) benzo[a]pyrene

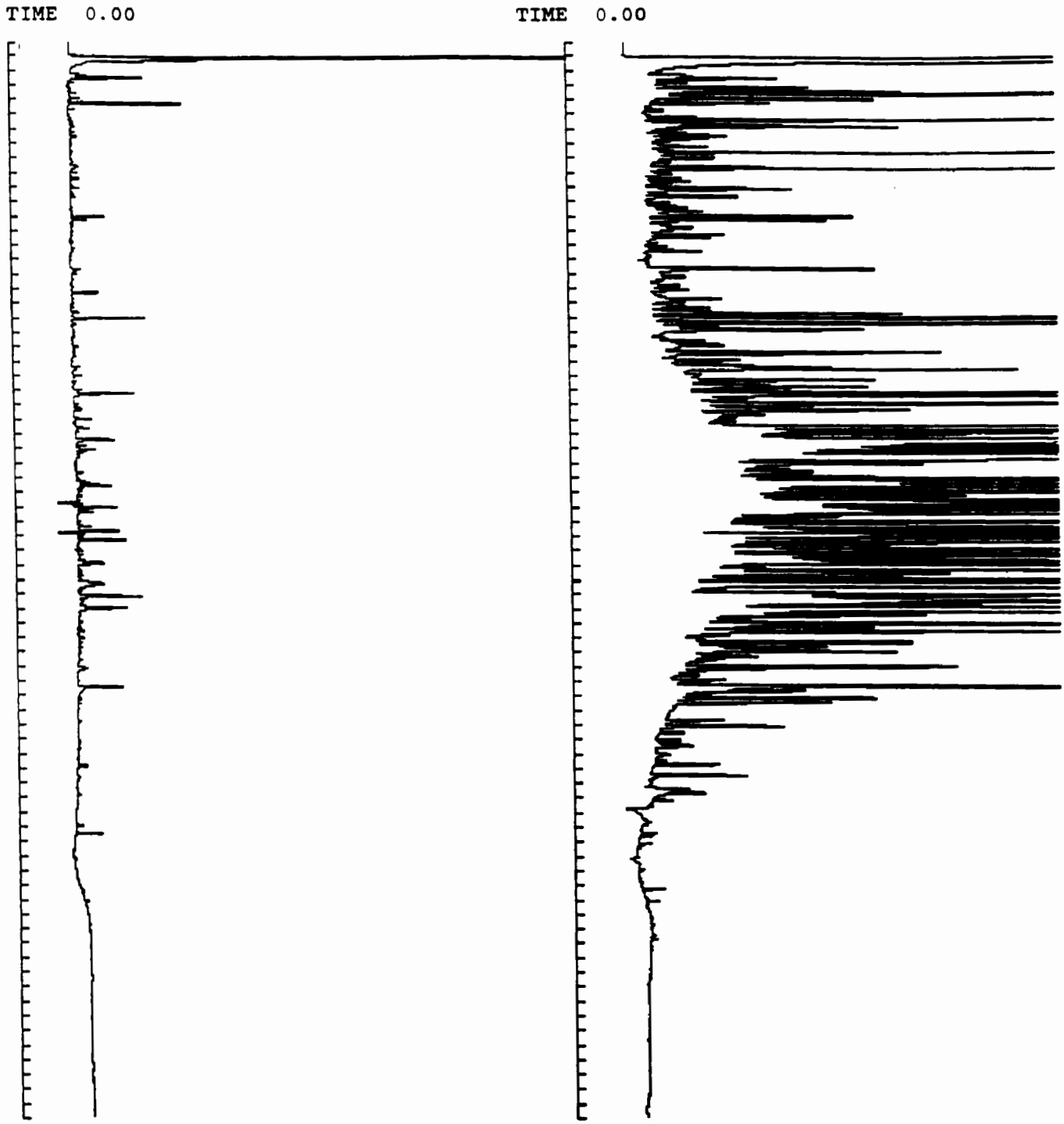


Figure 4: Chromatograms of dialysates from SPMDs exposed to laboratory air for 14 days (top) and blank SPMDs (bottom).

8 DEVELOPMENT OF A MONOCLONAL ANTIBODY IMMUNOASSAY FOR THE DETECTION OF POLYAROMATIC HYDROCARBONS IN SOIL

Randy L. Allen, Thomas N. Stewart, Tracy A. Withers, Wayne B. Manning, Steve B. Friedman, EnSys, Inc., P.O. Box 14063, Research Triangle Park, North Carolina 27709.

ABSTRACT

A sensitive and rapid enzyme immunoassay (EIA) was developed using a monoclonal antibody (MAb) reagent that detects polyaromatic hydrocarbons in soil. Derivatives of naphthalene, methyl naphthalene, phenanthrene and acenaphthene were synthesized with various types of spacers and conjugated to either bovine serum albumen (BSA) or bovine thyroglobulin (BTG). A total of 16 different conjugates were used for immunizing both Balb/c and Swiss Webster mice. Mice responding to immunizations were selected as splenocyte donors for MAb production. A panel of MAbs were produced that recognized PAH compounds in a competitive EIA.
An antibody specific for phenanthrene (F35-2Z11) was chosen for immunoassay development. The detection of phenanthrene in soil provided a reliable marker for PAH compounds because of its relatively low volatility and low susceptibility to leaching. An enzyme-hapten conjugate was prepared for MAb F35-2Z11 that demonstrated suitable characteristics of sensitivity, cross-reactivity and compatibility with extraction buffers. The resulting EIA demonstrated a sensitivity of less than 10ppm for phenanthrene in soil. Extracts of negative soil samples from different types of soil did not significantly alter the performance of the assay. Interference from polychlorinated biphenyls, pentachlorophenols and petroleum products were negligible. This method will offer speed and cost-effectiveness over current testing methods of PAH compounds in contaminated soil which will result in an increased efficiency of site management.

9 The Field Screening of a Large Site for Pentachlorophenol Contamination Using an Immunoassay-Based Analytical Method

Kevin R. Carter, EnSys Inc., Research Triangle Park, NC 27709

ABSTRACT

The contamination of soil and groundwater by pentachlorophenol as a result of wood preserving operations throughout the country has been a prominent environmental problem. A new method for the measurement of pentachlorophenol in environmental samples has been developed that employs immunoassay technology. Its high specificity, sensitivity, and freedom from matrix interferences as well as its speed and ease of use make it ideal for use as a field analysis tool to aid in the delineation of contaminated areas of soil at former wood treating sites. The application of this method in the field can result in the saving of both time and money. The results of a comparison between immunoassay-based testing performed in the field and GC analysis conducted in a field laboratory on a large wood treating facility showed that the field method can be used to accurately assess pentachlorophenol contamination.

INTRODUCTION

Pentachlorophenol (PCP) contamination of soil and water around operating and closed wood preserving plants has received much attention from regulatory authorities due to the potential health hazard posed by PCP and its co-contaminants, such as octachlorodioxin. The specific evaluation of PCP contamination in environmental samples has previously required the use of GC or GC/MS methods that are costly and subject to the normal delays associated with laboratory analytical methods. The recent development of rugged, accurate field analytical tests for PCP in soil and water has enabled the rapid screening of contaminated sites, as well as timely remediation monitoring, and pre-closure verification of clean-up (Mapes et al., 1992). These tests are based on immunoassay technology and rely on the specific binding properties of a biological compound known as an antibody to recognize the target analyte in an environmental sample. The presence of the analyte is visualized through a colorimetric enzymatic reaction and the results are compared with those obtained with a standard. The semi-quantitative result is interpreted with the aid of a battery-powered comparative photometer.

FIELD APPLICATION OF IMMUNOASSAY METHOD

The EPA's Environmental Response Team conducted extensive site characterization at several former wood preserving facilities in the Southeast during the summer of 1991. The first plant to be investigated (in Brunswick, GA) had recently ceased operations. Several areas on the 50 acre plant grounds were heavily contaminated with pentachlorophenol, creosote, and CCA (chromated copper arsenate). These included the area immediately surrounding the treating equipment, treated pole storage barns, the transfer yard, and a wastewater lagoon. The initial characterization was focused on rapidly assessing soil contamination from each of the wood-preserving chemicals. A mobile lab was established on-site at the facility in Brunswick to analyze samples by GC from all of the wood preserving facilities. Because the cost for this approach was so high and the need in the future for on-site analytical capability was foreseen, the immunoassay-based test developed by EnSys was evaluated on this project in parallel with the mobile lab.

The Brunswick site was sampled for PCP contamination assessment using a 100 foot grid with samples taken at the surface and at several depths. The EnSys immunoassay test system was employed to screen 200 soil samples as they were collected prior to GC analysis. The advantages of the screening test in this application included the ability of two field operators to screen up to 100 samples per day where two analytical chemists would only be able to analyze 25 samples per day for pentachlorophenol. In addition, the EPA contract field operators needed no sophisticated equipment and little training to use the field test. The test was capable of ranging the pentachlorophenol concentration in soil over several orders of magnitude, with a minimum detection limit of 0.5 ppm. For this project the test was used to assess pentachlorophenol concentration at thresholds of 25 and 100 ppm.

A high degree of correlation was observed between the GC-FID results and those obtained on-site with the immunoassay-based field test. Of the 176 samples analyzed using both methods, 147 (83%) exhibited excellent agreement. There were 21 (12%) false positives and 8 (5%) false negatives recorded. Several of these (6), however, must be considered provisional, because for these the field immunoassay results were within 25% of the GC results. The especially low incidence of false negative results highlights the utility of immunoassay-based field tests for the delineation of uncontaminated areas. It should be noted that the GC method was subject to inaccuracy primarily due to interferences caused by high levels of creosote and fuel oil in many samples, which makes 100% correlation between the two methods unlikely in any case. This side-by-side comparison conducted under actual field conditions demonstrates the accuracy of the screening method.

SUMMARY

A field analytical method for the semi-quantitative measurement of pentachlorophenol based on immunoassay technology has been tested at a wood preserving facility and the results compared to those obtained with GC-FID. The correlation observed was very good with an acceptably low level of false negative results.

REFERENCES

Mapes, J. P., K. D. McKenzie, L. R. McClelland, S. Movassaghi, R. A. Reddy, R. L. Allen, and S. B. Friedman. PENTA RIS^{c}™ Soil - A Rapid, On-Site Screening Test for Pentachlorophenol in Soil. Bulletin of Environmental Contamination and Toxicology, in press.

10 The Assessment of a Site for PCB Contamination Using an Immunoassay-Based Field Analytical Method

Kevin R. Carter, EnSys Inc., Research Triangle Park, NC 27709

ABSTRACT

The application of field analytical methods to site assessment projects can result in substantial savings of time and money relative to the conventional practice of collecting samples and submitting them for laboratory analysis. Where large numbers of samples must be collected and analyzed, the analytical turnaround time can severely handicap the progress of a project. A PCB-specific immunassay-based field analytical method was used to evaluate several hundred soil samples from a site on which electrical transformers had been stored. The field analysis of over one thousand samples from this site allowed the contaminated areas to be delineated in a relatively short time period. A PCB contamination map of the site was created that showed the pattern of PCB contamination clearly. A series of quality assurance/quality control (QA/QC) procedures were implemented to support the field analytical method. The QA data provided the necessary confidence in the field results.

INTRODUCTION

Immunoassay-based field analytical methods can be used to substantial time and money advantage in site assessment projects relative to the conventional practice of collecting samples and submitting them for laboratory analysis. While laboratory methods can provide definitive identification and quantitation of hazardous chemicals in soil and water, they require highly trained personnel, expensive capital equipment, and relatively laborious quality assurance/quality control (QA/QC) procedures to achieve these results. These factors contribute to substantial delays in obtaining results following the submission of a sample for analysis. Delays stemming from the laboratory analysis turnaround seriously reduce the time-effectiveness of site assessment work. This has a more pronounced effect where large numbers of samples must be collected and analyzed.

In order to complete the site assessment phase of an environmental clean-up project where hundreds of samples are required in a timely fashion, either the samples must be composited, sent to several analytical laboratories, or a field method must be employed. Although it certainly has valid applications, compositing of samples often creates detection limit problems. The use of several laboratories presents a significant QA/QC management

problem. With the appropriate simple quality assurance/quality control measures, immunoassay-based field screening of environmental samples can be accomplished at a reduced cost without an accompanying decrease in the quality of the data necessary to support the decision-making process.

IMMUNOASSAYS AS FIELD ANALYTICAL TOOLS

Immunoassay technology has only recently been applied to in-field sample analysis for environmental contaminants (US EPA, 1990 and Goolsby et al., 1991). Immunoassays rely on the specific binding properties of an antibody to identify contaminated samples. The presence of the target contaminant is visualized through a colorimetric enzymatic reaction and the semi-quantitative results are interpreted with the aid of a portable comparative photometer.

Immunoassay-based methods are appropiate for field analysis because:

- the reaction is extremely specific for the target contaminant
- there are few matrix interferences
- the test procedure is simple and rapid
- the method limits false negatives.

Immunoassays can, with a high degree of confidence, establish that sites or areas are free from contamination. Extensive testing by environmental consulting firms and by the EPA have shown that immunoassay-based products can correctly identify over 90% of samples tested as clean versus contaminated (Taylor et al., 1991).

SITE ASSESSMENT RESULTS

A west coast military base recently proposed to convert a surplus/salvage equipment storage area to another use. Because the 1.5 acre site had previously been used to store utility transformers and there was anecdotal evidence for transformer leakage, the state specified a phase 2 site assessment plan that included a total of up to 3700 samples to be collected and analyzed for PCBs. This sampling frequency was necessary to ensure that a small spill was detected. Since there was no existing record of where transformers had been stored on the site and surface staining provided no clues, the use of an intensive grid sampling design was required.

The environmental consultant was faced with the problem of analyzing a

large number of samples on a limited time scale with a budget that did not match these needs. The solution to the problem was a field analytical method that is specific for PCBs and provides the capability to analyze 35-50 samples per day on-site. Originally, a field method based on the detection of chlorine chemically stripped from PCBs was considered, but rejected due to the presence of significant levels of chloride ion in the soil that would act as a positive interferent. The immunoassay-based method was selected because of its accuracy, PCB-specificity, and sensitivity. This immunoassay field analytical system is manufactured by EnSys Inc.

The environmental consultant set up the two meter grid required by the sampling plan and a two-person crew collected surface samples for screening by the field method. The first round of samples was collected at eight meter intervals to roughly define contaminated areas. The action level for the site was 25 ppm PCBs. Analyses of each sample were made at 5 and 50 ppm to allow the mapping of contaminated zones. One large area and a few smaller areas were found to be contaminated with PCBs at levels greater than 50 ppm. Several samples that were shown to contain greater than 50 ppm PCBs on the eight meter grid were sent to a laboratory for confirmatory analysis by GC (results from the first batch are shown in Table 1). Over 75% of the field testing results were confirmed by the laboratory analysis. Where agreement between the two methods was not observed only false positives were obtained. The absence of false negatives is an important criterion for a successful field method.

To identify smaller areas of contamination and more sharply delineate the larger areas, samples were next collected and analyzed from points located at four meter intervals. Finally, a relatively small number of samples were collected at the two meter interval to sharply define any contaminated areas identified in the broader screens. The results of the field analytical testing are depicted in Figure 1.

In any project where field data are to be used for decision-making it is imperative that QA/QC be performed in the field to provide documentation regarding the validity of the field analytical data. Several different types of field QA/QC data were collected. The semi-quantative PCB field test kit contains duplicate calibration standards that are tested in parallel with each group of three samples. The evaluation of duplicate standards serves to provide internal test system quality control. The results are deemed valid if the difference in the results for the standards are within a predefined limit. In addition, during the course of this project the field test operators routinely tested performance evaluation (PE) samples supplied for the purpose of confirming that false negative/false positive specifications for the field test

were met (Table 2). This was primarily focused on the need to verify that samples with PCB concentrations near the action level, 25 ppm, were identified properly. This included ensuring that no false negative results at the 5 ppm test level were recorded for samples containing PCBs. The results of the PE sample analyses verified the expected performance relative to false negatives. The repeatability of the test was documented through the testing of duplicate subsamples at the rate of one for every twenty samples.

Because the PCB contamination covered areas substantially larger than the smallest grid interval, testing of samples from all of the nodes at that interval was unnecessary. The total number of samples screened over a 4 week period by the two-person field screening crew was slightly over 1000. More than half of those samples tested negative for PCBs. The ability to quickly identify areas contaminated with PCBs allowed the environmental consultant to focus on delineating the areas with PCB soil levels in excess of 5 ppm and 50 ppm.

The project might have proceeded quite differently at a sustantially greater cost had conventional laboratory-based GC analysis been employed. The performance of 1200 field analyses at $34 per analysis (including labor) and 150 laboratory confirmatory analyses at $150 per sample comes to under $64,000. By way of comparison, a strictly laboratory-based approach to this project would have cost $180,000 (1200 samples at $150 per sample). Due to the need for an approved laboratory and limited available laboratory capacity the project would have required an estimated 4 months to obtain all of the analytical data. This contrasts sharply to the 4 weeks required for the completion of the site assessment using the field analytical test.

SUMMARY

Following the field analysis of over one thousand samples using an immunassay-based field method, several areas of PCB contamination were clearly and completely delineated. The data obtained allowed a "map" of PCB contamination on the site to be constructed in a short period of time. Quality assurance data were collected during the course of the project to document the quality of the field analytical testing.

REFERENCES

US Environmental Protection Agency. Evaluation of the Westinghouse Bioanalytic Systems PCP Immunoassay. EPA 600/X-90/146, 1990.

Goolsby, D. A., E. M. Thurman, M. L. Clark, and M. L. Pomes. Immunoassay as a Screening Tool for Triazine Herbicides in Streams: Comparison with Gas Chromatographic-Mass Spectrometric Methods. in Immunoassays for Trace Chemical Analysis, M. Vanderlaan, L. H. Stanker, V. E.Watkins, and D. W. Roberts, eds. American Chemical Society, Washington, D.C., 1991.

M. J. Taylor, S. D. Wesson, and N. Monacella. Laboratory Evaluation of a Rapid Immunoassay Screen Test for Determination of Polychlorinated Biphenyls in Soil. GRI Contract No. 5089-253-1836, Task 4 (to be published), June 1991.

Table 1

QA Data: Confirmatory Laboratory Analyses

Sample	Field Test Results (ppm)		GC-ECD Results (ppm)
2-52	≥ 5	≥ 50	3310
4-28	≥ 5	≥ 50	1440
4-48	≥ 5	≥ 50	2900
6-24	≥ 5	≥ 50	492
6-32	≥ 5	≥ 50	616
6-36	≥ 5	≥ 50	237
8-48	≥ 5	≥ 50	40
10-32	≥ 5	≥ 50	112
10-36	≥ 5	≥ 50	145
12-48	≥ 5	≥ 50	19
14-32	≥ 5	≥ 50	114
20-4	≥ 5	< 50	< 0.5
24-40	≥ 5	≥ 50	86
28-4	< 5	< 50	< 0.5
32-4	< 5	< 50	< 0.5
34-32	≥ 5	≥ 50	3.5
38-36	< 5	< 50	4.5

Figure 1

PCB Contamination Map of Military Site

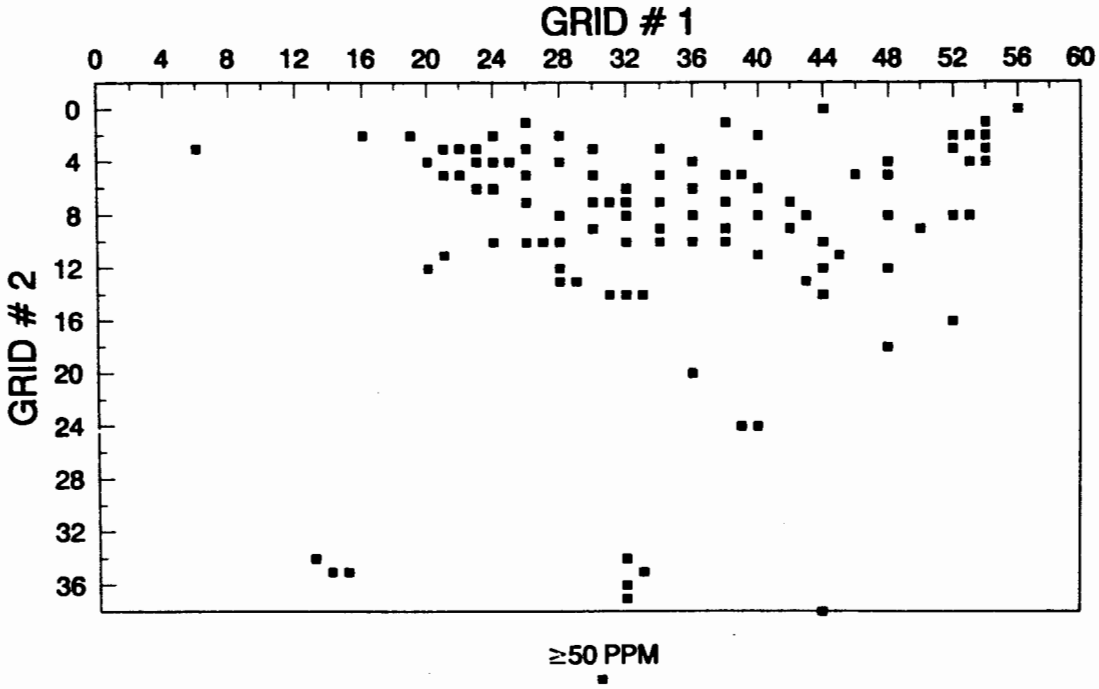


Table 2

QA Data: Performance Evaluation Sample Results

Sample Type	Field Test Results	
negative soil	< 5	< 50
negative soil	< 5	< 50
negative soil	≥ 5	< 50
negative soil	< 5	< 50
negative soil	< 5	< 50
negative soil	< 5	< 50
negative soil	< 5	< 50
negative soil	< 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	≥ 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
27.5 ppm Aroclor 1260 soil	≥ 5	≥ 50
27.5 ppm Aroclor 1260 soil	≥ 5	< 50
24.7 ppm Aroclor 1260 soil	≥ 5	≥ 50
24.7 ppm Aroclor 1260 soil	≥ 5	< 50
24.7 ppm Aroclor 1260 soil	≥ 5	< 50
24.7 ppm Aroclor 1260 soil	≥ 5	≥ 50
24.7 ppm Aroclor 1260 soil	≥ 5	< 50

11 The Application of Immunoassay-Based Field Analytical Methods

Kevin R. Carter. EnSys Inc., Research Triangle Park, NC 27709

ABSTRACT

The application of field analytical methods to hazardous waste site assessment can significantly enhance the quality of the site assessment effort and result in substantial savings of time relative to the conventional practice of collecting samples and submitting them for laboratory analysis. With the appropriate field method and adequate quality assurance/quality control (QA/QC) this can be accomplished without an accompanying decrease in the quality of the data necessary to support the decision-making process.

The recent development of several low-cost, rapid, analyte-specific field analytical tests based on immunoassay technology has provided on-site tools for the cost-effective assessment of soil and water contamination. Extensive application of immunoassay-based field analytical methods for pentachlorophenol, polychlorinated biphenyls, and petroleum hydrocarbons have shown them to be accurate, rugged, and reliable. In order to fully realize the advantages offered by these tests, a project must be designed from the beginning with field analysis in mind. There are two principal operational areas in which the typical sampling or remediation plan is significantly impacted by the use of a field analytical tool: the sampling frequency and quality assurance/quality control procedures.

The optimum sampling frequency for projects where field screening is employed is usually greater than it would have been using conventional practice. The rapid feedback regarding location and level of contamination that is available and the lower cost per sample collected and analyzed argues that a greater frequency of sampling, overall, is of benefit to the quality of the site assessment or remediation effort. Examples of modified sampling plans appropriate to immunoassay-based field testing will be presented and discussed.

In order for the results obtained with any analytical method to be reliable and accurate, a sampling QA/QC plan with data quality objectives (DQO) must be developed and followed. A specific plan should be developed based on the goals of the project for which it is to be used and the decisions that are anticipated to follow from the results. QA/QC procedures have been developed for immunoassay-based analytical methods to enable their application in the field with resulting data of documented quality.

INTRODUCTION

In many cases, the application of field analytical methods to site assessments can result in substantial savings of time and money relative to the conventional practice of collecting samples and submitting them for laboratory analysis. In order to fully realize these advantages, however, the project plan must be designed from the beginning with field analysis in mind. There are two principal operational areas in which the typical sampling plan is significantly impacted by the use of a field analytical tool: the sampling frequency and quality assurance/quality control (QA/QC) procedures. Immunoassay-based field tests possess the basic technical qualifications to make them extremely useful for the assessment of soil contamination.

IMMUNOASSAY-BASED FIELD ANALYTICAL METHODS

The environmental immunoassay technique relies on a molecule referred to as an antibody that is developed to have a high degree of affinity for the target analyte. The high specificity and high affinity of the antibody is coupled with a very sensitive colorimetric reaction that provides visualization of the result. All of this chemistry is accomplished with a small number of solutions that are applied to the processed sample or a dilution thereof. Soil samples require a simple extraction step and subsequent filtration of the extractant. A wide range of analyte concentration in samples is accommodated through conventional serial dilutions. Extraction, normalization, and sample dilutions can all be preformatted for ease of use in the field.

The attributes that make immunoassay tests ideal for field screening include:

- immunoassay-based tests are analyte-specific;
- they are accurate and precise;
- they are easy to use;
- they are rapid (<30 minutes);
- immunoassay-based tests are not significantly affected by the composition of the sample (soil or water) or the presence of most other compounds.

In addition to these characteristics, a properly designed immunoassay-based field screening method should possess a very low false negative detection rate. This property has the practical consequence of not treating a substantial volume of contaminated soil as though it were "clean." Viewed another way, this impacts the conduct of the site assessment in a positive fashion. It is not necessary to subject an area that has been screened and found to be free

of contamination relative to the action level to a large amount of confirmatory sampling and laboratory testing.

SAMPLING

The optimum sampling frequency for projects where field screening is employed is usually greater than it would have been using conventional site assessment practice. The rapid feedback regarding location and level of contamination that is available and the lower cost per sample collected and analyzed argues that a greater frequency of sampling, overall, is of benefit to the quality of the site assessment effort. It is widely acknowledged that in soil matrices the chief impediment to obtaining an accurate picture of contaminant distribution is the heterogeneity associated with the matrix. One approach to overcoming this problem is simply collecting and analyzing more samples. However, this solution carries with it a proportionally higher cost. The use of field methods makes it possible to get the additional data points within the original cost constraints. In addition, this information can be provided in the course of a single field mobilization with no added expense for demobilization and redeployment of the sampling team for successive sampling trips.

The application of an immunoassay-based field method requires a somewhat different approach in the design of a sampling plan. It is impossible to create a generic sampling plan to address the use of field analytical methods, because any sampling plan depends on several factors that are site-, analyte-, and matrix-specific. These factors include the pattern and magnitude of contamination and the relative cost of sampling/analysis relative to the anticipated cost of the remedy. Several general guidelines do exist, however. The most effective use of the strengths of field screening is obtained when the sampling/analysis activity is conducted to increasingly smaller intervals as it progresses, in an interactive fashion. The starting sampling interval is determined by consideration of many factors specific to the situation.

For example, a large site with relatively large areas of soil contamination might initially be sampled at the nodes of a 100 foot grid. Node samples testing "clean" would require no additional sampling in their adjacent areas. On the other hand, node samples analyzing above the action level would trigger the collection of additional samples at points 50 feet from the node in the direction of adjacent clean nodes. This type of iterative increase in sampling resolution allows the boundaries of contaminated areas to be defined relatively precisely with fewer samples (and at a lower total cost) than would be required to achieve the same degree of precision with uniform grid

sampling in a single trip, sampling/laboratory analysis scenario. But the increase in precision is obtained with more samples than would be collected/analyzed for the same cost using conventional laboratory analysis to evaluate the extent of contamination using a fixed grid sampling plan. As a result, the quality of the site assessment is enhanced by field testing without additional expenditure. The same principle of iterative sampling and field testing can be applied where soil contamination is expected to be more localized, as well. However in this case, a smaller beginning node spacing would be utilized.

QUALITY ASSURANCE AND QUALITY CONTROL

In order for the results obtained with any analytical method to be judged reliable and accurate, a sampling QA/QC plan must be developed and followed. The quality of data is dependent both on its analytical accuracy and precision and its utility to the user in making a decision with a defined degree of confidence. The use of a "high-powered" analytical technique does not ensure that the data derived therefrom are either accurate or useful. To obtain the maximum value from the money spent to collect data, it is necessary to define data quality in such a way as to not only specify accuracy and precision limits, but to include the intended use of the data, as well.

To ensure that data derived from field measurements using immunoassay-based methods are adequate for the task for which they are being obtained it is useful to follow the guidelines developed for the Superfund program by the EPA Quality Assurance Management Staff. A sampling QA/QC plan with data quality objectives (DQO) should be developed based on the goals of the project for which it is to be used. The EPA has developed the data quality objectives concept to enable the project manager to ensure that all measurements made in association with an environmental project produce data of established quality. The key factor in establishing the quality of data generated in the course of an environmental project is the level of QA/QC performed. The decisions to be made with the data and the consequences of failure dictate the level of QA/QC required for a given sampling plan. The EPA has defined three levels of QA/QC for the Superfund program (Ryti and Neptune, 1991) and Removal program (US EPA, 1990) that are valuable for other types of projects, as well. They are summarized briefly below:

QA1: This is a screening objective that is typically used for rapid, preliminary assessment of site contamination by field methods. Data collected for this objective have neither definitive identification of contaminants nor quantitation of their concentrations. No QA data are collected; a calibration

or performance check of the method is required along with verification of the detection level.

QA2: This is an objective that calls for the verification of the analytical results obtained by either field or laboratory methods. This objective is most frequently applied to field methods or quick laboratory methods. A portion of the results (≥10%) are selected for qualitative (identification) and quantitative (concentration level) verification. Assuming that the portion selected for verification is representative of the whole, the project manager is given a measure of confidence regarding the whole body of data.

QA3: This is a rigorous objective that specifies the assessment of the accuracy and and precision of the analytical determination, as well as the verification of the identity of the analyte. This level of QA/QC is usually only performed on data collected using laboratory methods. It provides the highest level of confidence, allowing critical decisions to be made based on results obtained.

Field analytical methods based on immunoassay techniques can readily be incorporated into projects to meet the data quality objectives for site assessments. Due to their analyte-specific nature, immunoassay-based field analytical methods are best-suited to situations where the nature of the contamination has already been determined using more general methods, such as GC/MS. Only where strong historical evidence exists for predominance of a single analyte should an immunoassay-based test be used for a Phase 1 type of site assessment.

The requirements necessary to satisfy QA1 level objectives are quite readily achieved using immunoassay-based field methods. In addition to sample documentation only calibration need be performed. Regular calibration is always a component of a properly designed immunoassay-based field method.

The decisions resulting from data generated as a consequence of a Phase 2 site assessment activity usually dictate that several elements of a QA2 level QA/QC plan be implemented in conjunction with immunoassay-based field testing. Such a plan contains the features detailed below:

A. Sample documentation
   1. Location, depth
   2. Time and date of collection and field analysis
B. Field analysis documentation - provide raw data, calibration, any calculations, and final results of field analysis for all samples screened (including QC samples)

C. Method calibration - frequent (several times daily) calibration; this should be an integral part of the immunoassay test

D. Site-specific matrix background field analysis - collect and field analyze uncontaminated sample from site matrix to document matrix effect

E. Duplicate sample field analysis - field analyze duplicate sample to document method repeatability; at least one of every 20 samples should be analyzed in duplicate

F. Confirmation of field analysis - provide confirmation of the quantitation of the analyte via an EPA-approved method different from the field method on at least 10% of the samples; choose 2% or at least two representative samples testing below the action level or lowest test level and 8% or at least two representative samples testing above the action level; provide chain of custody and documentation such as gas chromatograms, mass spectra, etc.

G. Performance evaluation sample field analysis (optional, but strongly recommended) - field analyze performance evaluation sample daily to document method/operator performance

H. Method blank, rinsate blank field analysis (optional)

I. Matrix spike field analysis (optional) - field analyze matrix spike to document matrix effect on analyte measurement

In addition to the QA/QC elements above, we have found that a simple quality control procedure used at the time of the analysis can markedly improve the performance of immunoassay-based field tests in the hands of field workers. Due to the temperature dependence of the immunochemistry, standards are normally tested alongside of samples in the field. For a semi-quantitative test a standard at a single concentration level is used to simplify the test for quick, easy field application. Little additional complication and time results from concurrently testing a duplicate of that standard, but the duplicate provides an easy field check of the operator's technique for that set of samples/dilutions tested.

Following the immunoassay-based field analytical method instructions and providing for the QA/QC requirements described above will result in cost-effective data at the level of confidence necessary for most Phase 2 site assessment-based decision-making.

SUMMARY

Field analytical methods provide a means for improving the quality of site assessment work with no cost or data quality penalty. Immunoassay-based field analytical methods have performance characteristics that are well-suited for their use in assessment of soil contamination. With the application of appropriate QA/QC procedures, immunoassay-based methods can be used to generate data that meets QA1 and QA2 level objectives.

REFERENCES

Ryti, R.T. and D. Neptune. Planning Issues for Superfund Site Remediation. Hazardous Materials Control 4 (6), 47-53, 1991.

US Environmental Protection Agency. Quality Assurance/Quality Control Guidance for Removal Activities. EPA/540/G-90/004, 1990.

12

A GUIDANCE AND METHODS COMPENDIUM: DOE METHODS FOR EVALUATING ENVIRONMENTAL AND WASTE MANAGEMENT SAMPLES

Steven C. Goheen, Margaret McCulloch, Sandra K. Fadeff, Deborah S. Sklarew, Berta L. Thomas, Roger M. Bean, Georgia K. Ruebsamen, Shantha M. Anantatmula, and Robert G. Riley. Pacific Northwest Laboratory[a], Richland, Washington 99352; Craig S. Leasure. Los Alamos National Laboratory, Los Alamos, New Mexico 87545; James S. Poppiti, Laboratory Management Branch, U.S. Department of Energy, Germantown, Maryland 20874

Abstract: The document DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods) is a guidance document planned for release in October 1992, with subsequent updates to be published every 6 months. DOE Methods contains guidance and validated methods for use by DOE and DOE contractor laboratories in waste and environmental sampling, and in analyzing the constituents of waste and environmental samples. The purpose of the document is to provide methods for the sampling and analysis of radioactive and radioactive-hazardous waste and environmental samples that are not currently provided by existing guidance manuals (i.e., EPA's SW-846). The development of DOE Methods is supported by the Laboratory Management Division (LMD) of DOE. LMD is charged with providing the required analytical facilities and analysis capabilities to cost effectively support DOE's environmental restoration and waste management (EM) programs. DOE Methods will support the activities that will determine whether EM actions are needed as defined by the DOE or the U.S. Environmental Protection Agency (EPA).

A database called the DOE Methods Compendium Database (database) is being developed in parallel with DOE Methods. Sampling and analytical methods have been and continue to be acquired from DOE and DOE contractor labs and entered into the database. Similar methods are consolidated and subjected to a review, validation, and approval process. Methods meeting certain validation criteria (i.e., QC data availability, internal/external laboratory verification) are selected for inclusion in DOE Methods.

INTRODUCTION

Until now, DOE and DOE contractor labs have relied on the EPA, other agencies, and professional societies for sources of compiled sampling and analysis methods. Historically, laboratories within the DOE complex have developed waste and environmental characterization procedures independent of one another. This practice has led to the accumulation across the DOE complex of a multitude of site-specific sampling and analysis procedures. Acquisition and consolidation of these procedures is the goal of the DOE Methods Compendium Program (DMCP). Through DOE Methods, DMCP will provide guidance for implementing sound sampling and analysis strategies and providing the most up-to-date methodologies in support of EM programs. Emphasis will be placed on incorporating radiochemical analysis methods, standard methods that have been modified to accommodate highly radioactive samples (i.e., methods from the EPA's SW-846 (1), Contract Laboratory Program (CLP), and 500 and 600 series), and field and waste sampling methods. Sampling methods will include those for both low and high levels of radioactivity.

Several documents were used in the development of DOE Methods (1-5) which comply with pertinent DOE regulations. DOE Methods will be reviewed quarterly and updated biannually. As part of the review process, new and revised methods and chapters will be subjected to external review each quarter. Reviewers comments will be incorporated so that the revised methods or chapters can be inserted in the next updated version of the document.

---

[a] Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06 76RLO 1830.

BACKGROUND

Program Roles and Responsibilities. Figure 1 depicts the overall organizational structure for the management and conduct of the DMCP. The LMD has overall responsibility for the DMCP. DOE has engaged the support of several organizations to meet the goal of this program. These groups and their responsibilities follow:

- Los Alamos National Laboratory (LANL) is the lead organization for the technical conduct of the program. LANL-specific responsibilities include database development, management, and application.

- Pacific Northwest Laboratory (PNL) is the custodian of DOE Methods and is responsible for its development, periodic updating, and issue. Both LANL and PNL work collaboratively to acquire procedures from laboratories across the DOE complex to support database and DOE Methods development.

- Assisting LANL and PNL is the National Air and Radiation Environmental Laboratory (NAREL). NAREL is responsible for independently assessing the methods, with special attention on providing guidance to the program on whether the methods are consistent with EPA monitoring and/or regulatory needs and quality assurance and related ANSI/ASTM standards. NAREL also provides the primary regulatory interface for radioactive and mixed-waste (or radioactive and hazardous sample) analysis methods.

Database and DOE Methods Dynamics. Since the middle of FY 1991, LANL and PNL have been acquiring procedures from the DOE and DOE contractor analytical laboratories within the DOE complex. Figure 2 indicates current LANL and PNL communication networks used to obtain procedures. PNL's network encompasses 6 operations offices and currently includes 25 laboratories and 1 program office. DOE sites targeted by LANL are also of similar scope. To date, the total number of procedures entered into the database based on the combined efforts of LANL and PNL is approximately 1,500.

Figure 3 summarizes the interrelationships of LANL and PNL database methods compendium development activities. Network-received procedures are entered into the database by LANL staff by transforming hardcopy information into text and image files and storing in the database. Both LANL and PNL maintain indexed hardcopy files of procedures. LANL's files are used in support of database development and to respond to user requests for procedures while PNL's repository is used in the development of DOE Methods. Hard copies of procedures from the LANL repository can be ordered through the database.

The database is accessed through the SEARCHmate™ system, which permits searching by procedure type or by selected procedure elements (i.e., analyte, matrix, detection limit). Through this process, users may identify existing procedures that meet their needs, thus avoiding costs associated with developing their own procedure or using an inferior procedure that would impact data quality. The database may also help to identify gaps in methodology, thus helping DOE identify where investments are needed in methods development projects. The database contains over 1,500 full-text procedures, most of which are radiochemical procedures. Figure 4 shows the distribution of a random sampling of 512 database procedures. For the development of DOE Methods, PNL is responsible for preparing all chapters and entering methods in the document. Network-received procedures are screened through a prioritization scheme that gives high-level mixed (radioactive-hazardous) waste and environmental methods (sampling and analysis) the highest priority, followed by low-level mixed waste methods. Methods for sampling and analysis of radioactive materials have third priority, and methods for non-radioactive samples are given fourth priority.

In situations where a number of common procedures have been received from DOE laboratories which are not available in commonly used documents, a single method will be developed that incorporates the attributes of all procedures in that batch. At the other extreme, unique methods will be evaluated on their own merit. Developed procedures are subjected to a review, validation, and approval process. A draft plan

has been prepared which defines 1) the mechanism by which procedures from the database become part of DOE Methods, and 2) the criteria used for establishing their level of validation (Figure 5). The placement of a procedure in a particular validation level is partially determined by submitted performance data. Methods that successfully complete the process are reformatted and incorporated into DOE Methods, then, where appropriate, submitted to EPA for inclusion in their methods documents (i.e., SW-846).

STRUCTURE AND PHILOSOPHY OF DOE METHODS

DOE Methods has been structured to complement EPA's Test Methods for Evaluating Solid Waste (SW-846), with emphasis on guidance for the sampling and analysis of radioactive and radioactive-hazardous waste and environmental samples. DOE Methods contains 11 chapters and 2 appendices. Chapter and appendix content are summarized in Figure 6. Chapters 1-6 provide guidance for the design of an EM sampling/analytical program. Chapters 7-11 contain sampling and analytical methods that can be used in EM program conduct. Each method is assigned a number according to the scheme shown in Figure 7.

Performance vs. Prescriptive Methods. DOE Methods will encourage a performance-based approach to methods application. Performance-based methods specify acceptable performance criteria for an analysis and allow the analyst flexibility in achieving that performance level. Analysts may use a recommended method or modify it to achieve a desired level of performance (i.e., any method can be used as long as its performance meets the data requirements of the project). In contrast, prescriptive methods specify in detail all the steps that must be followed, including quality control. Such methods are useful when the choices for analysis need to be limited, as is normally the case when contracting for analytical services. Most of EPA's methods, especially those used in the CLP, have been prescriptive.

The methods contained in DOE Methods will resemble prescriptive methods; however, they also will contain performance criteria. All relevant validation and performance information, to the extent that it is known, will be included for each method. At a minimum, a method developed by consolidating procedures will contain single-laboratory performance information. If the methods are not used as written, it will be necessary to demonstrate that data obtained from a subsequent adaptation will produce data comparable to that obtained when using recommended or other documented or approved methods. Such a practice increases the quality of data intercomparability across the DOE complex. Adoption of a performance-based approach will allow flexibility in how recommended methods are applied by DOE and DOE contractor labs to meet DOE needs.

CONCLUSION

DOE Methods contains guidance and sampling and analysis methods to address DOE's characterization needs for EM programs. It fills a gap currently not addressed by EPA guidance, thus aiding DOE in implementing cost-effective strategies for the monitoring, cleanup, and management of wastes and environmental contamination unique to the DOE complex. Supporting DOE Methods is a database configured so that any user from across the DOE complex can access it and review a particular method, or order a hard copy of a method. The DMCP provides the vehicle for DOE and DOE contractors to submit procedures to be considered for inclusion in DOE Methods. DOE Methods is expected to become a standard reference for guidance for the conduct of contaminant characterization at DOE sites.

REFERENCES

1 EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), 3rd Edition, 9/86

2 Pacific Northwest Laboratory Waste Management and Environmental Compliance, PNL-MA-8

3 Pacific Northwest Laboratory Radiation Protection, PNL-MA-6

4 Pacific Northwest Laboratory Health and Safety Management, PNL-MA-43

5 Measurement Quality Assurance for Radioassay ANSI Standard N42.2, Laboratories, 1/91.

DOE METHODS COMPENDIUM PROGRAM ORGANIZATION

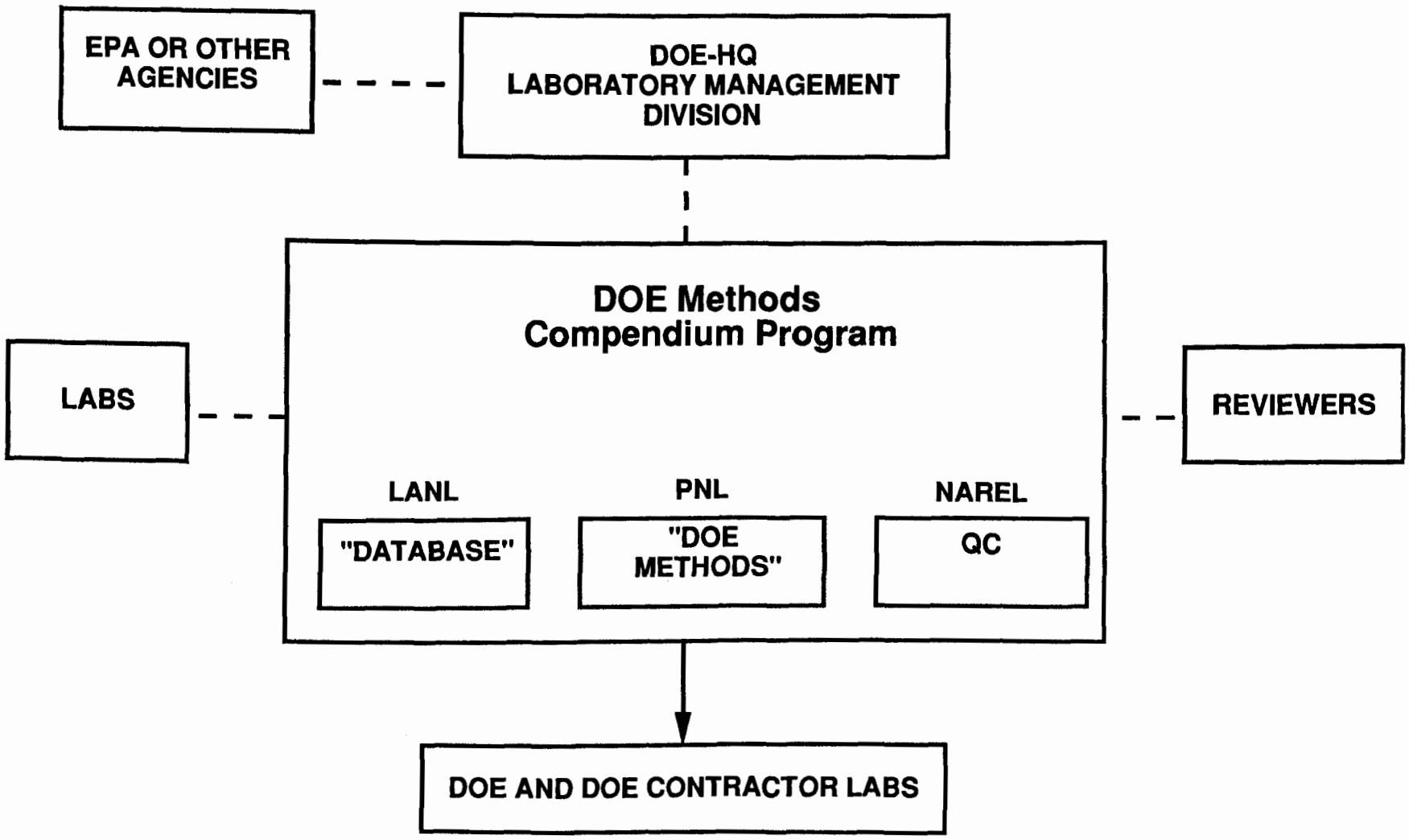


FIGURE 1

DOE METHODS COMPENDIUM PROGRAM LABORATORY NETWORK

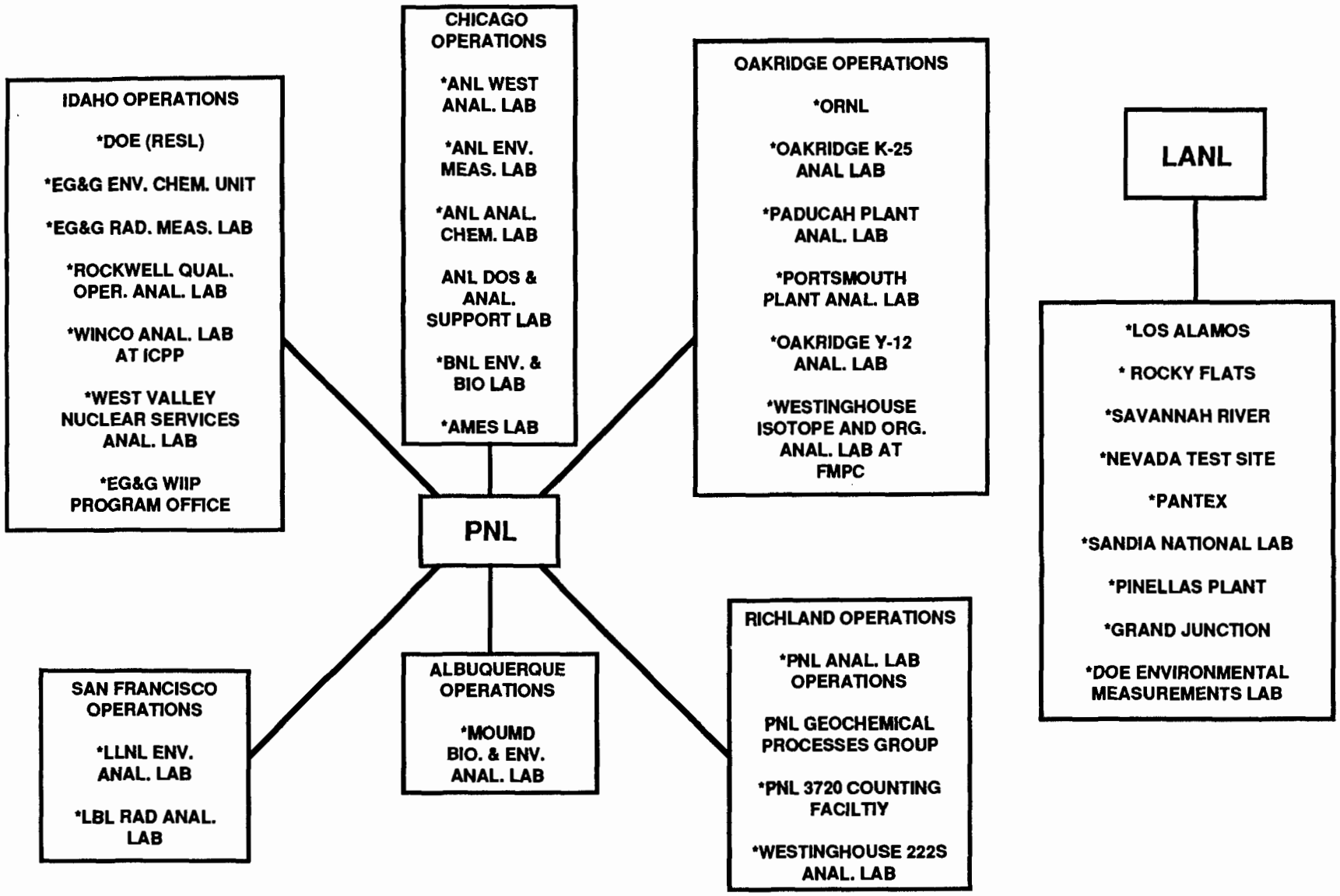


FIGURE 2

DATABASE AND METHODS COMPENDIUM DYNAMICS

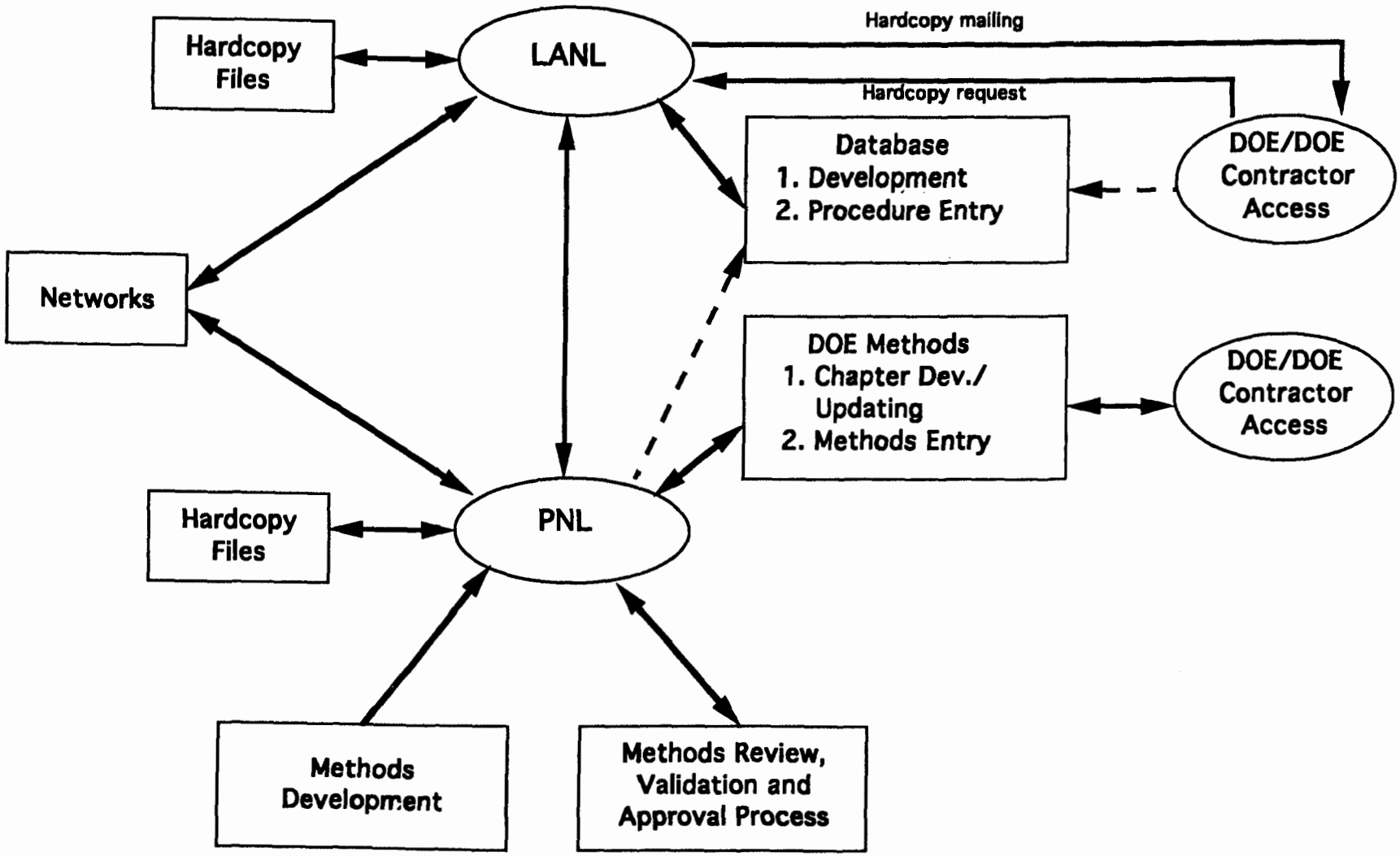


FIGURE 3

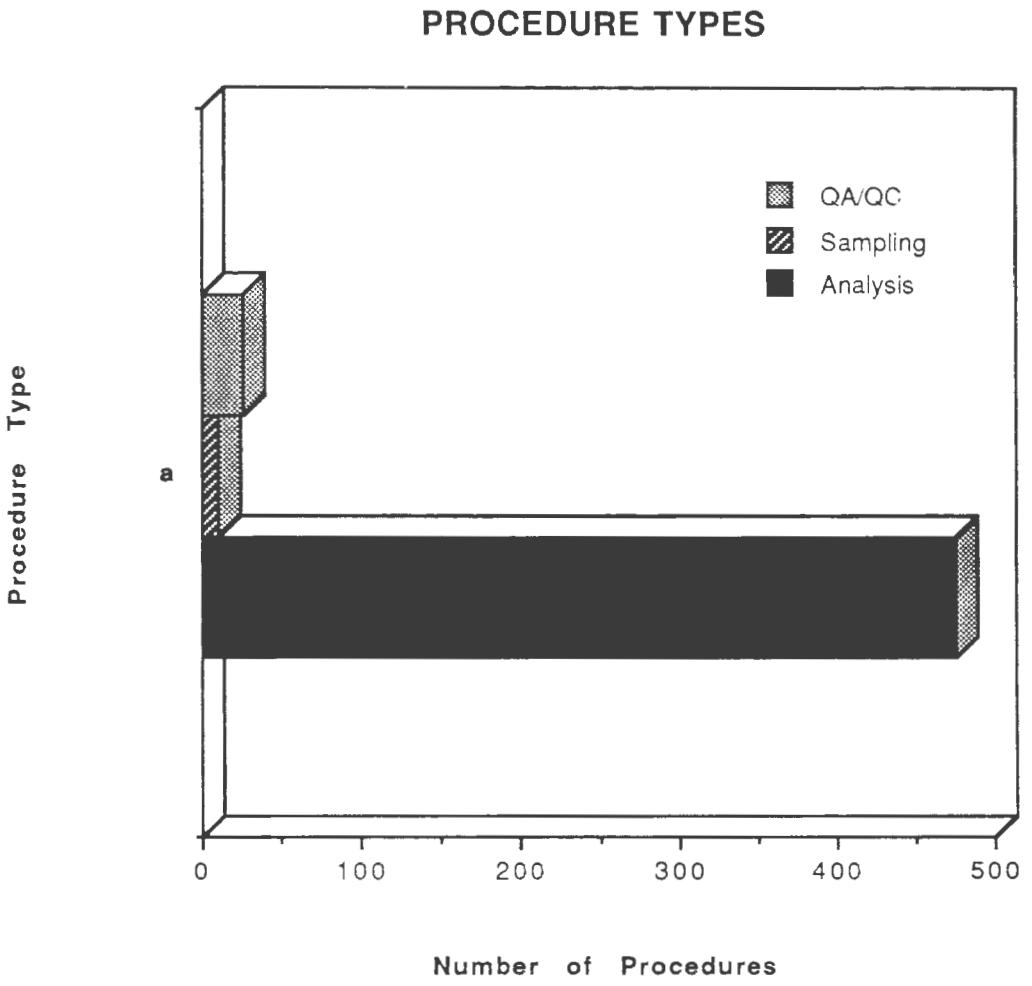

PROCEDURE TYPES
QA/QC
Sampling
Analysis
Procedure Type
a
0
100
200
300
400
500
Number of Procedures

FIGURE 4a

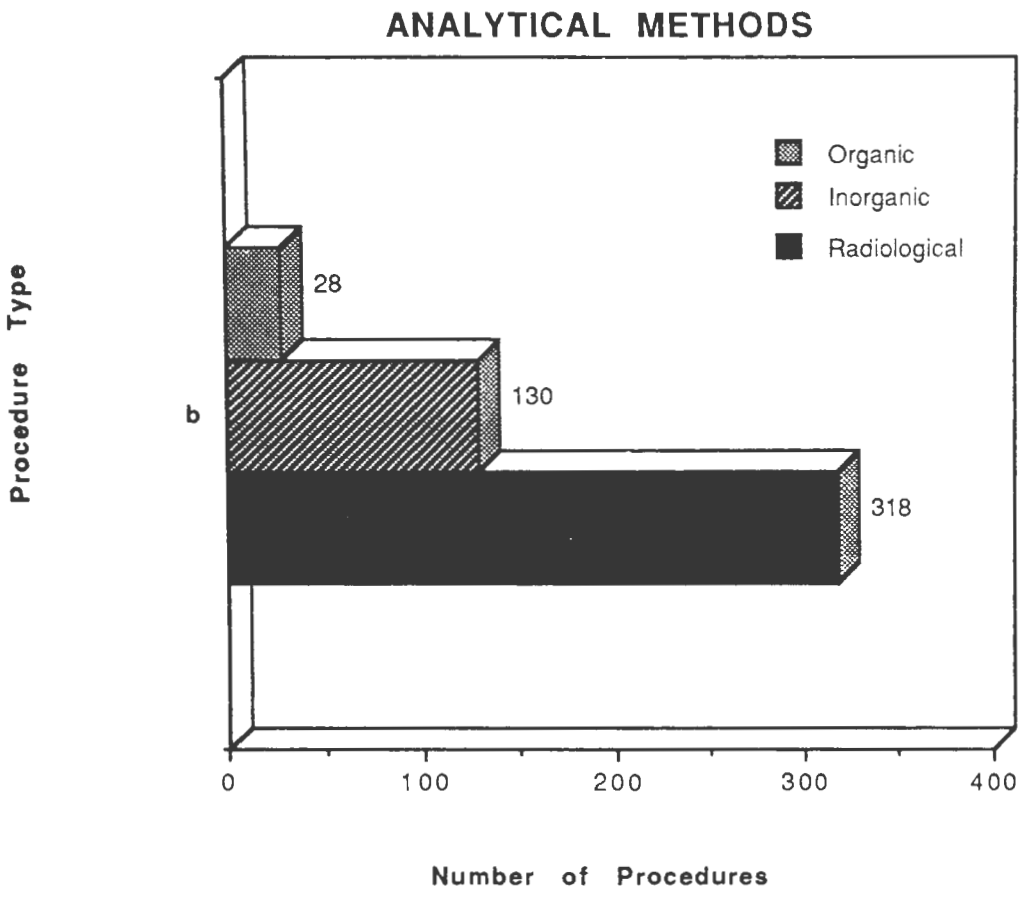

ANALYTICAL METHODS
Organic
Inorganic
Radiological
28
130
318
b
Procedure Type
0
100
200
300
400
Number of Procedures

FIGURE 4b

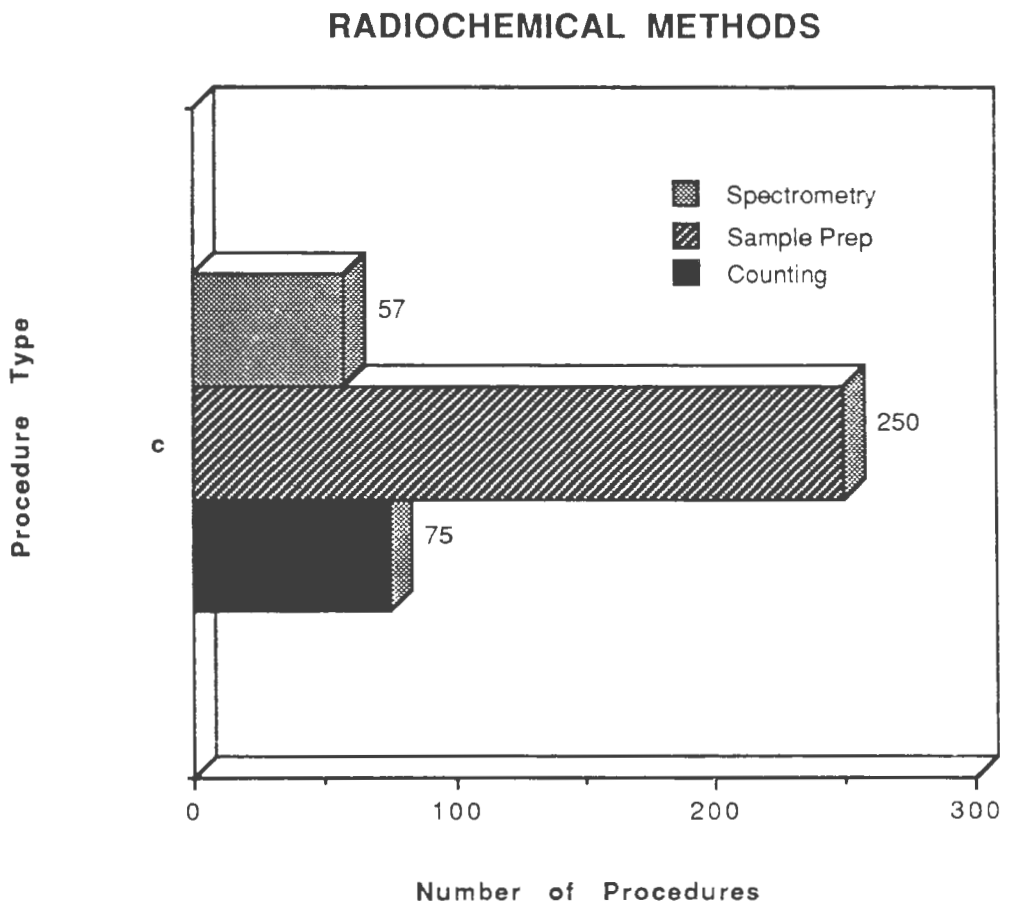

RADIOCHEMICAL METHODS
Spectrometry
Sample Prep
Counting
57
250
75
c
Procedure Type
0
100
200
300
Number of Procedures

FIGURE 4c

MOST COMMON RADIOCHEMISTRY ANALYTES

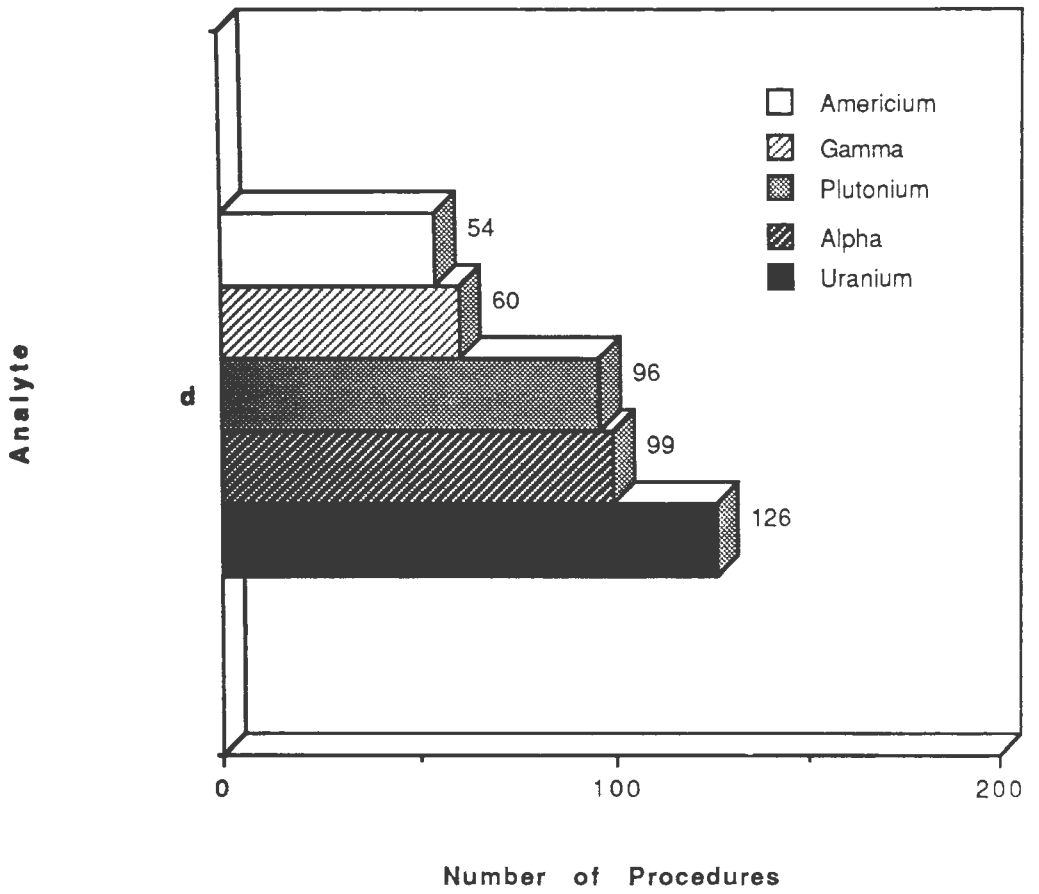


FIGURE 4d

VALIDATION LEVELS FOR PROCEDURES INCORPORATED INTO THE DATABASE

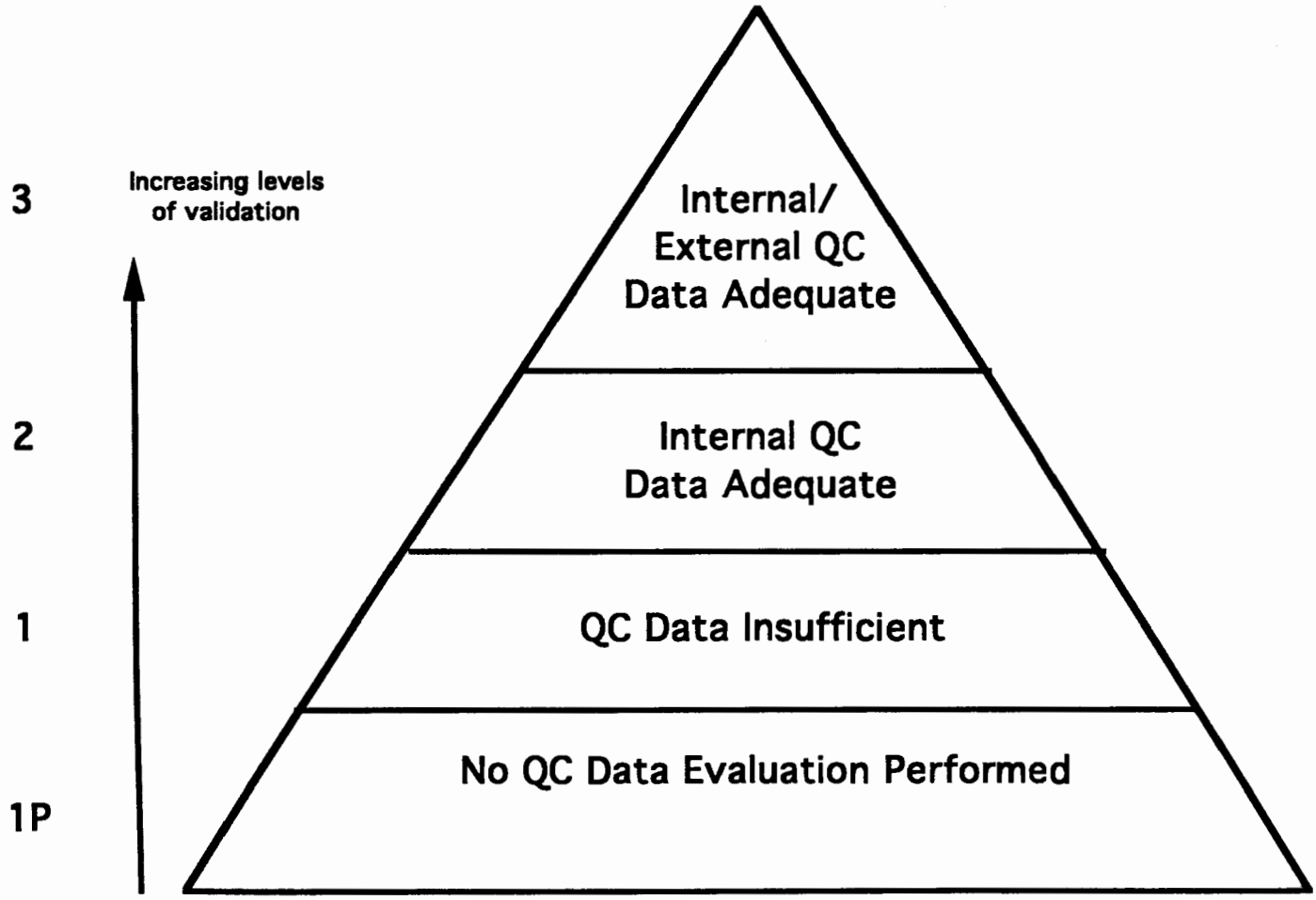


FIGURE 5

TABLE OF CONTENTS

DOE Methods for Evaluating
Environmental and Waste Management Samples

TABLE OF CONTENTS

ABSTRACT

PREFACE

INTRODUCTION

ACKNOWLEDGMENT

Chapter One QUALITY ASSURANCE

Chapter Two QUALITY CONTROL
Scope and Application
Definitions
Program Design
Quality Control Criteria
Data Reporting
QC Samples Submitted by Outside Organizations
References

Chapter Three SAFETY
Scope and Application
Radiation Protection
Dose Equivalent Limits, Controls, Policies, and Records
Hazardous Chemical Storage and Handling
References

Chapter Four WASTE HANDLING
Waste Minimization
Disposal Requirements
References

Chapter Five SAMPLING AND ANALYSIS PLAN
Scope and Application
General Considerations
Safety
Quality Control
Summary of Methods
Data Reporting
References

Chapter Six HOW TO CHOOSE METHODS
Purpose
Sampling Methods

FIGURE 6a

Analytical Methods
Radiological Screening
References

Chapter Seven SAMPLING METHODS
Scope and Application
General Considerations
Safety
Quality Control
Summary of Methods
Data Reporting
References

Chapter Eight ORGANIC ANALYTES
Scope and Application
Definitions
General Considerations
Safety
Quality Control
Summary of Methods
Sampling Considerations
Data Reporting
References
Method OG015R: Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography (DAI-GC)
Method PV030R: Purge-and-Trap
Method PE550R: Ultrasonic Extraction
Method PE541: Automated Soxhlet Extraction
Method OM260R: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique

Chapter Nine INORGANIC ANALYTES
Scope and Application
General Considerations
Safety
Quality Control
Summary of Methods
Sampling Considerations
Data Reporting
References
Method PM100R: Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes using TOPO

Chapter Ten RADIOCHEMISTRY METHODS
Scope and Application
General Consdierations
Safety
Quality Control
Summary of Methods
Sampling Consideations
Data Reporting
References

TABLE OF CONTENTS - 2

FIGURE 6b

Chapter Eleven MISCELLANEOUS METHODS
Scope and Application
Summary of Methods
General Considerations
Sampling Considerations
Safety
Quality Control
Definition of Terms
Data Reporting
References

APPENDIX A METHOD SELECTION AND VALIDATION
Method Selection Process
Method Validation Process
Method Approval Scheme
Process

APPENDIX B DEFINITION OF TERMS

TABLE OF CONTENTS - 3

FIGURE 6c

DOE METHODS NUMBERING SYSTEM

S	Sampling
SAxxx	Air Sampling
SWxxx	Water Sampling
SSxxx	Soil Sampling
SDxxx	Drum Sampling
O	Organics
OPxxx	Organic Sample Prep
OGxxx	GC Methods
OHxxx	HPLC Methods
OMxxx	GC-MS Methods
OIxxx	GC-IR or IR Methods
OSxxx	Screening
OVxxx	UV-Vis Methods
OXxxx	Organic Halides/Total Halides
M	Inorganics
MPxxx	Inorganic Sample Prep
MAxxx	AAA Methods
MCxxx	Ion Chromatography
MIxxx	ICP Methods
MMxxx	ICP-MS Methods
MSxxx	Screening
R	Radionuclides
RPxxx	Radionuclide Sample Prep
RGxxx	Energy Analysis (GEA)
RAxxx	Alpha Energy Analysis (AEA)
RLxxx	Liquid Scintillation Counting (LSC)
RSxxx	Screening--Alpha, Beta, Gamma
X	Miscellaneous Analytes and Tests
XBxxx	Biological (COD, etc.)
XOxxx	Nonspecific Organics, (TOC, Phenolics)
XPxxx	Properties (Corrosivity, Ignitability)
XHxxx	pH

FIGURE 7

13 ANALYSIS OF PCB'S BY ENZYME IMMUNOASSAY

Robert O. Harrison, ImmunoSystems, Inc., Scarborough, Maine
Robert E. Carlson, Ecochem Research, Inc., Chaska, Minnesota

ABSTRACT

A competitive inhibition Enzyme ImmunoAssay (EIA) has been developed for the determination of PolyChlorinated Biphenyls (PCB's). The test is capable of analyzing for PCB's in the field in 15 minutes from a prepared sample, using no specialized equipment. Validation data have been generated for soils using a rapid extraction procedure which can be done in the field with an inexpensive extraction device (drying of the soil is not required before analysis). Applications currently under development for other matrices include water, transformer oil, sediment, and surface wipes. The test specificity is restricted to PCB's, with high sensitivity for Aroclor's 1016, 1242, 1248, 1254, and 1260. Matrix and solvent interferences are minimal. The sensitivity and flexibility of the test allow analysis of PCB's with a wide variety of sample preparation methods. Sensitivity in the matrix of interest depends on the matrix and sample preparation method. The present rapid extraction and EIA, commercially available in kit form, is suitable for PCB screening of soils in many field and laboratory situations.

INTRODUCTION AND METHODS

Reagent Development

The assay development process followed the general procedure described previously by Harrison et al. (1988) and Jung et al. (1989). The development of the EIA for PCB's followed these steps: 1) PCB derivatives were synthesized for conjugation to proteins; 2) one of these PCB derivatives was conjugated to a carrier protein and the resulting conjugate was used to immunize animals, which then produced antibodies recognizing both the PCB derivative and PCB's; 3) a PCB derivative was conjugated to horseradish peroxidase (HRP) to make a conjugate which can be captured by anti-PCB antibodies; 4) the PCB-HRP conjugate was used to screen and select antibodies; 5) the selected system was optimized for sensitivity and matrix tolerance and characterized for specificity; 6) sample preparation methods were developed for specific sample types; 7) these methods were validated using field samples.

PCB EIA Procedure

Figure 1 schematically illustrates the procedure used for the analysis of samples containing PCB's. In summary: 1) rabbit antibodies which recognize the PCB structure are immobilized on the walls of plastic test tubes; 2) samples or calibrators are added to tubes with Assay Diluent, allowing PCB's to be captured by the immobilized antibodies (*incubation 1*). PCB's are specifically retained on the solid phase by the anti-PCB antibody when the rest of the sample is washed away; 3) PCB-enzyme conjugate is added to tubes and is bound by the anti-PCB antibody in the same manner as in step 2 (*incubation 2*). The unbound conjugate is washed away and the amount retained by the immobilized antibody is

inversely proportional to the amount of PCB bound in step 2; 4) enzyme substrate and chromogen are added to the tubes or wells for color development by the bound enzyme (*incubation 3*). The intensity of color is proportional to the amount of captured enzyme and is inversely proportional to the amount of PCB bound in step 2. Therefore, ***more color means less PCB.***

Field Soil Extraction

Soil samples were extracted for analysis by the following procedure using a simple extraction kit available with the EIA kit. Soil extraction consists of the following steps: 1) Weigh soil on the available pocket balance and place in extraction container. 2) Extract soil by adding an equal amount (w/v; e.g. 5 g soil + 5 mL) of methanol, and shaking vigorously for two minutes. Filter extract and collect using the filtration device contained in the soil extraction kit. 3) Analyze extract as described in step 2 of the EIA Procedure above, using a 1:100 dilution of extract.

Other Sample Types

Aroclor 1248 spiked into tap water was analyzed by extracting 500 mL water samples with a glass barrel solid phase extraction device containing C18 silica. Columns were conditioned with hexane followed by isopropanol and reagent water, then the sample was applied to the solid phase extraction device using Teflon tubing. After air drying, the extracted PCB was eluted with isopropanol, and the eluate was used directly in the assay by dilution into Assay Diluent.

The EIA kit has also been used for surface wipe tests. Standard surface sampling methods were employed, except for substitution of isopropanol for hexane for wiping. Additional isopropanol was used to extract the gauze wipe and this extract was used directly in the assay by dilution into Assay Diluent. Sediment analysis is currently under investigation using methods similar to the soil procedure described above.

RESULTS AND DISCUSSION

Matrix and Solvent Tolerance

The primary requirement for sample preparation for the PCB EIA is that the solvent used to introduce the sample into the test must be miscible with water. The test offers excellent resistance to the effects of blank soil extracts made with both DMSO and methanol. The test tolerates several solvents, including methanol, isopropanol, and DMSO, up to 20%, with no loss of sensitivity. Thus, adequate flexibility exists for the use of a variety of solvents and protocols in the development of new applications for different sample matrices.

Test Specificity and Sensitivity

The crossreactivity of the test for five commonly detected Aroclors was examined. Standard solutions of 200 ppm in methanol (Supelco) were used to make serial dilutions in methanol, which were tested in the EIA as described above. Table 1 shows the broad specificity of the EIA for the most common Aroclors.

Table 1. Crossreactivity of the EIA test for five Aroclors commonly found in soil. Values given are the stock concentrations required (when diluted 1:100 in sample diluent) to give 50% reduction in OD compared to the negative control (50%B_O).

Aroclor	1016	1242	1248	1254	1260
ppm of Aroclor stock giving 50%B_O	3.4	4.1	3.4	2.0	4.6

Based on the data of Table 1, using the specified 1:100 extract dilution, a soil extract concentration of 5 ppm of any of the Aroclors would give a test response of greater than 50% inhibition. Combining these crossreactivity data (least crossreactive Aroclor within twofold of 1248) and the standard curve of Figure 2 (detection of 0.2 ppm of 1248), yields a test sensitivity for any of the five Aroclors of 0.5 ppm or better. Specificity was also tested for selected congeners in the same manner as for the Aroclor's of Table 1. The congeners most strongly recognized were 2,2',5,5' tetrachlorobiphenyl, 2,3',4,4',5 pentachlorobiphenyl, and 2,2',4,4',5,5', hexachlorobiphenyl, showing that the Aroclor specificity reflects the congener specificity. Biphenyl and several chlorinated single ring compounds were also tested for crossreactivity in the EIA. All of the following compounds demonstrated less than 0.5% crossreactivity compared to Aroclor 1248: 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 3,3'-dichlorobenzidine, biphenyl, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. These results mean that *more than* 200 ppm of any of these compounds would be required to give the same test response as 1 ppm of Aroclor 1248. Also, *more than* 10,000 ppm of any of these compounds would be required to give the same test response as 50 ppm of Aroclor 1248.

Method Repeatability

Calibrator solutions of Aroclor 1248 in methanol were diluted 1:100 into Assay Diluent for EIA analysis as shown in Figure 1. The test was performed as described above over two weeks using three reagent lots. Figure 2 shows the means and standard deviations at four calibrator concentrations. Similar results were obtained over 5 months with calibrators in DMSO, using several calibrator preparations from two different sources. For the DMSO calibrators, pooled intraassay precision at 0, 7, and 45 ppm was 7.5% for 12 assays by two operators with two reagent lots. Interassay precision of determination of a control sample of approximately 20 ppm Aroclor 1248 in DMSO was 20% for 46 assays by two operators with two reagent lots. In another precision study, four field soil samples were extensively homogenized and analyzed using a methanol soil extraction and methanol calibrators. Extraction and analysis were performed by three analysts at three sites over 9 days using 3 reagent lots. Overall coefficients of variation averaged 33%, while interassay precision within lot and within site was as low as 16%.

Sensitivity for PCB's in Soils

Interference from soil extracts was tested using 12 clean PCB-free soils. Extracts using either methanol or DMSO showed minimal interference, equivalent to less than 1 ppm for DMSO and less than 0.5 ppm for methanol. As described in the previous section, all of the 5 Aroclors of Table 1 can be detected in DMSO or methanol at 0.5 ppm, using the 1:100

dilution into Assay Diluent described above. Thus, 0.5 ppm of any of the 5 Aroclors of Table 1 would be detected in a DMSO or methanol soil extract. The actual minimum detection level (MDL) for PCB in soil depends more on the variability of the soil and the variability and efficiency of the extraction than on the sensitivity of the EIA to PCB or soil interferences in the EIA.

Recovery of PCB Spikes from Soils

Aroclor 1248 standards in hexane were spiked onto 2 g aliquots of six different PCB-free soils at 20 and 100 µg/g. Extractions were performed one day to one week later according to the protocol described above. The mean recovery was 84% at 20 ppm and 95% at 100 ppm. Similar results were observed for 2 selected soils spiked at 50 ppm and analyzed after 5-8 months storage at 22° C.

Correlation of GC and EIA Results for Soil analysis

Comparisons were made between the PCB EIA with field extraction and GC-ECD, using both methods to analyze split field samples from a wide variety of sites. One study involving three outside groups gave the data shown in Figure 3 over the range from 0.1 ppm to 10,000 ppm. Similar data have been obtained for similar soils using methanol extraction. One example data set is shown in Figure 4 for samples containing more than 0.5 ppm Aroclor 1260 by GC.

Other Sample Types

Using the water method described above, the sensitivity of the test for Aroclor 1248 in clean water was estimated at 25 ng/L, based on analysis of solid phase extraction device blanks. Recoveries of Aroclor 1248 at this level were nearly quantitative. The utility of this method for environmental water samples containing high particle loads is still being evaluated. Evaluation of surface wipe tests and sediment methods are continuing.

CONCLUSIONS

The test is capable of analyzing for PCB's in soil in the field in approximately 20 minutes, using no specialized equipment. The test specificity is restricted to PCB's, with Aroclor's 1016, 1242, 1248, 1254, and 1260 recognized best. Congener specificity of the test reflects the Aroclor specificity. The sensitivity of the test for PCB in soil is better than 3 ppm, but varies with different soil type and Aroclor. Further work in this area will include improved soil analysis, oil analysis, surface wipe tests, sediment analysis, biological sample analysis, and field testing and validation for the above applications.

ACKNOWLEDGEMENT

The initial phase of development of this PCB immunoassay was partially supported by the US EPA through a sub-contract to ECOCHEM from Mid-Pacific Environmental Laboratories, Inc.

REFERENCES

1. Harrison, R.O.; Gee, S.J.; Hammock, B.D. "Immunochemical Methods of Pesticide Residue Analysis" Chapter 24 in *Biotechnology in Crop Protection: ACS Symposium Series Vol. 379*; Hedin, P.A., Menn, J.J., Hollingworth, R.M., eds., American Chemical Society: Washington, DC, **1988**.

2. Jung, F.; Gee, S.J.;, Harrison, R.O.; Goodrow, M.H.; Karu, A.E.; Braun, A.L.; Li, Q.X.; Hammock, B.D. "Use of Immunochemical Techniques for the Analysis of Pesticides". *Pesticide Science* **1989**, *26*, 303-317.

Figure 1. Schematic illustration of the Enzyme Immunoassay for PCB's. All three incubations are 5 minutes. Both washes are done with tap water. In summary: 1) rabbit antibodies which recognize the PCB structure are immobilized on the walls of plastic test tubes; 2) samples or calibrators are added to tubes with Assay Diluent, allowing PCB's to be captured by the immobilized antibodies (*incubation 1*). PCB's are specifically retained by the antibodies on the solid phase when the rest of the sample is washed away (*wash 1*); 3) PCB-enzyme conjugate is added to tubes and bound in the same manner as in step 2 (*incubation 2*). The unbound conjugate is washed away and the amount retained by the immobilized antibody is inversely proportional to the amount of PCB bound in step 2 (*wash 2*); 4) enzyme substrate and chromogen are added to the tubes or wells for color development by the bound enzyme (*incubation 3*). The intensity of color is proportional to the amount of captured enzyme and is inversely proportional to the amount of PCB bound in step 2. Therefore, ***more color means less PCB***.

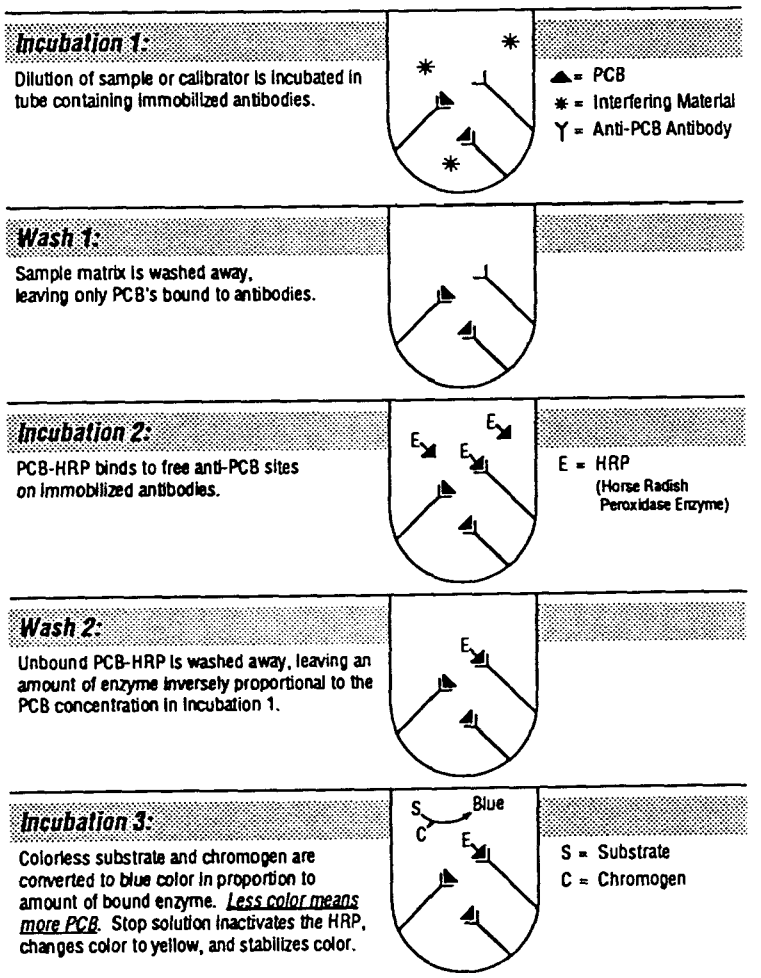


Figure 2. Mean Standard Curve of Aroclor 1248. The x axis values are concentrations of the standards which were diluted 1:100 in *incubation 1* as shown in Figure 1. These values equate directly to the concentrations in Table 1. These results are from a precision study which used 3 reagent lots to perform 27 assays over 9 days. Values for mean and SD are expressed as $\%B_O$ ((OD of standard/OD of negative control)x100), which is the color intensity of the standard as a percent of the color intensity of the negative control.

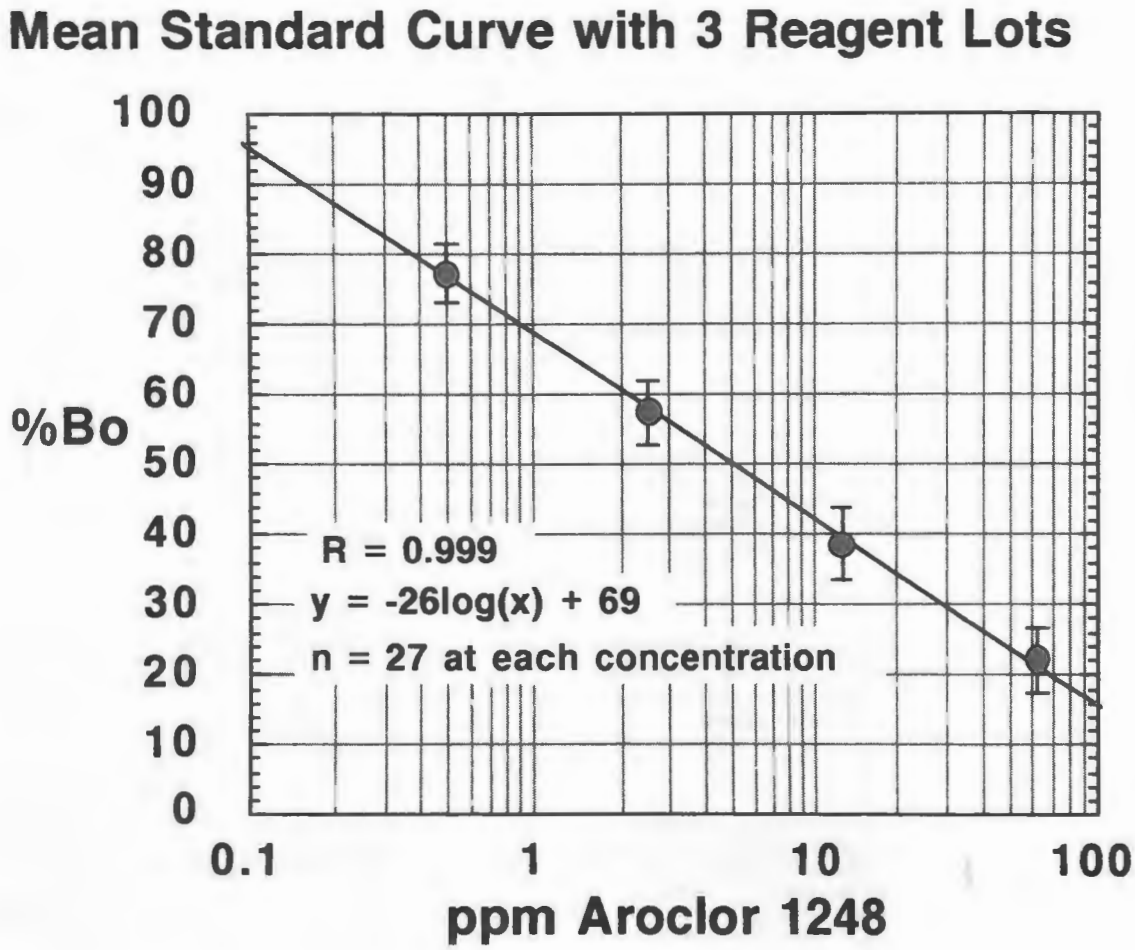


Figure 3. Correlation of GC and EIA Results for Soil Analysis. Results for analyses at three sites using multiple reagent lots over more than 3 months. Soils were analyzed as described in the materials and methods section except for the use of DMSO for extraction and standards, rather than methanol. Values over 50 ppm were determined by analysis of diluted extracts. Twelve additional samples were analyzed but not plotted because one or both of their results was expressed as a range only, e.g. <3 ppm or >50 ppm. Three of these samples were greater than 50 ppm by both methods, while nine were less than 3 ppm by both methods.

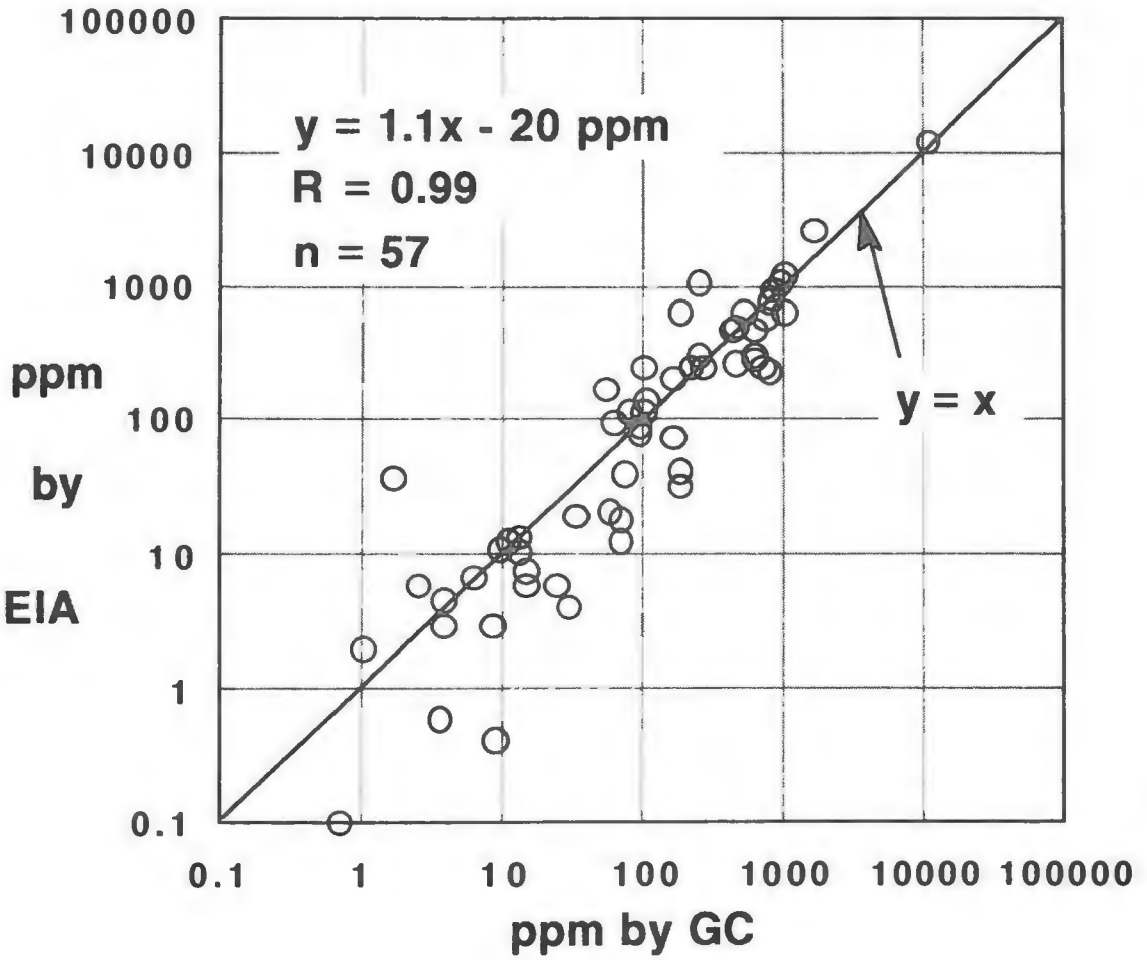
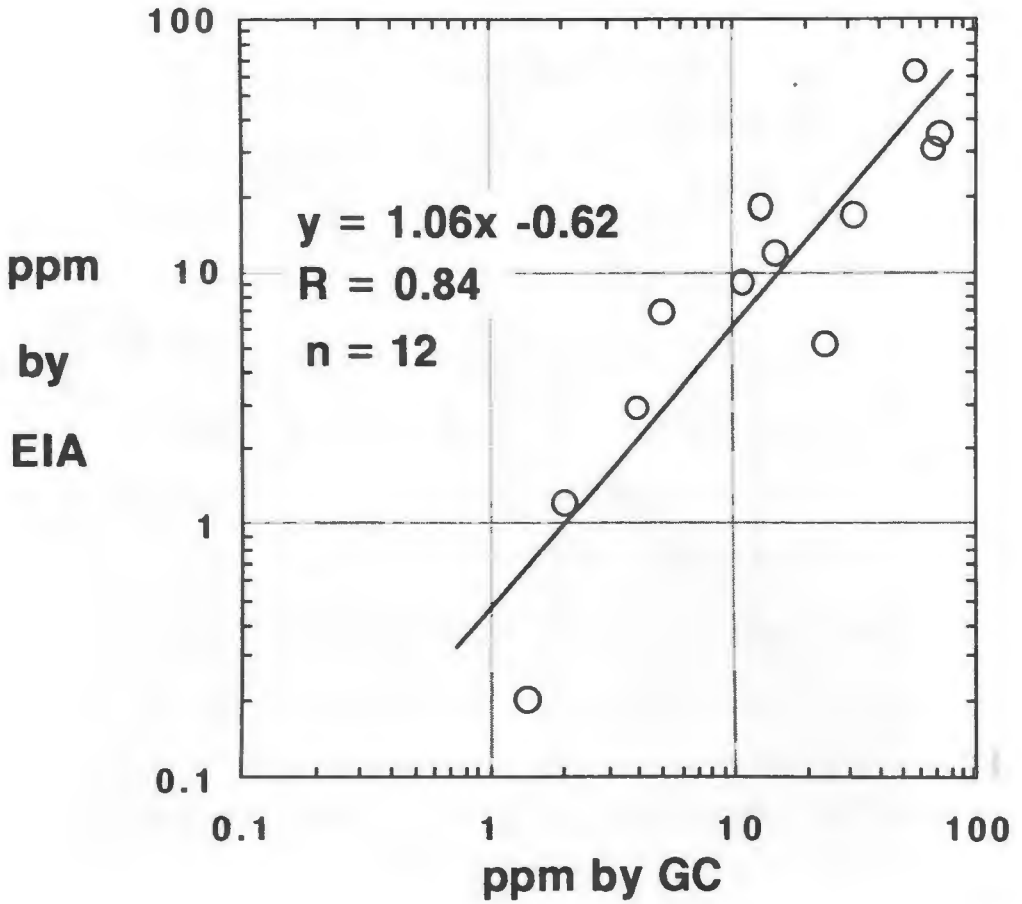


Figure 4. Correlation of GC and EIA Results for Soil Analysis. Twelve soil samples giving results between 0.5 and 100 ppm of Aroclor 1260 by GC were analyzed by EIA as described in the materials and methods section, using methanol for extraction and standards. These results indicate similar performance to Figure 3.



14 QUANTIFICATION OF 2,4-D AND RELATED CHLOROPHENOXYACETIC ACID HERBICIDES BY A MAGNETIC PARTICLE-BASED SOLID-PHASE ELISA.

Timothy S. Lawruk, Charles S. Hottenstein, David P. Herzog, Fernando M. Rubio, Ohmicron Corporation, 375 Pheasant Run, Newtown, PA 18940; James R. Fleeker, North Dakota State University, Biochemistry Dept., P.O. Box 5516, Fargo, ND 58105; J. Christopher Hall, University of Guelph, Dept. of Environmental Biology, Ontario, Canada N1G 2W1.

ABSTRACT

The intense pressure for increased pesticide residue testing in food, water and soil, together with the expense and delays associated with currently available testing methods, has focused attention on immunochemical methods which are sensitive, reliable, simple, cost-effective and at the same time provide more rapid results. Some of these desired features can be met with immunoassays formats currently available.

The performance characteristics of a magnetic particle-based solid-phase enzyme-linked immunosorbent assay (ELISA) requiring no sample preparation for the quantification of 2,4-D and related chlorophenoxy acid herbicides in groundwater samples are discussed.

INTRODUCTION

Pesticide testing in water, food and soil has increased dramatically over the past several years due to concerns over the potential contamination of wells and streams from spills, spraying and pesticide run-off. 2,4-D, a member of the chlorophenoxy acid class of compounds (CPHs), is a selective systematic herbicide commonly used for the post-emergence control of annual and perennial broadleaved weeds in cereals, maize, sorghum, grasslands, established turf grass, seed crops, orchards (specifically pome fruit and stone fruit), cranberries, asparagus, sugarcane, rice, forestry, and non-crop land including areas adjacent to water allowing the control of broad leaved aquatic weeds. 2,4-D is classified by the EPA as a category III contaminant with a maximum contaminant level of 70 ppb in water (USEPA, 1991). The Practical Quantiation Level for 2,4-D is 5 ppb (USEPA, 1991). 2,4-D has been shown to damage liver, kidneys and the nervous system of lab animals when exposed to large amounts. The National Cancer Institute has conducted studies showing that dogs in contact with 2,4-D are twice as likely to develop non-Hodgkins lymphoma and suggests that 2,4-D may be a human health hazard.

The principles of enzyme linked immunosorbent assay (ELISA) have been described (Hammock and Mumma, 1980) and applied to the detection of 2,4-D in water (Fleeker, 1987; Hall et al, 1989). Magnetic particle-based ELISA's have previously been described and applied to the detection of pesticide residues (Rubio et al, 1991; Itak et al, 1992; Lawruk et al, 1992). These ELISA's eliminate the imprecision problems of coated plates and tubes (Harrison et al, 1989) through the covalent coupling of antibody to the magnetic solid-phase. The uniform dispersion of particles throughout the reaction mixture allows for rapid reaction kinetics and precise addition of antibody.

MATERIALS AND METHODS

Amine terminated superparamagnetic particles of approximately 1 um diameter were obtained from Advanced Magnetics, Inc. (Cambridge, MA). Glutaraldehyde (Sigma Chemical, St. Louis, MO). Rabbit anti-2,4-D serum (Ohmicron, Newtown, PA). 2,4-D-HRP conjugate (available from Ohmicron, Newtown, PA). Hydrogen peroxide and TMB (Kirkegaard & Perry Labs, Gaithersburg, MD). 2,4-D and related compounds as well as non-related cross-reactants (Riedel-de-Haen, Hanover, GER).

The anti-2,4-D coupled magnetic particles were prepared by glutaraldehyde activation (Weston and Avrameas, 1971). The unbound glutaraldehyde was removed from the particles by magnetic separation and washing four times with 2-(N-morpholino)ethane sulfonic acid (MES) buffer. The 2,4-D antiserum was incubated overnight with agitation at room temperature with the activated particles. The unreacted glutaraldehyde was quenched with glycine buffer and the covalently coupled anti-2,4-D particles were washed and diluted with a Tris-saline/BSA preserved buffer.

Water samples (250 uL) and horseradish peroxidase (HRP) labeled 2,4-D (250 uL) are incubated for 30 minutes with the antibody coupled solid-phase (500 uL), (step 1). A magnetic field is applied to the magnetic solid-phase to wash and remove unbound 2,4-D-HRP and eliminate any potential interfering substances, (step 2). The enzyme substrate (hydrogen peroxide) and chromogen (3,3',5,5'- tetramethylbenzidine [TMB]) are then added and incubated for 20 minutes, (step 3). The reaction is stopped with the addition of acid and the final colored product is analyzed using the RPA-I™ Photometric Analyzer by determining the absorbance at 450 nm. The observed sample results were compared to a linear regression line using a log-linear standard curve prepared from calibrators containing 0, 1.0, 10.0, and 50.0 ppb of 2,4-D. If the assay is performed in the field (on-site), a battery powered photometer such as the RPA-III™ is used.

RESULTS AND DISCUSSION

Figure 1 illustrates the mean standard curve for the 2,4-D calibrators, collected over 55 runs, error bars represent 1 SD. The displacement at the 1.0 ppb level is significant (87% B/Bo, where B/Bo is the absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard). The assay sensitivity based on 90% B/Bo (Midgley et al, 1969) is 0.7 ppb.

A precision study in which surface and groundwater samples were spiked with 2,4-D at 3 concentrations, and each assayed 5 times in singlicate per assay on five different days is shown in Table 1. Coefficients of variation (%CV) within and between day (Bookbinder and Panosian, 1986) were less than 10% and 12% respectively.

Table 1

Pool #	1	2	3
Replicates	5	5	5
Days	5	5	5
N	25	25	25
Mean ppb	4.16	19.55	36.06
% CV Intra	9.5	8.7	7.7
% CV Inter	11.5	11.1	11.3

Correlation of 33 groundwater water samples with values obtained by the present ELISA method (y) and an established gas chromatography/mass spectronomy (x) method is illustrated in Figure 2. The regression analysis yields a correlation of 0.963 and a slope of 0.928 between methods.

Table 2 summarizes the accuracy of the 2,4-D ELISA. Added amounts of 2,4-D were recovered correctly in all cases with an average assay recovery of 103%.

Table 2

2,4-D added (ppb)	Mean (ppb)	SD (ppb)	% Recovery
5.0	4.64	0.44	93
15.0	16.81	1.47	112
30.0	32.96	3.32	110
40.0	39.36	3.21	98
Average			103

Values obtained from 3 groundwater samples diluted in the Diluent/Zero showed agreement between measured and expected values (Table 3).

Table 3

Sample	Observed 2,4-D ppb	Expected 2,4-D ppb	% Linearity
Sample 1	41.82	-	-
1:2	22.42	20.91	107
1:4	10.76	10.46	103
1:8	4.48	5.22	86
Sample 2	41.89	-	-
1:2	23.57	20.95	112
1:4	10.76	10.47	106
1:8	5.25	5.24	100
Sample 3	30.43	-	-
1:2	17.23	15.22	113
1:4	7.96	7.61	104
1:8	4.21	3.80	111
Average			105

Table 4, summarizes the cross-reactivity data using a variety of chlorophenoxy acid analogues. The percent cross-reactivity was determined as the amount of analogue required to achieve 90% B/Bo (Least Detectable Dose). Many non-structurally related agricultural compounds demonstrated no reactivity at concentrations up to 10,000 ppb.

Table 4

Compound	90% B/Bo LDD (ppb)	50% B/Bo LDD (ppb)	% Cross reactivity
2,4-D	0.50	15.0	100
2,4-D Propylene Glycol Ester	0.05	0.79	1962
2,4-D Ethyl Ester	0.05	0.82	1885
2,4-D Isopropyl Ester	0.07	1.44	1076
2,4-D Methyl Ester	0.12	1.64	945
2,4-D Butyl Ester	0.19	2.40	646
2,4-D Sec-Butyl Ester	0.13	2.20	705
2,4-D Butoxyethyl Ester	0.13	3.10	500
2,4,5-T Methyl			

Ester	0.98	18.1	106
2,4-D Butoxy-propylene Ester	1.21	31.1	50
2,4-D Isooctyl Ester	2.08	30.0	52
2,4,5-T	2.98	190	8.2
2,4-DB	3.95	139	11.2
MCPA	7.8	159	10.0
Silvex Methyl Ester	12.4	1000	1.9
MCPB	56.8	1470	1.1
4-Chlorophenoxy-acetic acid	61.1	1220	1.3
Dichlorprop	117	7500	0.2
Silvex (2,4,5-TP)	167	2060	0.8
Dichlorophenol	217	3570	0.4
Triclopyr	830	NR	<0.1
MCPP	1160	NR	<0.1
Pentachlorophenol	NR	NR	<0.1
Picloram	NR	NR	<0.1

Table 5 summarizes that no interferences are present up to the tested levels of various common water components. The concentrations of the compounds chosen are those that would most likely exceed levels found in groundwater samples (American Public Health Association, 1989).

Table 5

Compound	Max. Conc. tested	Interfered
Nitrate	250 ppm	No
Copper	250 ppm	No
Nickel	100 ppm	No
Thiosulfate	250 ppm	No
Sulfite	250 ppm	No
Sulfide	250 ppm	No
Sulfate	10,000 ppm	No
Iron	250 ppm	No
Magnesium	250 ppm	No
Calcium	250 ppm	No
NaCl	1.0 M	No
Humic acid	50 ppm	No
Silicates	1,000 ppm	No

Summary

This ELISA demonstrates both the feasibility of using magnetic particles as a solid-phase in an immunoassay for the detection of pesticide residues, and its performance characteristics in the quantitation of 2,4-D in groundwater samples. The assay compares favorably to GC/MS determinations and exhibits excellent precision and accuracy

which guarantees consistent monitoring of environmental samples. The assay sensitivity of 0.7 ppb (90% B/Bo) in water exceeds the EPA Maximum Contaminent Level of 70 ppb and the Practical Quantitation Level of 5 ppb. The antibody employed allows for the detection of 2,4-D and related chlorophenoxy acids in the presence of other pesticides and commonly found groundwater components. This ELISA is ideally suited for the adaptation to on-site monitoring of 2,4-D in water, providing results in less than 60 minutes.

References

American Public Health Association (1989) Standard Methods for Examination of Water and Wastewater. American Public Health Association, Washington DC.

Bookbinder, M.J., Panosian, K.J., (1986) Correct and incorrect estimation of within-day and between-day variation, Clin. Chem., 32:1734-1737.

Fleeker, J. (1987) Two enzyme immunoassays to screen for 2,4-Dichlorophenoxyacetic acid in water, J. Assoc. Anal. Chem., 70:874-878.

Hall, J.C., Deschamps, R.J.A., Krieg, K.K. (1989) Immunoassays for the detection of 2,4-D and picloram in river water and urine, J. Agric. Food Chem., 37:981-984.

Hammock, B.D., Mumma, R.O. (1980) Potential of immunochemical technology for pesticide analysis. In Pesticide Identification at the Residue Level, ACS Symposium Series, Vol. 136 (Harvey, I. & Zweig, G., Eds.) American Chemical Society, Washington, DC, pp. 321-352.

Harrison, R.O., Braun, A.L., Gee, S.J., O'Brien, D.J., Hammock, B.D. (1989) Evaluation of an enzyme-linked immunosorbent assay (ELISA) for the direct analysis of molinate (Odram®) in rice field water, Food & Agricultural Immunology, 1:37-51.

Itak, J.A., Selisker, M.Y., Herzog, D.P. (1992) Development and evaluation of a magnetic particle based enzyme immunoassay for aldicarb, aldicarb sulfone and aldicarb sulfoxide, Chemosphere, 24:11-21.

Lawruk, T.S., Hottenstein, C.S., Herzog, D.P., Rubio, F.M. (1992) Quantification of alachlor in water by a novel magnetic particle-based ELISA, Bull. Enviro. Contam. Toxicol. Vol. 48:643-650.

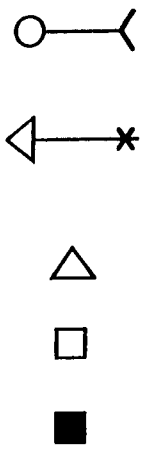
Midgley, A.R., Niswender, G.D., Rebar, R.W. (1969) Principles for the assessment of reliability of radioimmunoassay methods (precision, accuracy, sensitivity, specificity), Acta Endocrinologica, 63:163-179.

Rubio, F.M., Itak, J.A., Scutellaro, A.M., Selisker, M.Y., Herzog, D.P. (1991) Performance characteristics of a novel magnetic particle-based enzyme-linked immunosorbent assay for the quantitative analysis of atrazine and related triazines in water samples, Food & Agricultural Immunology, 3:113-125.

USEPA, National Primary Drinking Water Regulations; Final Rule, Federal Register, 40 CFR parts 141-143, Vol. 56, No. 20, January 30, 1991.

Weston, P.D., Avrameas, S. (1971) Proteins coupled to polyacrylamide beads using glutaraldehyde, Biochem. Biophys. Res. Commun., 45:1574-1580.

Magnetic Particle Immunoassay



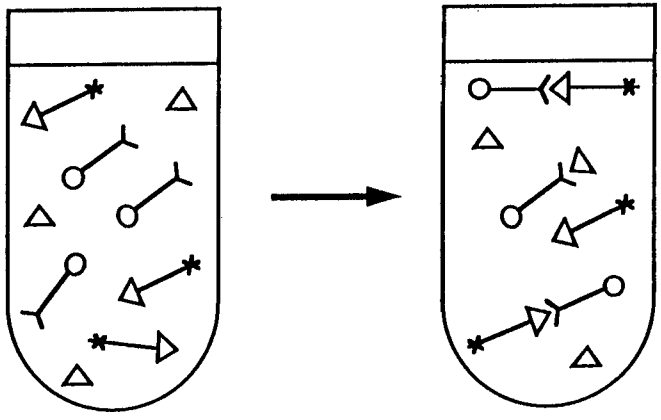
Magnetic Particle with Antibody Attached

Pesticide Conjugated with Enzyme

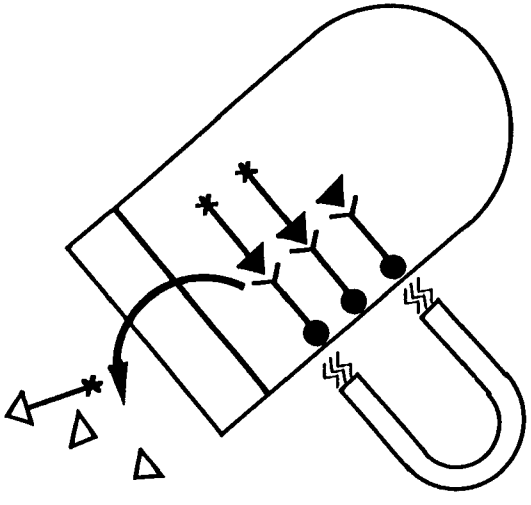
Pesticide

Chromogen/Substrate

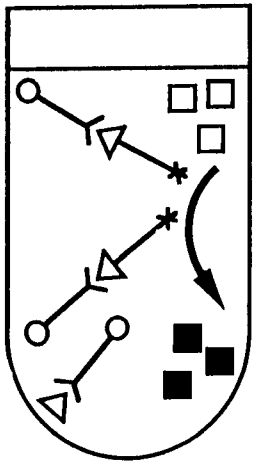
Colored Product



1. Immunological Reaction



2. Separation



3. Color Development

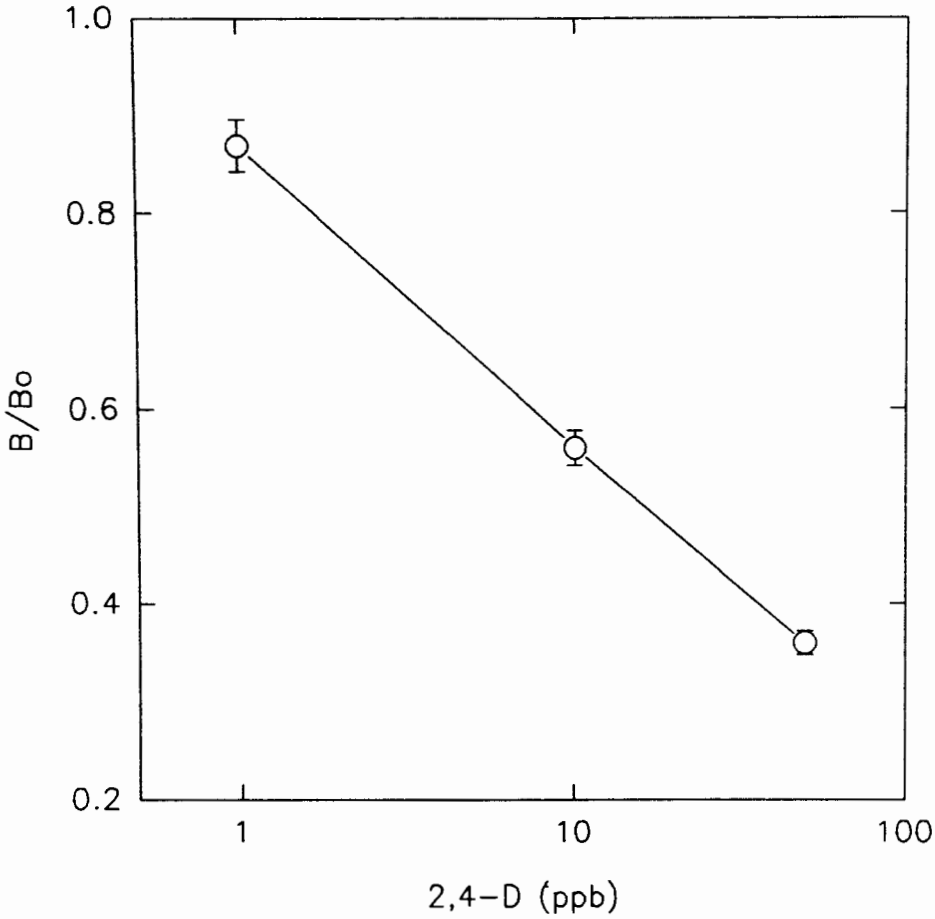


Figure 1. Dose response curve for 2,4-D. Each point represents the mean of 55 determinations. Vertical bars indicate +/- 1 SD about the mean.

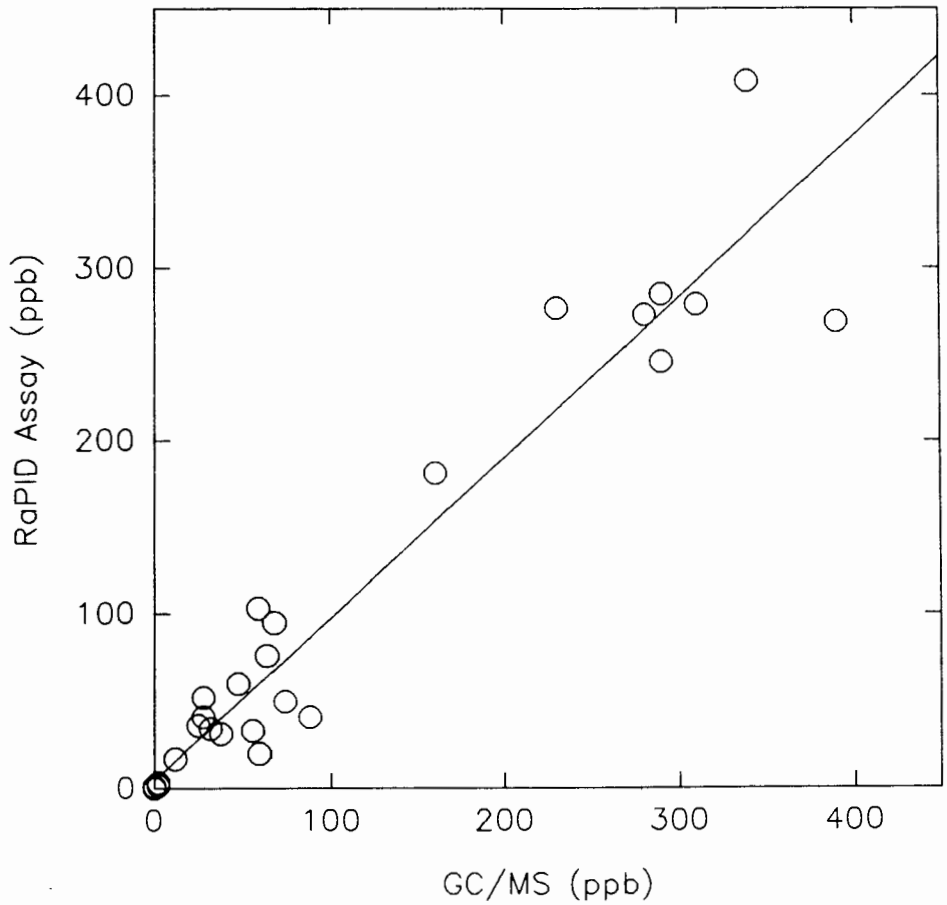


Figure 2. Correlation between 2,4-D concentrations as determined by ELISA and GC methods. n = 33, r = 0.970, y = 0.938x + 2.21.

QUALITY ASSURANCE

15

AUTOMATING ANALYTICAL QUALITY CONTROL ON A LOCAL AREA NETWORK BASED LIMS SYSTEM

Richard D. Beaty, Ph.D., Director Product Development, and Mary R. Schoen, Software Engineer, Telecation Inc., 19423 N. Turkey Creek, Suite C, Morrison, Colorado, 80465. (303) 697-8080

ABSTRACT

Quality control is a calculation and data management intensive operation of an analytical laboratory. Analytical quality control involves some procedures which are standard, accepted practice, and others which may be specific to an individual laboratory addressing a special application. In addition to their own in-house procedures, a given laboratory may have to comply with a number of QC protocols simultaneously, including those defined for "Good Laboratory Practice" (GLP) and special government regulatory programs with their own QC procedures.

An important contribution of a LIMS system is to increase the overall efficiency and integrity of the laboratory's QC program, by automating the data management and statistical functions which accompany quality control. The procedures used for analytical quality control can generally be grouped into two categories: 1) those involving treatment of actual analytical unknowns and observing the response of the treated samples; and 2) the inclusion of additional samples within an analytical run for purely quality control purposes. Both types involve the generation of QC data and appropriate statistical calculations, which provide a measure of the "goodness" of the data as determined by the QC calculation. Typically, sample results will be flagged according to rules defined for the QC measurements which accompany the sample analysis.

One of the most frequently used and statistically cumbersome QC procedures is the maintenance of x-bar or "Shewhart" charts. A Shewhart chart involves mean and standard deviation calculations on historical data to determine "warning" and "control" limits, within which subsequent determinations of the control sample are

---

Informix & SmartWare are registered trademarks of Informix Software, Inc.

expected to agree. This routine task involves not only the statistical calculations, but also the determination of a "rolling average" of the twenty most recent determinations. This paper discusses techniques for dynamically updating the LIMS data to be included in the most recent Shewhart chart and automatically flagging data which exceeds warning and control limits.

The total QC process involves assignment of the various QC procedures to analytical runs, calculation of QC statistics, flagging data which fails QC protocols, and maintaining historical QC trends. The ultimate goal of QC management with a LIMS is to totally automate this process. This paper will define an approach which not only achieves this goal for predefined, standardized protocols, but also allows the flexibility to deal with emerging techniques and unique QC applications.

INTRODUCTION

Quality control is a calculation and data management intensive operation of an analytical laboratory. Analytical quality control involves some procedures which are standard, accepted practice, and others which may be specific to an individual laboratory addressing a special application. In addition to their own in-house procedures, a given laboratory may have to comply with a number of QC protocols simultaneously, including those defined for "Good Laboratory Practice" (GLP) and special government regulatory programs with their own QC procedures.

An important contribution of a LIMS system is to increase the overall efficiency and integrity of its QC program by automating the data management and statistical functions which accompany quality control. The challenge a LIMS vendor faces, when attempting to automate these functions, is that not all laboratories conduct the same types of QC. Even for so-called "standard" techniques, different laboratories use variations in their approaches. In general, achieving the greatest amount of automation requires defining the functions to be automated, and then programming those functions. However, a commercial LIMS to be used by many laboratories must leave functionality open, in order to accommodate the varying QC procedures from laboratory to laboratory. This fact precludes "hard coding" all of the QC functions into the system. This paper will discuss one technique, which optimizes automation of "standard" QC procedures, while leaving the system open to user modification for specific procedures.

THE SYSTEM

Standard practice in LIMS design today calls for use of a commercial data base controlled by a fourth generation language. TELECATION has traditionally used Informix's "SmartWare" (R) system, which offers not only a powerful data base and fourth generation language, but also provides built-in integration and seamless transfer of data between the data base module and the spreadsheet and word processor modules. The same fourth generation programming language which controls the data base is used to generate turnkey applications involving other modules. The spreadsheet/graphing module is especially powerful for QC applications.

For this investigation, TELECATION used Informix's "SmartWare II" system, which offers the same degree of integration between data base and spreadsheet, but with dramatically expanded data base and programming capabilities. The LIMS functions were developed and tested on a local area network consisting of Novell 386 operating in an Ethernet environment. The file server consisted of an 80386 processor, with 4MB of RAM and a 300MB hard drive. The network workstations consisted of a variety of 80286 and 80386 machines, each with 4MB of memory.

STANDARD QC TECHNIQUES

The procedures used for analytical quality control can generally be grouped into two categories: 1) those involving treatment of actual analytical unknowns and observing the response of the treated samples; and 2) the inclusion of additional samples within an analytical run for purely quality control purposes. Both types involve the generation of QC data and appropriate statistical calculations which provide a measure of the "goodness" of the data, as determined by the QC calculation. Typically, sample results will be flagged according to rules defined for the QC measurements, which accompany the sample analysis.

Standard techniques involving the treatment of unknown samples include running sample duplicates (for determining the percent difference between the replicate runs), sample spikes (for determining percent recovery of the spiked analyte), and matrix spike duplicates (for determining the percent difference between two similarly spiked samples). In addition to defining the formulas for calculation of the QC parameters characteristic of each technique, analytical data which is outside

predefined limits of acceptability is typically flagged, to call attention to QC failure. Therefore, the conditions which initiate data flagging, as well as the flags, themselves, must somehow be programmed into the QC automation system.

Standard techniques involving the testing of incremental QC include the analysis of control samples. These controls may be monitored over many days for determination of long term precision. Alternately, the experimental results of the control sample may be compared to the "known", or certified value, as a measure of the accuracy of the determination.

Depending on the parameters being measured and the analytical techniques used for these measurements, a variety of QC measurements selected from the above types are included in each analytical run. For QC techniques involving treatment of actual samples, not every sample in the run is treated for QC measurements, as this would unduly burden the productivity of the laboratory. Instead, certain samples are selected as representative of all samples in the run, and the success or failure of the QC measured on the selected samples is extrapolated to indicate the validity of analytical results for all similar samples in the run. The significance of this fact to the automation of quality control, is that each sample measured in a single analytical run must somehow be linked to all other samples measured in the run, so that the results of quality control measurements, which validate the analytical results, can be tracked. The relational data base of SmartWare II makes this type of linkage possible.

DATA BASE STRUCTURE AND DESIGN

With the above considerations in mind, a LIMS data base was designed, which would not only provide all of the standard data storage and retrieval requirements of a LIMS, but would also optimize the mechanism for automating analytical quality control. For storing all of the basic information about samples and their analytical results, three data bases were defined. These data base files were named "Samples", "Tests", and "Parameters", signifying the basic information stored in each.

```
SAMPLES.DB - information specific to entire sample

        examples: sample ID
                  source
                  collect date/time
                  login date/time
                  storage location

TESTS.DB - information regarding test methods to be
           run on each sample

        examples: test ID
                  lab section
                  preparation method
                  analytical method
                  hold time
                  preparation date/time
                  analysis date/time

PARAMS.DB - detailed information on each parameter to
            be determined in a test.

        examples: parameter ID
                  results
                  check limits
                  detection limits
                  reportable significant figures
                  reportable decimals
```

FIGURE 1. Definition of sample-related data bases.

"Samples" is used to store information specific to an entire sample to be analyzed. "Tests" stores the name of each test to be run on the sample, along with critical information about that test. "Parameters" stores the name of each parameter to be determined in a test, along with the results of that determination and other critical parameter-specific details. Figure 1 illustrates the basic definition of these data bases.

Each "sample" record is uniquely identified by a "lab#" field. "Test" and "Parameter" records, which are a part of the sample, are linked to the "Sample" record through the "lab#" field. Additionally, each "parameter" record can be linked to the "test", in which it is determined, through a "test_id" field. This relationship is illustrated in Figure 2.

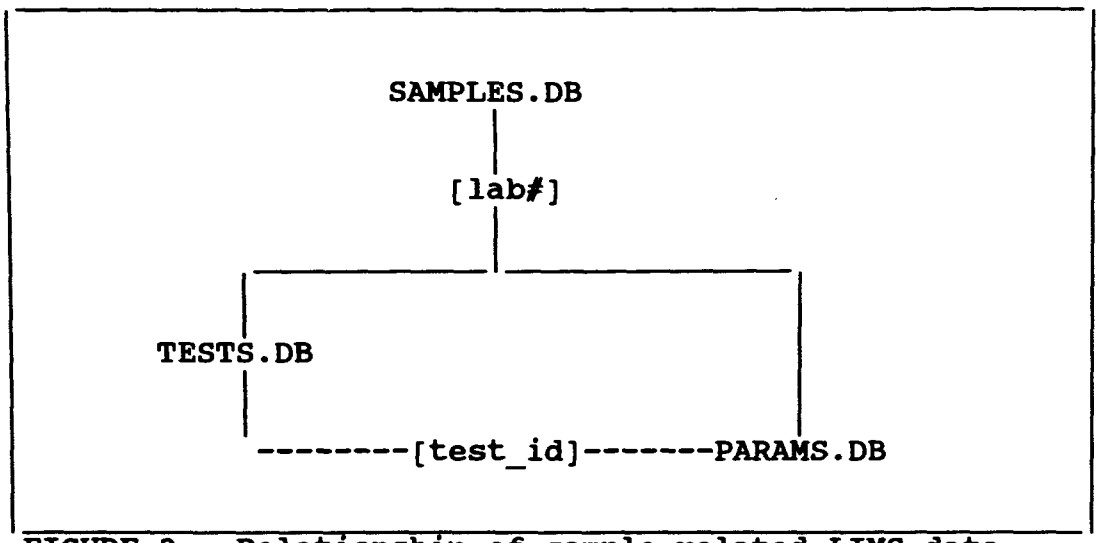


FIGURE 2. Relationship of sample-related LIMS data base files.

To provide for the needs of run-oriented data entry and quality control, two more data bases are defined. These include the "Runs" and "QC Parameters" data bases. Each record of the "runs" data base contains a "run#" field to uniquely identify a run, a "test_id" field to identify the test being run in the "run#", and other run status fields. The "QC Parameters" data base contains fields to store the results of standard QC measurements, and additional fields to control the calculation of each. The "QC Parameters" data base is structured to contain one record for every "parameter" subjected to a quality control measurement. Definition of the "runs" and "QC Parameters" data bases is illustrated in Figure 3.

The "parameter" records from unknown samples being determined in the "run" and the "QC Parameter" records determined in the "run" are linked together by a common "run#", as shown in Figure 4.

```
RUNS.DB - list of run#'s with run status information

        examples: run#
                  test_id
                  analyst name
                  analysis date
                  approval name
                  approval date

QCPARAMS.DB - results of QC measurements for each
              parameter

        examples: duplicate / %difference / flag
                  spike / %recovery / flag
                  spike dup / %difference / flag
                  blank
                  control / true value / %accuracy
                  warning & control flags
```

FIGURE 3. Definition of "Runs" and "QC Parameters" data bases.

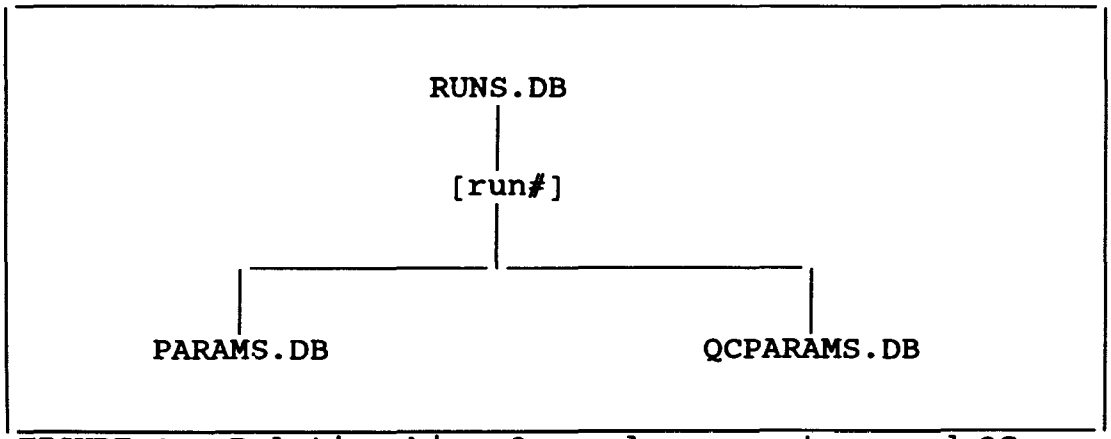


FIGURE 4. Relationship of sample parameters and QC parameters measured in common analytical run.

ASSIGNING QC MEASUREMENTS TO A RUN

The parameters on which QC measurements are to be made, as well as the QC to be performed on each parameter, will vary with the nature of the analytical procedure, or "test", being run. Therefore, a flexible mechanism is required to determine both which parameter records are added and what QC measurements are to be run for each.

Most QC procedures call for adding QC parameters according to one of two schemes. For those procedures involving the measurement of existing sample parameters (such as sample duplicates, spikes, etc.), it is usually desirable to select a representative sample or samples, and make appropriate QC measurements on the selected samples only, for every parameter being measured in the run. Alternately, many organic analyses call for the determination of "surrogates", or parameters which are normally absent in the original samples. Controlled amounts of these surrogate parameters are added to all samples, and their recovery measured. To accommodate the different schemes for QC parameter addition, an "Add-QC" menu provides the user with the option of assigning QC measurements to a run, according to the requirements of "Representative Samples" or "Surrogate Parameters". The differences are summarized in Figure 5. By simply making the menu choice, the program automatically adds the necessary parameter records to the QC parameters file.

ADD QC" MENU OPTIONS

REPRESENTATIVE-SAMPLES - for selected sample only, adds one parameter record to QC Parameters file for every unique parameter in run.

SURROGATE-PARAMETERS - for every sample in run, adds surrogate parameter records according to list defined for test in surrogate reference file.

FIGURE 5. Menu selectable routines for adding QC parameters to run.

For the "Representative Sample" option, a number of possible QC measurement techniques might apply. Yet, every technique may not be used in every case. To allow easy assignment of the desired QC to be measured on a selected sample, a simple "checkoff" menu of predefined QC procedures (Figure 6) is presented to the user who requests to "ADD QC" to a representative sample. Only those techniques checked will then be activated for the selected sample.

```
Check (x) QC to be assigned to LAB#: 92-20945

        DUPLICATE
            SPIKE x
        SPIKE_DUP x
            BLANK x
          CONTROL
```

FIGURE 6. Checkoff menu for user selection of QC assignments to representative sample.

DEFINING QC MEASUREMENTS AND CALCULATIONS

The heart of the automated QC system is the definition of the various QC measurements and the associated formulas which control the calculation of QC variables. The generation of QC flags, which alert the user to out of control conditions, must also be defined. To the LIMS vendor designing a LIMS for use across a wide variety of application areas, it is also critical to consider the necessity of user-modifiability, so that QC details can be configured for individual needs.

To provide both preconfigured automation of standard QC techniques and user flexibility for tailoring to specific needs, the details of all QC techniques are contained in the definition of the "QC Parameters" data base. A view of the "QC Parameters" data base for a selected parameter record is shown in Figure 7. In this view, the user may enter results for sample duplicate, spike, spike duplicate, blank, and control. Other fields in the view are either referenced directly through relationships to other files, or calculated from the entered values through predefined formulas. The sources of values for the "QC Parameters" fields are summarized in Figure 8.

QC PARAMETERS

PARAM_ID PB	PARAM_NAME		
QCLAB# QC00000104	DATE 05/14/1992	TEST_ID Inorganics	RUN 92050041
		Transferred to FINISHED	

DILUTION 1.000 VOLUME 1.0000 WEIGHT 1.0000 SOLIDS 100.00%

SAMPLE QC	LAB# 92-9002	CALC_RESULT 0.5020	UNITS ug/L	
Check to assign	xDUPLICATE 0.4640			DIFF% 7.87
	x SPIKE 1.3000	SPK_AMT 0.7500		RECOV% 106.40
	xSPIKE_DUP 1.2400			SPKDUP% 4.72

CONTROL QC	xBLANK 0.0080			
Check to assign	CONTLAB# 920501	HISTORY	TRUE_VALUE 5.0000	
	xCONTROL_RESULT 4.3300	SAVED	ACCURACY% 86.60	W

CONTROL HISTORY

QC_LAB#	QC_DATE	RESULT
QC0000000029	04/29/1992	4.6600
QC0000000032	04/30/1992	4.9200
QC0000000038	05/01/1992	5.2100
QC0000000043	05/02/1992	4.9500
QC0000000047	05/03/1992	5.6600
QC0000000056	05/04/1992	5.2200
QC0000000063	05/05/1992	4.8500
QC0000000085	05/06/1992	4.9600
QC0000000086	05/07/1992	5.1300
QC0000000091	05/08/1992	4.9200
QC0000000106	05/09/1992	4.8800
QC0000000109	05/10/1992	5.0600
QC0000000115	05/11/1992	5.7200
QC0000000119	05/12/1992	4.8900
QC0000000120	05/13/1992	5.1400
QC0000000131	05/14/1992	5.0800
QC0000000138	05/15/1992	4.9700

X-BAR RESULTS

TOTAL_CONTROLS	17	PROCESS_LAST	20
MEAN	5.0718	WARNING	0.5449
		CONTROL	0.8174

FIGURE 7. "QC Parameters" data base record. QC results are automatically calculated from predefined formulas.

SOURCE OF QC PARAMETERS FIELD INFORMATION
FOR AUTOMATION OF QC CALCULATIONS

QC Procedure	Field	Source
SAMPLE REFERENCE	LAB#	selected when ADD-QC
	CALC_RESULT	direct link to PARAMS
DUPLICATES	DUPLICATE	user entry
	DIFF%	calculated
	DUP_FLAG	calculated
SPIKES	SPIKE	user entry
	SPIKE_AMT	user entry
	RECOV%	calculated
	SPIKE_FLAG	calculated
SPIKE DUPLICATES	SPIKE_DUP	user entry
	SPKDUP%	calculated
	SPKDUP_FLAG	calculated
BLANKS	BLANK	user entry
CONTROL SAMPLES	CONTrol LAB#	user entry
	CONTROL_RESULT	user entry
	TRUE_VALUE	direct link to ref
	ACCURACY%	calculated file
	CONTROL_FLAG	calculated
LONG-TERM PREC. (X-BAR CHART)	CONTROL HISTORY	direct link to history
	MEAN	calculated
	WARNING window	calculated
	CONTROL window	calculated

FIGURE 8. Source of QC Parameters field information.

It should be noted that since all of the "intelligence" regarding the determination of QC results is built into the definition of the QC Parameters view, as opposed to being hard coded in the program, the system remains open to modification of formulas for existing QC measurements, or even addition of completely incremental QC techniques, which were not originally defined in the system. The system defined above is preconfigured, and therefore requires no user intervention to implement. However, the system may be easily modified and expanded, either by the vendor, or by the trained user.

DEFINITION OF "SHEWHART" CHARTS

The purpose of the "Shewhart," or x-bar chart, is to monitor long-term precision. This is done by recording the results of a control sample over a period of days or weeks, calculating the mean of the results over that period of time, and determining "warning" and "control" limits, defined as 2x and 3x the standard deviation of results, respectively. The x-bar chart is a particular challenge to automate fully, since it involves data, not all from the same run, but from many past runs. To further complicate the challenge, not all past results are included in the determination. The x-bar data is usually calculated only from the last 20 measurements of the control.

In spite of the difficulty of the challenge, a system which would automate the x-bar process and automatically flag controls exceeding warning or control limits would be immensely valuable to the QC manager, attempting to make decisions on the validity of current data. This has been achieved by linking the "QC Parameters" file to a "Control History" file, which contains past runs of the sample. The lower half of the "QC Parameters" record, illustrated in Figure 7, illustrates this link.

From Figure 7, it can be seen that all of the results from past determinations of the same parameter in the same control sample are automatically available. In addition, fields for the calculation of x-bar parameters (including the mean, warning, and control limits), are defined in a manner similar to other QC fields, discussed above. It should be noted that no manual entry is required, in order to exercise the automatic determination of warning and control flags. All values necessary for the process to occur are obtained, either by direct link to the necessary data file, or by automatic computation through predefined calculated fields.

The net result of the design concepts described above can be seen in Figure 9. Results for sample test parameters assigned to a run can be entered or reviewed in the "Sample Parameters" window. By simply selecting "QC-View" from the menu, the "QC Parameters" accompanying the run (lower half of Figure 9) are instantly shown. The percent difference of sample duplicates, percent recovery of spikes, percent difference of spike duplicates, and the value of the blank are tabulated for each parameter measured. The percent accuracy of laboratory controls is also shown. Finally, automatically computed flags ("*" in Figure 9) alert the

Enter RESULTS

TEST_ID VOA LAB_SECTION GC/MS RUN 92050045 STATUS
LAB# TUTOR-005 MATRIX WATER SAMPLE_ID Organic CLP Analyses
CLIENT_ID Jones CLIENT_NAME
COLLECT_DATE 05/12/1992 HOLD_DAYS 10 HOLD_DATE 05/22/1992

SAMPLE PARAMETERS

PARAM_ID	INITIAL	DIL	VOL	WT	SOL%	CALCULATED	REPORTED	F
111TCA	24	1	1	1	100.00	24.0000		24
1122PC	55	1	1	1	100.00	55.0000		55
112TCA	62	1	1	1	100.00	62.0000		62
11DCA	8	1	1	1	100.00	8.0000		10U
11DCE=	44	1	1	1	100.00	44.0000		44
12DCA	29	1	1	1	100.00	29.0000		29
12DCE=	4	1	1	1	100.00	4.0000		10U
12DCP	26	1	1	1	100.00	26.0000		26
2-HEXANONE	52	1	1	1	100.00	52.0000		52
2BUTANONE	12	1	1	1	100.00	12.0000		12
4M2P	35	1	1	1	100.00	35.0000		35
ACETONE	22	1	1	1	100.00	22.0000		22
BENZENE	59	1	1	1	100.00	59.0000		59

QC PARAMETERS

QCLAB#	LAB_#	PARAMID	DIFF%	DRECOV%	SSPKDUP%	MBLANK	ACCURACYC
QC00000107	TUTOR-005	CH3Cr		95.00	8.96	2.0000	
QC00000107	TUTOR-005	CH3Br		110.00	10.12	0.0000	
QC00000107	TUTOR-005	VNYLCL		118.00	9.21	5.0000	
QC00000107	TUTOR-005	C1ETHANE		90.00	6.54	4.0000	
QC00000107	TUTOR-005	CH2C12		120.00	6.27	6.0000	
QC00000107	TUTOR-005	ACETONE		93.50	6.93	0.0000	86.67C
QC00000107	TUTOR-005	CDSF		108.00	9.67	2.0000	
QC00000107	TUTOR-005	11DCE=		107.00	9.33	2.0000	
QC00000107	TUTOR-005	11DCA		91.00	7.33	0.0000	
QC00000107	TUTOR-005	12DCE=		41.00*	74.13*	0.0000	
QC00000107	TUTOR-005	CHC13		156.00*	12.12	4.0000	
QC00000107	TUTOR-005	12DCA		121.00*	10.53	2.0000	
QC00000107	TUTOR-005	2BUTANONE		112.00	4.12	0.0000	
QC00000107	TUTOR-005	111TCA		95.50	7.73	3.0000	
QC00000107	TUTOR-005	CC14		88.00	10.12	0.0000	115.79W
QC00000107	TUTOR-005	CHBrC1		185.00*	23.30*	5.0000	
QC00000107	TUTOR-005	12DCP		94.00	11.76	4.0000	
QC00000107	TUTOR-005	c13DCP		74.00*	15.79	0.0000	

FIGURE 9. The data entry and review screen allows simultaneous viewing of sample and QC parameters and QC flags, to alert reviewer to out of control results.

data reviewer to results which failed quality tests. The "W" and "C" flags in the last column, immediately identify control values which exceed "warning" and "control" limits, respectively, as determined by the automatic computation of x-bar information.

SUMMARY

The purpose of analytical quality control is to provide a quantitative tool to the data reviewer, and to assist that person in making critical decisions regarding the validity and acceptance of laboratory analyses. In order for this goal to be achieved, the necessary data must be easily and quickly accessed by the data reviewer at the time decisions on data acceptability are being made. The above described system meets this requirement.

Inasmuch as the QC programs of all laboratories do not follow a single, predefined standard, it is absolutely necessary that any commercial LIMS, addressing quality control automation, do so in a manner which leaves the system open for user-personalization of the details. The techniques described in this paper provide the necessary flexibility to meet this need.

Quality control is a time-consuming task in the operation of an analytical laboratory. Nothing can compensate for the time required to conduct QC analyses. However, the overhead in managing the data, making the calculations, and providing ready access to the results, can be expedited through a relational data base LIMS, that has been designed around the way a testing laboratory works. Quality control is one of the most tedious, detailed, and time-consuming functions of a laboratory. If the purpose of a LIMS is to increase laboratory efficiency, automation of analytical quality control is a critical part of the full-functioning LIMS system.

16

PERFORMANCE EVALUATION OF ANALYTICAL METHODS FOR RCRA REGULATORY PROGRAMS FOR THE PETROLEUM INDUSTRY

Gary Walters, Enseco Rocky Mountain Analytical Laboratory, 4955 Yarrow Street, Arvada, CO 80002; Allen Verstuyft, Ph.D., Chevron Research Corporation, 576 Standard Avenue, Richmond, CA 94802, Dianna Kocurek, Tischler / Kocurek, 116 East Main, Round Rock, Texas 78664

ABSTRACT. Monitoring is required by petroleum refineries to support a variety of RCRA program initiatives. An evaluation was performed to better define the data quality objectives (DQOs) for three specific regulations which impact the petroleum industry. Specifically, work was performed to evaluate the monitoring requirements associated with the Appendix IX Groundwater monitoring rule, the toxicity characteristic (TCLP) and the land disposal ban program. Subsequent work documented the performance of the SW-846 methods relative to the monitoring requirements for each of these three regulatory programs relative to petroleum industry needs. In many cases, the performance characteristics can be applied to samples of a similar matrix to aid in the design of cost effective programs for similar monitoring programs.

Once the DQOs were defined, laboratory work was performed to document the performance of the analytical methods for selected target analytes relative to four matrices of concern to the petroleum industry. Volatiles, semivolatiles, and metals of concern to the petroleum industry were evaluated. Analytes were selected from the Appendix IX list and the "Skinner" list or Refinery list, which is a subset of Appendix VIII constituents used for delisting refinery wastes, land treatment demonstrations, and site closures related to petroleum refinery RCRA programs. The four matrices were soil, treated waste, oily waste, and TCLP leachates. For semivolatiles, various sample preparation techniques (Method 3550 with 1:1 acetone:methylene chloride, a modified Method 3550 with methylene chloride only, EPA Handbook for the Analysis of Petroleum Refinery Residuals) and clean-up procedures (Method 3611 Alumina column cleanup and Method 3640 GPC column cleanup) were evaluated for the treated waste and oily waste matrices to determine the relative advantages and disadvantages of these various options. For each matrix a method detection limit (MDL) study based on 40 CFR 136, Appendix B was performed for all target analytes. These MDL values were evaluated by comparing the precision of each matrix to reagent water.

INTRODUCTION

Petroleum refineries must perform testing under RCRA to respond to various EPA initiatives. In some cases, the testing requirements are not well understood either by those who must use the data or by those who perform the analyses. This work was funded by the American Petroleum Institute to prepare a series of guidance documents. Currently, a document on evaluation of analytical methods for Appendix IX analysis [1] has been released and another document on the Toxicity Characteristic Leaching Procedure is in preparation. These documents contain a summary of the Practical Quantitation Limits (PQLs) plus analytical precision and

accuracy data present in SW-846 [2] and 40 CFR Part 136[3]. These criteria are all based on the analysis of water , and they are useful as Data Quality Objectives (DQOs) for the analysis of other matrices. However, they should be used with caution in the estimation of quantitation and uncertainty of data for matrices other than water.

The focus of this work was to develop baseline performance data for other Appendix IX analytes in matrices other than water: TCLP leachate, clean soil, treated refinery waste, and oily waste. The primary emphasis was on analytes of interest to the petroleum refinery industry. In addition, some alternate extraction and cleanup techniques were investigated for semivolatile analytes.

STUDY DESIGN

Method Performance

The four matrices studied were: 1) an oily waste (mixed separator sludge and slop oil emulsion), 2) a treated oily waste (the cake from a solvent extraction process), 3) a clean loamy soil, and 4) the TCLP leaching solution. Data for reagent water is also presented for comparison; however, this data was generated for a different study at different spiking levels. The studies consisted of seven replicates with compounds spiked at concentrations relative to the nature of the matrix as defined below. (1,4-Dioxane was spiked 20 times higher than the other volatile analytes in the first four matrices. In the reagent water matrix, 1,4-dioxane, acetone, and 2-butanone were spiked at higher levels-see Table 7.) The study analytes are listed in Table 1. The analytes were selected by the API Environmental Monitoring Task Force as representative analytes of concern to the petroleum industry.

Semivolatiles		Volatiles	
Oily Waste	25 ppm	Oily Waste	5 ppm
Treated Waste	5 ppm	Treated Waste	1.25 ppm
Clean Soil	1 ppm	Clean Soil	20 ppb
TCLP Leachate	100 ppb	TCLP Leachate	100 ppb
Reagent Water	5 ppb	Reagent Water	5 ppb

The spike levels for the metals varied based on the technique and the metal and are shown in Table 2. Three metals (antimony, arsenic and selenium) were evaluated by both Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP) and Graphite Furnace Atomic Absorption (GFAA) techniques.

The oily and treated waste samples contained background levels of some target organic compounds. All solid matrices contained background levels of the metals. Accordingly, an initial analysis of each sample was performed to determine background concentrations. These data were used to evaluate the spiking levels. The MDL was calculated as 3.14 times the standard deviations from the seven replicates, as described in 40 CFR 136 [3]. The results for each matrix were evaluated by a comparison of precision and accuracy.

TABLE 1. STUDY ANALYTES

Metals

Antimony
Arsenic
Chromium
Cobalt
Lead
Nickel
Selenium

Volatile Organics

Acetone
Benzene
2-Butanone
Carbon disulfide
1,2-Dibromoethane
1,4-Dioxane
Ethyl benzene
Methylene chloride
Styrene
Toluene
m-Xylene
o-Xylene
p-Xylene

Acenaphthene
Acenaphthylene
Anthracene
Benzenethiol
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Bis(2-ethylhexyl)phthalate
Chrysene
m-Cresol (3-methyl phenol)
o-Cresol (2-methyl phenol)
p-Cresol (4-methyl phenol)
Dibenz(a,h)anthracene
Dibenzofuran
7,12-Dimethylbenz(a)anthracene
2,4-Dimethylphenol
Fluoranthene
Fluorene
Indene
Indeno(1,2,3-cd)pyrene
3-Methylchloanthrene
1-Methylnaphthalene
2-Methylnaphthalene
Naphthalene
Phenanthrene
Phenol
Pyrene

TABLE 2. SPIKING LEVELS FOR METALS
Spike Concentration, ppm

ICP Metals	Reagent Water	TCLP Leachate	Soil	Treated Waste	Oily Waste
Antimony	0.05	0.5	50	50	50
Arsenic	0.05	0.5	50	50	50
Chromium	0.05	0.2	20	0*	0*
Cobalt	0.05	0.2	20	20	20
Lead	0.05	0.5	50	50	50
Nickel	0.05	0.5	50	50	50
Selenium	0.5	2.0	200	200	200
GFAA Metals					
Antimony	0.02	0.5	50	50	50
Arsenic	0.01	0.5	5	50	50
Selenium	0.02	0.2	2	2	2

* Not spiked due to high levels in sample

Evaluation Of Extraction And Cleanup Techniques For Semivolatile Organics

As a group, the analysis of semivolatile organics presents a significant analytical challenge. The group contains the largest number of analytes. The analytes include many analytes of concern to the petroleum industry (Polynuclear Aromatics-PNAs and phenols). Interferences present in many refinery samples (aliphatic hydrocarbons) can significantly impact the method performance, and the methods allow for various sample preparation and cleanup procedures. The method performance resulting from the use of these various analytical options has not been thoroughly evaluated. The work was therefore designed to evaluate some of these options. The evaluation focused on the extraction techniques for soil, treated waste and oily waste, plus cleanup techniques for the waste matrices.

Three approaches were evaluated for the extraction of the solid matrices. The first approach was a sonic probe extraction of a 30 gram sample aliquot using 1:1 methylene chloride:acetone as described in SW-846 Method 3550. The second approach was the same extraction with 100% methylene chloride. Method 3550 states that the first approach provides a "more rigorous extraction procedure." However, it is well documented that the acetone reacts with itself during the extraction process to form aldol condensation products. The reaction products are manifested as a series of early eluting interfering compounds. The third extraction approach was from the "Handbook for the Analysis of Petroleum Refinery Residuals and Waste"[4]. The procedure in this guidance manual is a simultaneous extraction/acid-base partition preparation which includes the sonication and phase separation of a sample with methylene chloride and aqueous sodium hydroxide for "base/neutral" compounds followed by extraction of the acidified aqueous layer for the "acid" compounds. Soxhlet extraction using SW-846 Method 3540 was not evaluated. Comparisons of soxhlet versus sonication extraction have been previously reported [5,6]. For the oily waste samples, only the 100% methylene chloride and the refinery Handbook extractions were evaluated. In each case, duplicate samples were analyzed from each alternate extraction technique. The "best" technique was selected; only the five remaining replicates from the "best" technique were analyzed and evaluated.

SW-846 contains two cleanup procedures which are relevant to the analysis of refinery wastes, Method 3640-Gel Permeation Cleanup and Method 3611-Alumina Column Cleanup and Separation of Petroleum Wastes. Method 3611 has been widely used to remove interferences from aliphatic hydrocarbons in oily wastes for the determination of a select list of semivolatile analytes. The application of this cleanup to a broader suite of analytes (e.g., Appendix IX) has not been studied. Method 3640 was developed in the CLP protocol to remove lipids and related materials. The technique is in widespread use in the CLP for a limited suite of analytes, and its use for Appendix VIII analytes has been discussed [7]. Its utility for samples containing aliphatic hydrocarbons has not been thoroughly evaluated. Furthermore, the improved reliability for using either cleanup as opposed to no cleanup has also not been studied.

The first part of the cleanup evaluation consisted of subjecting a standard solution containing the semivolatile analytes to both procedures. This work eliminated bias due to sample interferences or extraction efficiency. The second phase of the cleanup evaluation used data obtained from the treated and oily waste matrices. The evaluation of extraction techniques described previously and the generation of MDL data described earlier assumes the use of Method 3611 for the treated and oily waste matrices. The results from these analyses provide baseline overall method performance. The improvement resulting from the GPC cleanup and the impact of no cleanup was evaluated against this basic approach by analyzing split extracts. For each matrix, four of the extracts were analyzed by Method 8270 with no cleanup. Three extracts were subjected to the GPC cleanup before analysis.

RESULTS

Metals

Recovery and precision performance for ICP (Method 6010) and GFAA (Methods 7041, 7060, 7740) are summarized in Tables 3 and 4. Method 3050 was used for acid digestion of the solid samples. Average and standard deviation are based on seven samples (eight for reagent water). The overall standard deviation for all metals is the pooled standard deviation. As seen in both tables, antimony was recovered poorly or not at all in the solid matrices. This is noted in Method 7040, as there is currently not an approved digestion procedure for the analysis of antimony in solids. Antimony was evaluated in a USEPA study [8] of Method 3050; however, antimony was not recommended for analysis by Method 3050.

Aside from antimony, recoveries were generally in expected ranges. Recoveries higher than normal were seen with arsenic/ICP and GFAA in reagent water and oily waste, nickel and selenium/ICP in treated waste, and selenium/ICP in oily waste. Low recoveries were seen with arsenic/GFAA, lead, and selenium/GFAA in oily waste; and arsenic/GFAA and selenium/GFAA in clean soil. Chromium was not spiked in treated and oily wastes because of high background levels of this metal; therefore, recoveries could not be determined for these matrices.

There were a number of statistically significant difference in metal recoveries between matrices. In general, a difference of 10 percentage points between any of the recoveries shown in Tables 3 and 4 tested significant.

Standard deviations (within-analyte precisions) for the ICP metals ranged from 2% to 16%; GFAA performance was similar with a range of 3% to 21%. Pooled estimates across all metals except antimony and chromium are shown in the last column of each table. For the ICP metals included in these estimates - arsenic, cobalt, lead, nickel, and selenium - the range was 4-9% for the matrices with a difference greater than two percentage points between matrices being significant. The range for pooled estimates for arsenic and selenium by GFAA were similar, 4-11%, with two percentage points also considered significant.

Table 5 groups the metals analyzed by both methods (antimony, arsenic, and selenium) for comparison. In overall recovery, GFAA performed better with antimony and arsenic; ICP was better with selenium, but was spiked at much higher levels. ICP had recoveries greater than 100% for both arsenic and selenium. As noted above, ICP and GFAA had zero recovery with antimony in clean soil; ICP also had nearly zero recovery in treated and oily wastes. Although precision differences existed within individual matrices for these two methods, the pooled precision estimates indicate that overall performance was similar.

TABLE 3. COMPARISON OF METAL RECOVERIES BY ICP

	Metals Analyzed by ICP							All Metals Except Sb, Cr
	Antimony (Sb)	Arsenic (As)	Chromium (Cr)	Cobalt (Co)	Lead (Pb)	Nickel (Ni)	Selenium (Se)	
Reagent Water								
Average	89%	120%	96%	98%	93%	98%	103%	102%
Std. Deviation	(7%)	(12%)	(4%)	(2%)	(7%)	(3%)	(3%)	(7%)
TCLP Leachate								
Average	108%	108%	107%	97%	98%	100%	107%	102%
Std. Deviation	(3%)	(8%)	(4%)	(4%)	(5%)	(4%)	(6%)	(6%)
Clean Soil								
Average	0%	109%	109%	96%	98%	100%	111%	103%
Std. Deviation	NC	(4%)	(6%)	(3%)	(7%)	(2%)	(2%)	(4%)
Treated Waste								
Average	8%	113%	NA	110%	98%	126%	116%	113%
Std. Deviation	(16%)	(11%)	NA	(14%)	(6%)	(7%)	(6%)	(9%)
Oily Waste								
Average	5%	125%	NA	90%	58%	102%	118%	99%
Std. Deviation	(3%)	(7%)	NA	(4%)	(5%)	(5%)	(4%)	(5%)

NA = Not Applicable, Not spiked

TABLE 4. COMPARISON OF METAL RECOVERIES BY GFAA

	Metals Analyzed by GFAA			
	Antimony (Sb)	Arsenic (As)	Selenium(Se)	Average Excluding (Sb)
Reagent Water				
Average	105%	120%	86%	103%
Standard Deviation	(5%)	(8%)	(6%)	(7%)
TCLP Leachate				
Average	100%	98%	91%	94%
Standard Deviation	(4%)	(3%)	(5%)	(4%)
Clean Soil				
Average	0%	76%	61%	68%
Standard Deviation	NC	(5%)	(3%)	(4%)
Treated Waste				
Average	70%	93%	94%	94%
Standard Deviation	(21%)	(3%)	(16%)	(11%)
Oily Waste				
Average	59%	82%	54%	68%
Standard Deviation	(6%)	(3%)	(10%)	(7%)

TABLE 5. COMPARISON OF ICP AND GFAA PERFORMANCE

Matrix	Recovery +/- Standard Deviation(%)		
	Antimony	Arsenic	Selenium
Reagent Water			
GFAA	105% ± 5%	120% ± 8%	86% ± 6%
ICP	89% ± 7%	120% ± 12%	103% ± 3%
TCLP Leachate			
GFAA	100% ± 4%	98% ± 3%	91% ± 5%
ICP	108% ± 3%	108 %± 8%	107% ± 6%
Clean Soil			
GFAA	NC, 0%	76% ± 5%	61% ± 3%
ICP	NC, 0%	109% ± 4%	111% ± 2%
Treated Waste			
GFAA	70% ± 21%	93% ± 3%	94% ± 16%
ICP	8% ± 16%	113% ± 11%	116% ± 6%
Oily Waste			
GFAA	59% ± 6%	82% ± 3%	54% ± 10%
ICP	5% ± 3%	125% ± 7%	118% ± 4%
Overall Average Recovery			
GFAA	67%	94%	77%
ICP	42%	115%	111%
Pooled Standard Deviation			
GFAA	10%	5%	9%
ICP	8%	9%	4%

NC = Not calculated, 0% recovery

MDLs calculated from the standard deviation of the replicate samples are shown in Table 6 for both ICP and GFAA. For comparison with the aqueous matrices, reagent water and TCLP leachate, detection limits published in the analytical methods are given in the last column. The published detection limits are for a clean, interference-free matrix and are directly comparable to reagent water.

The MDLs for reagent water compared well with the published detection limits. For ICP, MDLs for all the metals were lower, in some cases significantly lower, than the published values. The MDLs for the three metals analyzed by GFAA also compared well with values published in the methods. Although arsenic and selenium MDLs in this study were twice the published values, the absolute difference was not great (1-2 ug/L).

TCLP leachates were spiked 4-20 times higher than reagent water, and MDLs were 4-20 times higher than reagent water. Clean soil MDLs were generally lower than the waste matrices; however, the waste matrices contained higher background levels of many of the analytes which elevates the MDL value. In some cases, GFAA spiking levels were the same as spiking levels used for ICP and MDL values were generally similar. However, GFAA is the more sensitive method of the two.

TABLE 6. METAL MDL'S

Note different units for liquids and solids -->	Reagent Water (ug/L)	TCLP Leachate (ug/L)	Clean Soil (mg/kg)	Treated Waste (mg/kg)	Oily Waste (mg/kg)	MDL Given in Method (ug/L)
ICP Analysis						
Spike level for all metals except as noted below.	50 ug/L 500 ug/L (Se)	500 ug/L 200 ug/L (Cr,Co) 2,000 ug/L (Se)	50 mg/kg 20 mg/kg (Cr,Co) 200 mg/kg (Se)	50 mg/kg 20 mg/kg (Co) 200 mg/kg (Se) Cr not spiked	50 mg/kg 20 mg/kg (Co) 200 mg/kg (Se) Cr not spiked	
Antimony	11	45	#	25	4	32
Arsenic	18	120	6	17	10	53
Chromium	6	23	4	62	86	7
Cobalt	3	28	2	9	2	7
Lead	10	82	11	10	8	42
Nickel	4	63	3	11	8	15
Selenium	43	365	16	35	27	75
GFAA Analysis						
Spike level for all metals except as noted.	20 ug/L 10 ug/L (As)	500 ug/L 200 ug/L (Se)	50 mg/kg (Sb) 5 mg/kg (As) 2 mg/kg (Se)	50 mg/kg 2 mg/kg (Se)	50 mg/kg 2 mg/kg (Se)	
Antimony	3	61	#	33	10	3
Arsenic	2	49	1	4	5	1
Selenium	4	33	0.2	1	1	2

Zero for all replicates

TABLE 7. VOLATILE RECOVERY REFINERY ANALYTES

	Recovery (%)				
	Reagent Water	TCLP Leachate	Clean Soil	Treated Waste	Oily Waste
Spike Level	5 ug/L*	100 ug/L**	20 ug/kg	1,250 ug/kg	5,000 ug/kg
ng on column	25	100	100	50	50
Acetone	104	83	215	76	160
Benzene	110	96	97	93	105
2-butanone	104	119	137	70	48
Carbon disulfide	86	68	103	60	79
1,2-dibromoethane	98	105	88	79	92
1,4-dioxane***	86	71	116	54	92
Ethylbenzene	99	109	104	111	124
Methylene chloride	108	100	138	307	109
Styrene	83	91	85	82	103
Toluene	107	95	102	94	106
m + p Xylenes	119	160	151	155	178
o-Xylene	97	122	109	115	128
Median	101	98	106	88	105

* Most analytes in reagent water spiked at 5 ug/L, some at higher levels (acetone and 2-butanone 25; 1,4-dioxane 500)
** TCLP leachate diluted 1:5 in reagent water
*** Except for Reagent Water, 1,4-dioxane spiked 20 X higher

TABLE 8. VOLATILE PERFORMANCE BY MATRIX

Matrix	Recovery +/- Standard Deviation (%)*
Reagent water	99% ± 21%
TCLP leachate	99% ± 11%
Clean soil	95% ± 6%
Treated waste	92% ± 3%
Oily waste	106% ± 8%

*Excluding outliers

Volatiles

Seven samples of each of the five matrices were used for recovery and precision evaluation of volatiles. Average recoveries are shown in Table 7. Some problems were encountered with several of these analytes as seen by the abnormally low and high recoveries in the table. Calibration problems were experienced with the xylenes and blank contamination was suspected with acetone and methylene chloride analyses. Subsequent outlier analyses identified 2-butanone; carbon disulfide, and 1,4-dioxane with recovery outside the normal performance for some matrices. (Grubbs

test for outliers [9] was used for this and subsequent outlier testing.) The median was used to describe the overall performance for each matrix prior to testing for outliers.

Matrix effects on recovery and precision for refinery volatiles were analyzed only with the five analytes that did not have calibration, blank or other problems. These five were benzene, 1,2-dibromoethane, ethylbenzene, styrene, and toluene. A summary of the performance of each matrix is shown in Table 8 together with a pooled estimate of within-analyte precision. Although the range in average recovery was 92% (treated waste) to 106% (oily waste), no statistical difference was found between matrices for these refinery volatiles. Note that the variable recoveries for some outliers may be attributable to particular matrices. For example, recovery of carbon disulfide is lower in TCLP leachate (68%) and treated waste (60%)than the other matrices (79-103%). Similar results for some matrices were observed with 2-butanone and 1,4-dioxane.

The tests for difference in precision showed that the precision for TCLP leachate and oily waste were equivalent and that the precision of clean soil and oily waste were equivalent; all other precision tests showed significant differences. Treated waste had the best precision, followed by clean soil and oily waste, then TCLP leachate, and finally reagent water. This relatively poor performance with reagent water was not expected because it was the simplest matrix. The poorer precision is probably the result of spiking levels 2 to 4 times lower in reagent water in comparison to the levels spiked in other matrices. Table 7 lists the spike level and nanograms (ng) on column for a direct comparison of spiking level by matrix. Given that precision often degrades as concentration decreases and that the spiking levels for reagent water were near the method detection limit, it is likely that this is the cause of the apparently "poorer" precision performance for reagent water.

MDLs for the volatile analytes are shown in Table 9. The MDLs for 1,4-dioxane were much higher than for the other analytes; however, the MDLs were consistent with the higher spike levels used for 1,4-dioxane. Ranges in MDLs, excluding 1,4-dioxane, were:

Reagent water	2-9 ug/L
TCLP leachate	30-87 ug/L
Clean soil	3-13 ug/Kg
Treated waste	69-1600 ug/Kg
Oily waste	390-9600 ug/Kg

Semivolatiles

Extraction

The performance of the three sample preparation methods (initial duplicates) for clean soil, treated waste, and oily waste for refinery analytes is compared in Table 10. Overall, there was no significant differences among the three methods. This is shown by the range of the average recoveries across all matrices (73-79%) and the variability in recoveries when looking at individual matrices and methods. An analysis of variance on the recoveries showed no difference between methods or between matrices.

TABLE 9. VOLATILE MDL'S

	Method Detection Limits (MDLs)				
	Reagent Water (ug/L)	TCLP Leachate (ug/L)	Clean Soil (ug/kg)	Treated Waste (ug/kg)	Oily Waste (ug/kg)
Acetone	7	87	8	700	3400
Benzene	2	33	5	110	830
2-butanone	9	51	12	1100	9500
Carbon disulfide	3	30	13	69	1800
1,2-dibromoethane	4	34	4	140	2500
1,4-dioxane	220	2600	460	14000	47000
Ethylbenzene	4	36	5	150	620
Methylene chloride	3	45	4	1600	2800
Styrene	3	34	3	89	850
Toluene	3	32	4	120	390
m + p Xylenes	4	54	8	230	830
o-Xylene	3	43	4	110	930
Median	3	40	5	140	1400

See Table 7 for spike level.

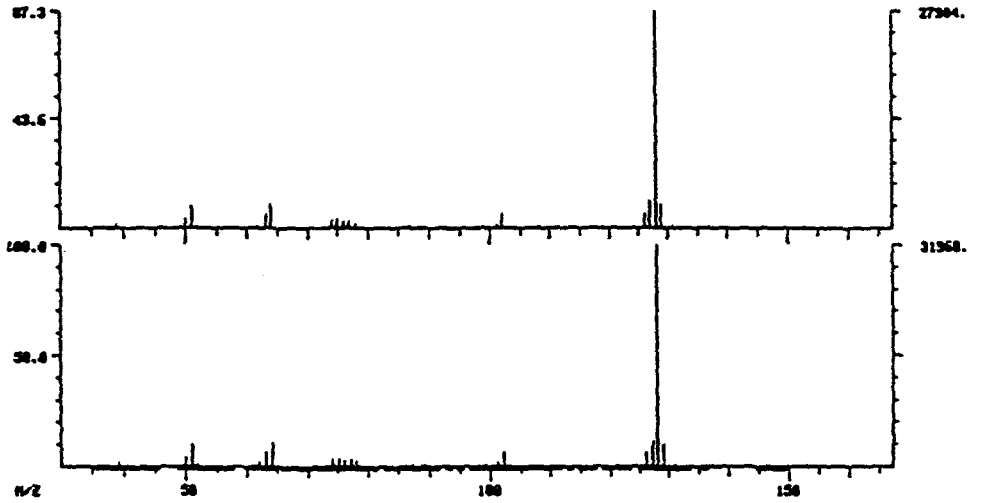
TABLE 10. COMPARISON OF EXTRACTION PROCEDURES FOR SEMIVOLATILES

	Extraction Method		
	3550 MC:AC	3550 MC	Handbook Acid/Base
	Recovery ± Standard Deviation (%)		
Clean soil	82% ± 3%	74% ± 10%	73% ± 3%
Treated waste	71% ± 11%	80% ± 5%	84% ± 9%
Oily waste	--	63% ± 4%	79% ± 18%
All Matrices	77% ± 8%	73% ± 7%	79% ± 12%

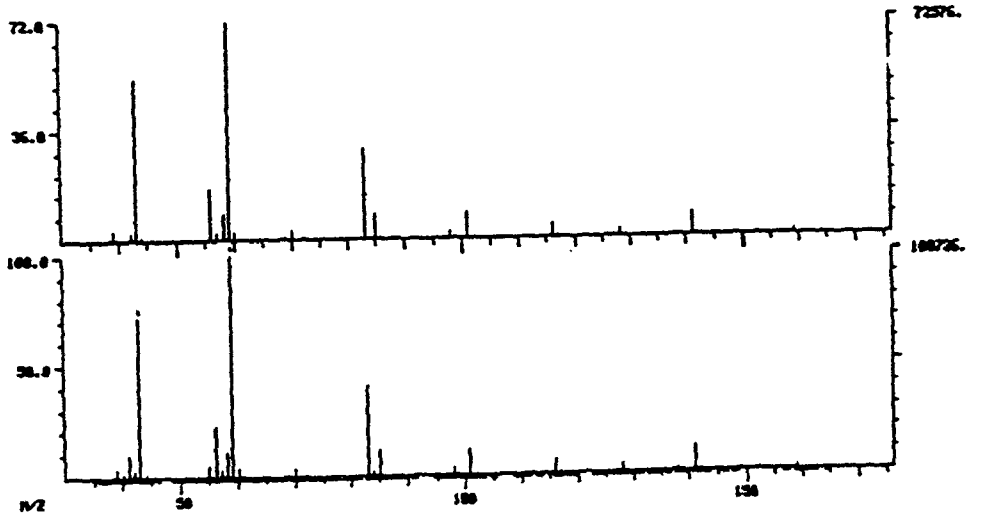
The standard deviations in the table represent the pooled estimate of precision for individual analytes (within-analyte precision). Precision ranged from 3% to 18%. Statistically, there were some differences among the matrices:methods, suggesting that the handbook method was less precise than SW-846 Method 3550. However, there was no strong trend in the data and given the small number of samples (2) for each combination, the statistical differences may not be borne out in long-term performance.

In the comparison of extraction methods, five of the refinery analytes were excluded. Acenaphthylene and benzenethiol were excluded because of calibration problems with these analytes and three other analytes were excluded because they were outliers: bis(2-ethylhexyl)phthalate; 7,12-dimethylbenzanthracene; naphthalene. Naphthalene was an outlier because the compound was not detected due to aldol condensate interference in the methylene chloride:acetone (MC:AC) extractions.

Since no extraction was statistically different, the MC only Method 3550 extraction was selected for continued evaluation. The MC:AC procedure did produce aldol condensate interference as expected. This is shown in Figure 1 by comparing the mass spectra of naphthalene from the MC only extract to the MC:acetone extract. The handbook technique was more labor intensive and was not selected because there was not demonstrated method improvement.



A. Methylene Chloride Only Extraction



B. Methylene Chloride:Acetone Extraction/Aldol Condensate Interference

FIGURE 1. MASS SPECTRUM FOR NAPHTHALENE

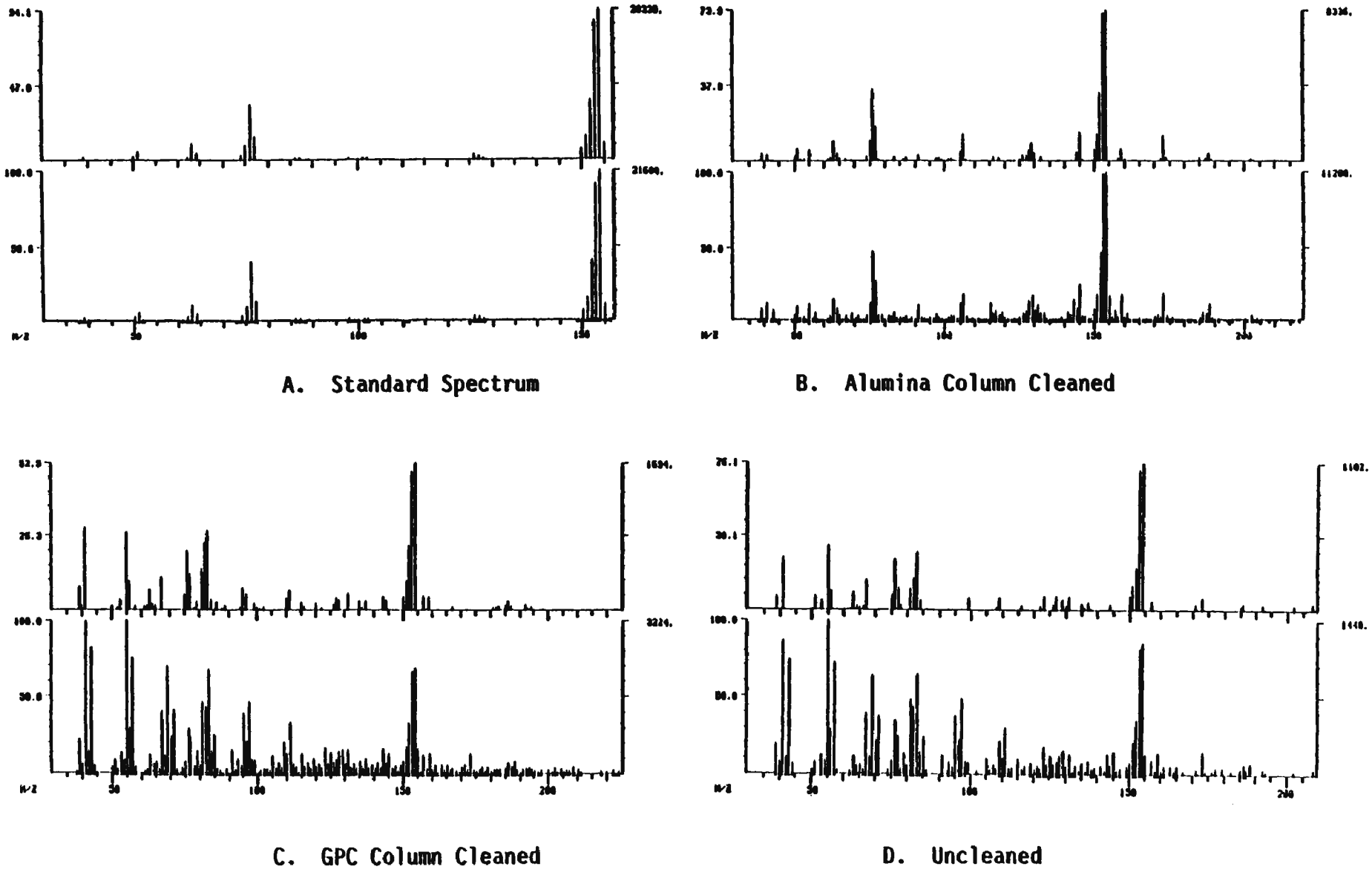


FIGURE 2. MASS SPECTRA FOR ACENAPTHENE, BASE MASS 154. TOP SPECTRUM IS ENHANCED (BACKGROUND SUBTRACTED), BOTTOM SPECTRUM IS NOT ENHANCED. ON GPC AND UNCLEANED SPECTRA, ENHANCEMENT DOES NOT REMOVE ALL COELUTING INTERFERENCE.

Cleanup

Cleanup for semivolatile analysis using GPC and alumina columns were compared for treated and oily wastes. One of the objectives of this comparison was to see which analytes were not recovered by each column. A second objective was to see what improvement in recovery, precision, and detection limits was achieved at the cost of losing analytes during the cleanup procedure.

Baseline performance of the GPC and alumina columns was first determined with a standard solution. The average recovery for GPC and alumina was 83% and 78%, respectively; however, this was not a statistically significant difference. The outliers and compounds with calibration problems were excluded as were phenols. For the standard test only, acid/base partitioning was not done prior to the alumina column cleanup. Excluding the phenols, all compounds were recovered.

The second objective was evaluated using the treated waste and oily waste data obtained from the seven replicates (analyzed after alumina column cleanup) plus the splits analyzed after GPC (3 or 4) plus the splits analyzed without cleanup (3 or 4). Results are summarized in Table 11. Of the 28 analytes, 7 were omitted due to the outlier test or calibration problems. Based on these results, the column cleanups did not have a significant impact on the precision of the data. After cleanup, single-analyte precision was either poorer or unchanged when compared to no cleanup. Column cleanup did a poorer job of recovering four of the PNAs from oily waste than no cleanup at all. These PNAs were 7,12-dimethylbenzanthracene; 1-methyl naphthalene, phenanthrene, and pyrene. In overall recovery, neither GPC nor alumina column cleanup showed a statistical difference in overall recovery for treated and oily wastes when compared to no cleanup (Table 11).

However, column cleanups do offer some advantages that are not easily quantifiable. For example, the uncleaned samples were not analyzed at the same concentration as samples which had been "cleaned" of interference compounds. For example, the oily waste samples were analyzed at the following sample weight/solvent volume ratios: uncleaned, 1 g/10 mL; GPC cleaned, 1 g/2 mL; alumina cleanup, 1 g/1 mL. As a result, the uncleaned samples had higher PQLs than the column cleaned samples. In this study, results for the uncleaned samples were reported below the PQL, which was not necessary for the column cleaned samples. The spectra obtained below the reporting limit are in general poor quality, and at times, technically questionable (see Figure 2).

TABLE 11. COMPARISON OF CLEANUP PROCEDURES FOR SEMIVOLATILES

	Cleanup Method			
	No Cleanup	GPC	Alumina	All Methods
	Recovery ± Standard Deviation			
Treated Waste (number of samples)	83% + 33% (3)	87% + 14% (4)	78% + 14% (7)	82% + 22% (14)
Oily Waste (number of samples)	61% + 16% (4)	48% + 22% (3)	52% + 15% (7)	53% + 18% (14)
All Matrices (number of samples)	72% + 26% (7)	68% + 18% (7)	65% + 15% (14)	

The GPC column cleanup removes high molecular weight interference, while the alumina column cleanup removes interference from high concentrations of aliphatic hydrocarbons. See Figure 3 for comparison of the cleanups based on the total ion chromatograms and mass 57 (hydrocarbon) chromatogram. Both cleanups are useful for their intended purpose, and both may be necessary based on the materials in the sample. As discussed in Method 3600 (cleanup), cleanups are designed to purify extracts to prevent deterioration of column efficiency and loss of detector sensitivity. Cleanups can also increase the lifetime of expensive columns. While eliminating cleanups may apparently improve precision by eliminating extra steps, the constant introduction of contaminants into the measurement system will eventually degrade the performance of the system and results in poorer detectability of analytes.

Recovery and Precision by Matrix

Seven samples were analyzed for each matrix with the exception of TCLP leachate which had eight samples. The solid samples were extracted with 100% methylene chloride using the low level sonication Method 3550. Following the extraction, the waste samples were cleaned using acid-base partitioning and alumina column cleanup. Average recoveries for the analytes are in Table 12. Semivolatile performance is shown in Table 13. The standard deviations in Table 13 are pooled estimates of the within analyte precision, excluding eight of the 28 analytes eliminated as outliers or due to calibration problems. Statistical differences were found between matrices in both recovery and precision. The recovery for oily waste was lower than the other four matrices. The recoveries for TCLP leachate, clean soil and treated waste were statistically the same. In precision performance, TCLP leachate ranked first, followed by clean soil. Reagent water precision tested equivalent to treated and oily wastes. As noted for the volatiles, this poorer precision is related to the lower spiking levels used for reagent water.

MDLs for the semivolatiles are shown in Table 14. Ranges in MDLs were:

Reagent Water	1-11 ug/L
TCLP Leachate	4-54 ug/L
Clean Soil	90-830 ug/Kg
Treated Waste	300-16000 ug/Kg
Oily waste	2800-59000 ug/Kg

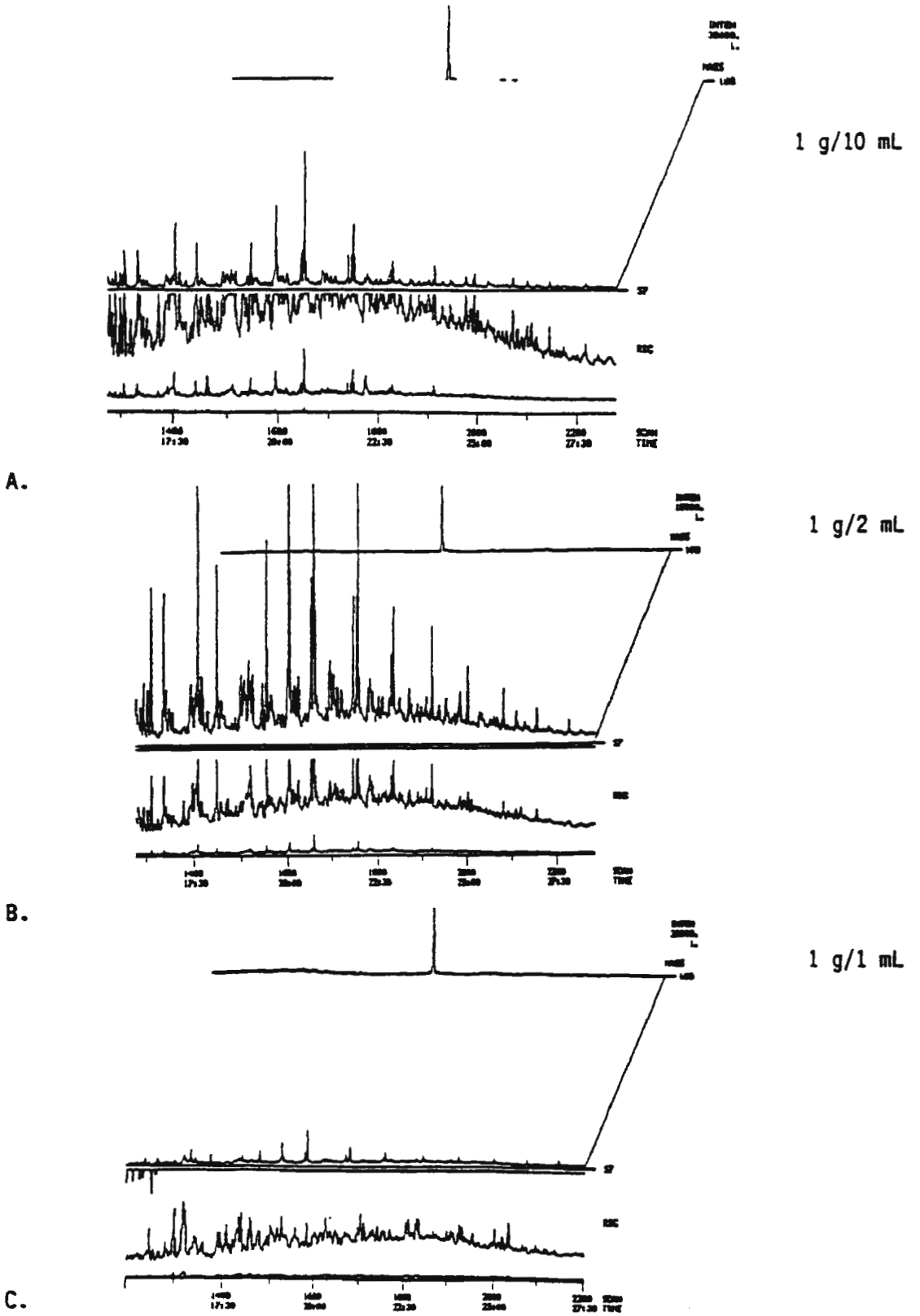


FIGURE 3. MASS CHROMATOGRAM (57) AND TOTAL ION CHROMATOGRAM OF OILY WASTE EXTRACTS: A - UNCLEANED EXTRACT, B - GPC EXTRACT, C - ALUMINA CLEANED EXTRACT. SAMPLE WEIGHT/VOLUME NOTED. CHROMATOGRAMS SCALED TO HEIGHT OF PHENANTHRENE D10-MASS 188 (INTERNAL STANDARD).

TABLE 12
SEMIVOLATILE MEDIAN RECOVERY REFINERY ANALYTES

	Reagent Water	TCLP Leachate	Clean Soil	Treated Waste	Oily Waste
Spike Amount	5 ug/L	100 ug/L	1,000 ug/kg	5,000 ug/kg	25,000 ug/kg
Acenaphthene	96	73	83	83	45
Acenaphthylene	100	18	26	20	20
Anthracene	100	68	84	78	52
Benzenethiol	**	147	159	219	226
Benzo(a)anthracene	95	73	89	81	58
Benzo(b)fluoranthene	86	68	100	97	62
Benzo(k)fluoranthene	87	78	83	100	72
Benzo(g,h,i)perylene	75	70	86	78	17
Benzo(a)pyrene	83	65	82	80	50
Bis(2-ethylhexyl)phthalate	291	87	90	78	73
Chrysene	107	83	91	89	49
Dibenzo(a,h)anthracene	73	73	87	76	67
Dibenzofuran	96	85	83	89	76
7,12-Dimethylbenzanthracene	77	60	69	45	43
2,4-Dimethylphenol	81	57	79	81	50
Fluoranthene	97	75	87	81	55
Fluorene	93	75	83	85	40
1h-indene	**	68	100	88	77
Indeno(1,2,3-cd)pyrene	67	73	86	71	60
3-Methylchloanthrene	53	46	61	51	36
1-Methylnaphthalene	**	59	82	39	24
2-Methylnaphthalene	87	78	83	77	56
3-&4-methylphenol	102	78	80	73	55
2-methylphenol	86	76	77	76	57
Naphthalene	86	64	79	76	52
Phenanthrene	103	72	87	88	20
Phenol	95	80	77	62	47
Pyrene	104	74	94	91	38
Median	93	73	83	79	52

* Most analytes in reagent water spiked at 5 ug/L, 3-methylchloanthrene spiked at 10 ug/L.
** Not spiked

TABLE 13. SEMIVOLATILE PERFORMANCE BY MATRIX REFINERY ANALYTES

Matrix	Recovery ± Standard Deviation (%)
Reagent Water	91% ± 13%
TCLP Leachate	73% ± 5%
Clean Soil	83% ± 8%
Treated Waste	79% ± 11%
Oily Waste	52% ± 15%

TABLE 14. SEMIVOLATILE MDL'S REFINERY ANALYTES

Note different units for liquids and solids -->	Reagent Water (ug/L)	TCLP Leachate (ug/L)	Clean Soil (ug/kg)	Treated Waste (ug/kg)	Oily Waste (ug/kg)
Spike Amount (in units shown)	5*	100	1,000	5,000	25,000
Acenaphthene	2	13	240	920	12000
Acenaphthylene	3	4	94	320	2800
Anthracene	2	12	230	980	10000
Benzenethiol	**	51	830	16000	35000
Benzo(a)anthracene	2	16	240	1300	10000
Benzo(b)fluoranthene	2	17	340	6400	9700
Benzo(k)fluoranthene	2	12	260	2800	13000
Benzo(g,h,i)perylene	1	11	210	4000	26000
Benzo(a)pyrene	1	14	240	1200	10000
Bis(2-ethylhexyl)phthalate	11	54	250	6200	59000
Chrysene	2	19	250	1600	15000
Dibenzo(a,h)anthracene	2	22	250	2300	7800
Dibenzofuran	2	14	220	790	8600
7,12-Dimethylbenzanthracene	1	13	310	2800	17000
2,4-Dimethylphenol	3	9	360	1400	7000
Fluoranthene	1	15	250	1400	11000
Fluorene	2	14	220	980	16000
1h-indene	**	17	360	1100	9100
Indeno(1,2,3-cd)pyrene	2	15	240	2300	7000
3-Methylchloanthrene	4	9	180	2300	6100
1-Methylnaphthalene	**	10	260	1200	17000
2-Methylnaphthalene	2	16	300	2800	10000
3-& 4-methylphenol	2	19	260	1200	9600
2-methylphenol	3	31	530	1900	21000
Naphthalene	2	15	290	1800	8600
Phenanthrene	2	15	260	1600	23000
Phenol	2	18	260	990	9500
Pyrene	2	13	250	2600	18000
Median	2	15	250	1600	10000

* Most analytes in reagent water spiked at 5 ug/L, 3-methylchloanthrene spiked at 10 ug/L.

** Not spiked in reagent water

CONCLUSIONS

For metals, there were some statistically significant differences in recovery and precision; however, in general, the performance on the different matrices was similar. A notable exception was the low recovery of antimony in solid matrices. For the five volatiles which did not have calibration, blank, or other problems, there was no statistical difference between recovery for the various matrices. Using the same five volatiles, treated waste had the best precision, followed by clean soil and oily waste, then TCLP leachate, and finally reagent water. The poor performance for reagent water was apparently related to the absolute spiking level; similar performance was seen for the semivolatiles. For the semivolatile extraction, no clear differences in extraction techniques were seen, but the MC only extraction was chosen as the simplest and because it did not produce the aldol condensate products in the MC:AC extraction. The evaluation of cleanup techniques indicated that cleanup procedures do not improve precision. However, the cleanups do allow the samples to be run efficiently with lower PQLs. The cleanups, particularly the alumina cleanup for refinery wastes, do remove interferences which eventually can degrade the performance of the GC/MS system. For the semivolatile matrix evaluation, statistical differences were found between matrices in both recovery and precision. The recovery for oily waste was lower than the other four matrices. The recoveries for TCLP leachate, clean soil and treated waste were statistically the same. In precision, TCLP leachate ranked first, followed by clean soil. Reagent water precision tested equivalent to treated and oily waste. As noted above for volatiles, this poor precision for reagent water appeared to be related to the spiking level.

Overall, the data indicates that, in some cases, precision and accuracy values based on the analysis of water can be extended to other matrices for the analytes studies. However, with particular analytes and particular matrices, there may be significant differences in precision and accuracy. These can generally only be determined by a detailed study of the matrix and the analytes in question.

REFERENCES

1. "Evaluation of Analytical Methods for Measuring Appendix IX Constituents in Groundwater," API Publication No. 4499, July 1989.

2. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," USEPA, OSW/Washington, DC, SW846, 3rd Edition, November 1986.

3. 40 Code of Federal Regulations Part 136

4. "Handbook for the Analysis of Petroleum Refinery Residuals and Wastes," Radian Corporation for EPA/OSW, October 1984.

5. Hein, C.S. and A.B. Shartleff, "Extraction of Semivolatile Appendix IX Compounds from Solid Samples," USEPA Symposium on Waste Testing and Quality Assurance, Vol. II, July 1988

6. Brilis, G. M. and P. J. Marsden, "Comparative Evaluation of Soxhlet and Sonication Extraction in the Determination of Polynuclear Aromatic Hydrocarbons in Soil," Chemosphere, 1990, Vol. 21 1/2.

7. Marsden, R.J. and J. Longbottom, "Evaluation of Method 3640 (GPC Cleanup) for Appendix VIII Analytes," USEPA Symposium on Waste Testing and Quality Assurance, Vol. II, July, 1987.

8. "USEPA Method Study 37, Sw-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils," EPA/600/54-89/012 July 1989, NTIS Order No. PB 89-181 952/AS.

9. Grubbs, F. E., and G. Beck, "Extension of Sample Sizes and Percentage Points for Significance Tests of Outlying Observations." Technometrics, TCMTA, 14 (No. 4):847-54 (November 1972).

17 THE IMPORTANCE OF SELECTING REPRESENTATIVE SAMPLES IN THE DEVELOPMENT OF A SUCCESSFUL TREATABILITY STUDY

Lance A. Hines, Ph.D., Chemistry Section Manager, Steven E. Morrissette, Senior Staff Geologist, and Curtis J. Clowe, Chemist, Environmental Division, Woodward-Clyde Consultants, 101 South 108th Avenue, Omaha, Nebraska 68154

ABSTRACT

Quality assurance issues associated with the identification and collection of representative samples for treatability testing don't always receive the appropriate attention. The ramifications can be monumental in terms of lost time and expenditures and more importantly, the failure to properly remediate a site. Treatability studies in general are very difficult to plan and perform, usually due to the number of potential variables, an inadequate amount of funding needed to address all of the critical variables, and extreme pressures from an already tight schedule. This predicament is exacerbated by the limited understanding or the inadequate amount of time and resources used in the development of the data quality objectives (DQOs) at the outset of the RI/FS. Because of these factors, the importance of the representativeness of the treatability samples that are collected becomes even more critical. The treatability study discussed herein was performed under all of the aforementioned pressures and was successful in part because of the recognition of the need for representativeness. The purpose of this treatability study was initially to confirm a previous study replacing the former performance criteria of the Extraction Procedure Toxicity (EPTOX) test with that of the Toxicity Characteristic Leaching Procedure (TCLP). The study involved the development of a solidification/stabilization mix design capable of passing the TCLP test. The site was a former lead battery breaking and reclamation operation located along the James River in Virginia. The lead concentration in the surface and near surface soil reached concentrations of over 13 percent. Preliminary results of the test samples indicated failures of the TCLP test of over 5000 percent including the mix originally purported as achieving leaching concentrations of under 5 mg/L using EPTOX methodology. A review of the strict QA/QC procedures used in sampling and analysis provided clues as to the cause of the failures. Samples for the treatability tests were based on incorrect RI/FS data characterizing the concentrations of lead and the surface and subsurface distribution of these concentrations. After a limited field investigation, a better understanding of site conditions afforded the collection of samples which were more representative. More appropriate mix preparations, coupled with a better understanding of the site chemistry, facilitated the development of remedial mix designs capable of meeting TCLP performance criteria. The results of the treatability study will be presented and the lessons learned will be discussed. This study was performed under contract with the US Army Corps of Engineers for the USEPA Region III.

INTRODUCTION

A limited bench-scale treatability study conducted in support of the remedial design for a Superfund site in Virginia was intended as substantiative work to a previous stabilization/solidification study. The study was designed to confirm the recommended stabilization mix components of Type II Portland cement, soil, and either lime or sodium phosphate as presented in the EPA Record of Decision (ROD) for the site. In accordance with the ROD, the contaminated material was to be stabilized and transported for off-site disposal. Due to changes in RCRA regulatory requirements, i.e. the adherence to the TCLP criteria in lieu of the EPTOX, it was important to refine and confirm the recommended treatability mix.

During the excavation of the initial treatability test pit, a distinct underlying clay layer was encountered at about 2 feet. This appeared to be inconsistent with existing site information. As it was desired to

obtain the most representative sampling and analysis of soils in selected areas across the site, this clay layer was of concern. As such, additional activities including the installation of test pits and borings and subsequent soil sampling and analysis were performed to better characterize site conditions which might affect the overall treatment design and afford the evaluation of representativeness of treatability samples. We present here the results of the treatability study.

Site Background

The site, located in EPA Region III, is approximately 11 acres in size and is located along the James River in Virginia. The site is bordered on the west and north by dense woods, on the northeast by sparser woods, and on the south and east by open fields and several buildings. The general area around the site is used for industrial purposes.

The site is nearly level and is included in the Coastal Plain physiographic region of Virginia. The Coastal Plain of Virginia is made up of various Pleistocene and Holocene Age sedimentary deposits overlying older sedimentary deposits which overlie the granitic basement rock. In the region around the site, and especially in areas near the James River, the granitic basement rock was expected to be shallow. Borings and test pits indicated that the shallow subsurface profile included man-placed or disturbed fill over alluvial deposits. The fill consisted of a mixture of sand, silt, and clay with varying amounts of crushed rock, cobbles, and battery casing fragments. The observed thickness of the fill ranged from 2 to 4 feet. The alluvium is typically low to medium plastic sandy silty clay and extended to the maximum depth of the test pits and borings 15 feet below ground surface. The actual extent was not determined. This clay horizon appeared to be continuous under the site. The original RI/FS boring logs indicated silty sand which was not consistent with observations made of treatability sample test pits.

The site was used from the early 1970s to 1985 for the recycling of used auto and truck batteries which were delivered in bulk shipments. After cutting the batteries open and draining the acid into an on-site retention pond, the lead-containing components of the batteries were removed and stored on site for later processing. The empty battery casings were then shredded and also stored on site. Battery casing fragments are currently present on the surface and in the shallow subsurface. Whole battery casings were occasionally unearthed during test pit excavations.

Previous Stabilization/Solidification Treatability Studies

During the remedial investigation/feasibility study (RI/FS) an initial stabilization/solidification treatability study was conducted at the site. This study investigated various combinations of soil, Type I Portland cement, fly ash, lime, and a proprietary component. Based on preliminary results, it was necessary to perform additional testing since results with Type I Portland cement and fly ash were inconclusive. The additional stabilization mixes consisted of soil, Type II Portland cement, lime, sodium silicate, and sodium phosphate in various combinations. The results of this study indicated that the two mixes having the greatest reduction in lead mobility by the Extraction Procedure Toxicity (EPTOX) test contained 36 and 48 percent Type II Portland cement combined with about 5 percent sodium silicate and about 3 percent lime, respectively. Other mixes including one with sodium phosphate also were effective with the level of Portland cement at 48 percent.

These studies seemed to indicate that the likelihood of achieving stabilization of lead was high using Type II Portland cement combined with an additive such as lime to control the pH. It was determined that fly ash was not a viable alternative.

Treatability Study Approach

The overall objective of the study was to better define the stabilization/solidification mix ratio of Type II Portland cement, soil/sediment, and additives. A subsequent objective of the study was to provide insight into the potential limitations of the design process by better characterizing subsurface soils with respect to debris, contamination, and soil type. The general approach to this treatability study was phased to provide the representative mix ratio recommendations under the given cost and time constraints. The following paragraphs outline some of the various phases of the approach.

The first phase, which ran concurrently with the subsequent phases, involved the representative sampling and analysis of soils in selected areas across the site. This phase included the screening and characterization of soil components as well as the determination of levels of metals. This phase included drilling and sampling of soil, water, and waste debris within the site and the nearby property. The study also included physical and chemical laboratory testing of untreated soil, water, waste and stabilized/solidified mixtures. Information concerning properties of the site soils/materials provided data important for treatability, as well as the potential for volume increase of the treated material.

A second phase of the study involved the preparation of various stabilization/solidification mix ratios of Type II Portland cement, hydrated lime, sodium phosphate and, subsequently, calcium phosphate designed to focus the mix ratio recommendation based on the previous treatability study. The intent during this phase, which included a series of physical and chemical tests, was to provide treatability information on two areas of greatest concern with respect to chemical fixation as well as material handling. Based on preliminary test results, the treatability study design was modified to include calcium phosphate in lieu of sodium phosphate. Further physical and chemical tests of the potentially successful stabilized/solidified mixes were used to assess feasibility in the treatability process.

The first of the two areas of concern centered on the drainage ditch where sediments posed treatability and handling questions. The second area of concern addressed as part of this phase was in the vicinity of some former acid ponds. Typical remedial concerns in this area were battery chip content (from processed casings), cobble content, soil pH, and high lead levels. This area was selected to provide a representative sample indicative of the worst-case soils to be remediated. The recommendation of the typical remedial mix ratio was to be based on results obtained on the representative sample taken from this area.

METHODS

Samples were obtained initially from two test pits (TP-1 and TP-2), one from the reported acid pond area and another from the drainage ditch in order to address possible differences in treatability based on soil type, pH, and lead levels. In an attempt to obtain representative treatability samples, material was composited from the face of the test pits in proportions consistent with reported contamination levels as well as practical considerations with respect to excavation operations. As previously discussed, additional test pits (TP-3 through TP-7 and TP-4A, TP-5A and TP-6A) were excavated to better characterize any lateral variabilities which might affect treatability. Soil borings were drilled to investigate the shallow subsurface conditions. Undisturbed samples of the soil directly beneath the contaminated soils were obtained from the borings using 3-inch-diameter Shelby tubes to evaluate soil characteristics.

The laboratory testing program of the untreated soil samples consisted of physical and chemical tests, including tests of soils from both the upper disturbed soil horizon and the underlying clay. The physical

properties determined included the classification (Unified Soil Classification System), moisture content, density, permeability, and shear strength. The chemical tests consisted of pH, total metals, TCLP metals, TCLP alkalinity, and TCLP pH. Activities also included the screening on-site of untreated soils to provide information on the potential extent of non-process materials requiring pretreatment such as battery casing chips and cobbles. Testing of untreated materials was also important for assessing the representativeness of materials selected for treatability testing.

Additional test pits TP-4A, TP-5A, and TP-6A were located near the previously excavated TP-4, TP-5, and TP-6. These locations were selected based on their potential for "representativeness". These test pits were excavated to depths where lead contamination was equal to or just below the site action level, based on information obtained from laboratory testing and previous investigations. Samples from the additional test pits were separated into two groups: upper fill material (disturbed materials) and lower, undisturbed, natural soils or clay. Two additional test pits, TP-9 and TP-10, were excavated to characterize the subsurface conditions in the reported acid and neutralization pond areas. The depths of all the test pits ranged from about 4 to 6 feet. In addition to test pits, soil borings were drilled and soil samples were taken to assess the "representativeness" of soils requiring remediation.

Soil borings were drilled immediately adjacent to test pits TP-4A, TP-5A, and TP-6A, respectively. The purpose of these borings was to obtain undisturbed Shelby tube samples from the natural soil material at these sites for laboratory testing to better characterize conditions which might affect the remedial process. Laboratory tests consisted of physical and chemical tests of both untreated and treated soils/waste. The physical tests included particle size, Atterberg limits, moisture content, permeability, unconfined compressive strength, density, and moisture-density relationships for compacted materials. Physical tests were performed according to American Society of Testing Materials (ASTM) standard procedures, if applicable. The chemical tests included total metals analysis, pH, TCLP metals (predominantly lead), TCLP pH, and TCLP alkalinity.

Samples were shipped to the laboratory for physical tests, bench-scale treatability mix preparations and subsequently for chemical analysis. The untreated material was subdivided into four types: fill material, natural soil or clay, composited material, and water. The treated material consisted of soil-cement mixtures with hydrated lime, sodium phosphate, or calcium phosphate.

The mixing procedures for the soil-cement-lime-sodium phosphate and soil-cement-lime-calcium phosphate mixtures were relatively similar. After geophysical testing, soil samples were dried for a short period of time and sieved through a No. 4 (4.76 mm) sieve. The appropriate proportions of the additives were mixed with the sieved sample. The ratios of the mix were based on the dry weight of the sieved soil sample. For the soil-cement-lime-sodium phosphate mixtures, all the materials were added at the same time. For the soil-cement-lime-calcium phosphate mixtures, lime and/or calcium phosphate and a small amount of water were added to the soil 1 hour before the addition of cement to enhance the exposure of the soil to the stabilizing additives. Twelve treatability samples were prepared using the soil-cement-lime-sodium phosphate mix and subsequently 23 samples were prepared using the soil-cement-lime-calcium phosphate mix. The secondary mixes were prepared from disturbed soils composited from TP-4A, TP-5A, and TP-6A. This combined sample, prepared exclusively from the upper material, was identified as TP-456. It was determined from preliminary data that these soils would be most "representative" of the soils requiring stabilization/solidification based on additional site characterization data.

RESULTS

Analysis Of Waste Stream Characteristics

Physical Classification and Moisture Content

Physical classifications and moisture content tests were conducted on both disturbed, "upper" material and natural, undisturbed soils. The results of the physical classification and moisture content tests are listed in Table 1. The results indicate that the composited subsurface soils are generally low plastic (lean) sandy clay or sandy silt with 1 percent or less gravel (the coarser materials were removed on site). The particle size ranges from about 2 mm (medium-grained sand) to less than 0.001 mm (silt or clay particles). The characteristics of the gradation curves (coefficient of uniformity >15 and a coefficient of curvature near 1) and the broad particle size range show that the soil is generally well graded. With these observed particle size characteristics, the on-site soils are likely to show favorable physical characteristics after stabilization/solidification.

Measured moisture contents of the shallow soils depend on the amount of rainfall and can vary throughout the year. Due to the low permeability of the underlying soils, saturation of the shallow soils is frequent. Soils received for geophysical and treatability testing ranged in moisture content from about 13 to 23 percent. The variability of the site soil moisture indicates a requirement of moisture adjustment during the remedial process.

Unconfined Compressive Strength (ASTM 2166-85)

The tests indicated that on-site soils exhibit a stiff to very stiff consistency, implying that this soil would be expected to provide reasonable support to most construction equipment during removal of the contaminated soils.

Bulk Density

The measured dry unit weights and moisture contents are contained in Tables 2a and 2b along with the corresponding total unit weight (bulk density). The dry unit weight of the test pit samples ranged from about 94 to 110 pounds per cubic foot, with an average of 104 pounds per cubic foot. The dry unit weight of the Shelby tube samples (average sample depth about 4 to 5 feet) varied from about 103 to 110 pounds per cubic foot, with an average of about 106 pounds per cubic foot.

Permeability (SW9100)

Samples were taken at the soil borings (via Shelby tube) from the soils directly beneath the disturbed upper layer at the site for laboratory permeability analysis. The measured permeabilities ranged from 7.1×10^{-8} to 2.0×10^{-6} cm/sec. Thus, the soil beneath the disturbed upper layer can be considered a relatively impermeable plastic clay that will not allow free migration of water.

TCLP Metals Analysis of Untreated Soil Samples

Untreated soil samples were collected from test pits and soil borings and analyzed to determine the lead concentrations present (Table 3). TCLP results for lead of the composite samples ranged from 56.4 mg/L at TP-1 to 345 mg/L at TP-4.

The pH of untreated soils at the site was typically about 6. A lower pH (pH<3) was obtained in the drainage ditch (TP-1) and the deeper natural clays. Alkalinity values for TCLP leachates had a considerable range of ND to 92.0 mg/L reflecting the heterogeneity of the surface soils.

Lead concentrations are presented in Table 3 for samples from upper fill material, samples from natural soils at depths between 3 to 8 feet, and composite samples. The samples were obtained from the soil borings as well as test pits within the site. Lead contamination at the site was limited to the upper fill material that ranged in thickness between 2 to 4 feet. Lead contamination was also confined to the top 2 feet at off-site locations. None of the samples from the 3- to 5-foot depth have lead levels greater than 120 mg/kg.

Analysis Of Treatability Study Data

Moisture-Density Relationships of Compacted Soil-Cement Mixtures (ASTM D 558-82)

Compaction tests were performed on the soil-cement mixtures. Samples from TP-1 and TP-2 were mixed with various amounts of cement, lime, and sodium phosphate. The results of compaction tests of TP-1 and TP-2 samples show that increases in cement ratio produce minor changes in the optimum moisture content and maximum dry density. However, increases in lime and sodium phosphate ratios generally increase the optimum moisture content and decreases the maximum dry density. Similar trends were observed for the TP-456 (exclusively upper material) sample. Maximum dry density for TP-1 and TP-2 mixtures ranged between 102 and 110 pounds per cubic foot, with optimum moisture content between 17 and 22 percent. The maximum dry density of the TP-456 mixes varied from 108 to 122 pounds per cubic foot and the optimum water content between 13 and 20 percent. Because the TP-456 sandy silt and TP-1 and TP-2 samples are sandy clays, the above difference in moisture-density values are expected. TP-456 material was considered "representative" of the soils to be remediated at the site.

The TCLP tests and economic considerations indicated that the soil-cement mixture containing 15 percent cement and 10 percent calcium phosphate had a high potential for meeting remedial requirements. The optimum moisture content and maximum dry density for this mixture were 14.3 percent and 112.7 pounds per cubic foot, respectively. An estimate of the volume of materials to be handled during the site stabilization/solidification process was calculated based on the moisture-density curve for the above sample and the average dry density of untreated samples. The average dry density of the on-site soils was determined in the field. Based on the available data, the final volume of solidified/stabilized mixture in the field is expected to be 10 to 20 percent larger than the volume of untreated soils. This estimate assumes that the solidified/stabilized mixture will be compacted to at least 95 percent of the maximum dry density obtained from the laboratory moisture-density tests using the above ASTM D 558-82 test procedure. The moisture content is assumed to be within $\pm$ 3 percent of the optimum moisture determined from the above test. It was also assumed that the mix ratios are based on the dry weight of soil.

Permeability of Stabilized/Solidified Mixture (SW-9100)

The permeability of the recommended soil-cement mixture (15 percent cement and 10 percent calcium phosphate) was evaluated using a flexible wall permeability test. The measured coefficient of permeability was approximately 1.4×10^{-5} cm/sec. Although this value is slightly higher than the maximum permeability of $1.0\ 10^{-5}$ cm/sec recommended by the EPA, the stabilized material must meet TCLP criteria rendering it a noncharacteristic waste.

Unconfined Compressive Strength of Stabilized/Solidified Mixture (ASTM D 1633-84)

Two unconfined compression tests were conducted to evaluate the strength of the recommended soil-cement mixture (15 percent cement and 10 percent calcium phosphate). The average unconfined compressive strength was about 340 pounds per square inch (psi), about 25 times higher than the strength of untreated soil. The measured unconfined compressive strength is well above the minimum recommended by EPA (about 50 psi). The stabilized/solidified material is expected to provide stable support for construction equipment, cover material, overburden, and any other materials that might be placed upon it.

TCLP of Soil-Cement Mixtures

The results of TCLP tests for stabilized/solidified soil-cement mixtures are presented in Tables 4 and 5. Only two samples of the soil-cement-lime-sodium phosphate (Table 4) resulted in TCLP lead values less than the regulatory level (5 mg/L). The measured TCLP lead value for both mixtures was 3.3 mg/L and contained 40 percent cement with 5 percent lime or sodium phosphate, respectively. The remaining mixtures exhibited significantly higher TCLP lead values (up to 316 mg/L).

Based on the results shown in Table 4, the mix design was re-evaluated and sodium phosphate was replaced with calcium phosphate in the additional soil-cement mixtures. As shown in Table 5, the TCLP lead values were below detection limit in the following samples: 50 percent cement; 15 percent cement and 20 percent calcium phosphate; and 15 percent cement and 10 percent calcium phosphate. Several other samples contained low levels of TCLP lead (samples with cement ratios between 15 and 20 percent and calcium phosphate between 10 and 20 percent). The mixture that contained 15 percent cement and 10 percent calcium phosphate was considered the most suitable mixture for remedial design because of the lower mix ratios and, therefore, lower cost. The mixture also had acceptable physical characteristics such as strength, low permeability, and density. Also, the net increase in volume of treated material would be lower for this mix ratio, thereby reducing costs of off-site disposal.

DISCUSSION

This limited bench-scale treatability study was intended as substantiative work to a previous stabilization/solidification study and to confirm adherence to the TCLP criteria in lieu of the EPTOX. Additional activities included the installation of test pits and borings and subsequent soil sampling and analysis were performed to better characterize site conditions which might affect the overall treatment design and afford the evaluation of representativeness of treatability samples. Test pits dug for this purpose were designed to simulate practical excavation conditions based on the depth of lead contamination above action limits as presented in the RI/FS. The collected site material was sieved prior to shipping in order to estimate the composition and extent of battery casing fragments and cobbles in contaminated soils throughout the site. Physical characteristics of the site soils were also examined to assess effects of soil type on the stabilization of lead.

Initial mixes containing 20, 30, and 40 percent Type II Portland cement with respective additional components of 1 and 5 percent lime or 5 percent sodium phosphate were prepared for soils from two locations, the drainage ditch (Test Pit 1) and in the vicinity of the former acid pond (Test Pit 2). Preliminary results indicated that only two mixes from TP-1 soils containing 10,000 mg/kg lead passed the TCLP criteria of 5 mg/L. No mixes from TP-2 containing 24,000 mg/kg lead gave TCLP leachate levels below 50 mg/L. The two mixes which passed, having identical TCLP leachate values of 3.3 mg/L, contained 40 percent Portland cement and either 5 percent lime or 5 percent sodium phosphate.

Based upon these results, two trends were further evaluated which indicated a response with respect to TCLP criteria. One was the effect of the percentage of Portland cement, and the other was the presence of phosphate. As sodium phosphate is not readily available, calcium phosphate, supplied as a fertilizer known as triple superphosphate, was selected for additional testing. Triple superphosphate is readily available and, according to the literature, calcium phosphate typically forms a more stable mineral complex than sodium phosphate at a lower pH range.

Additional treatability mixes were then planned to examine a wider range of Portland cement content (15 - 50 percent) with respect to lime and calcium phosphate. Initially, three site areas were selected as representative for site treatability. However, further characterization of the site surface soils and underlying clay horizon necessitated treatability testing of only the upper 2 to 4 feet of site soils. Therefore, the additional treatability mixes were prepared with sieved soils composited from the upper 2 feet from Test Pits 4, 5, and 6 (TP-456). This material appeared to be more representative of materials to be encountered during full-scale remediations.

Preliminary results from the additional treatability testing of the more contaminated soils indicated a strong stabilization effect with increasing calcium phosphate levels at a lower Portland cement content of 15 percent. Based on these results, which included one mix with 10 percent calcium phosphate meeting TCLP criteria, a final set of 5 mix ratios was prepared with 15 to 20 percent Portland cement and 10 to 20 percent calcium phosphate, respectively:

- Mix 1 - 60 percent soil, 15 percent Portland cement, 15 percent $CaPO_4$
- Mix 2 - 65 percent soil, 15 percent Portland cement, 20 percent $CaPO_4$
- Mix 3 - 70 percent soil, 20 percent Portland cement, 10 percent $CaPO_4$
- Mix 4 - 65 percent soil, 20 percent Portland cement, 15 percent $CaPO_4$
- Mix 5 - 60 percent soil, 20 percent Portland cement, 20 percent $CaPO_4$

Results of TCLP testing on these mix preparations following a seven-day cure indicated that all met TCLP criteria with four showing nondetect (ND) for lead.

Based on these results and the results of the previous stabilization study, a mix of 15 percent Portland cement and 10 percent calcium phosphate was selected for confirmatory testing given its potential for remedial success at this battery site.

Further confirmatory physical and TCLP leachate testing was performed on this selected mix. The TCLP leachate contained 8.3 mg/L of lead, which was higher than the regulatory criteria of 5 mg/L. Even though this mix has shown TCLP results of ND and 8.3 mg/L, this particular mix and the other five mixes containing calcium phosphate are presented below for informational purposes as having potential remedial success. The slight failure (comparatively) can be attributed, based on results of further site characterization, to the heterogeneity of the upper 2 to 4 feet of site soils with respect to lead contamination. Test results have indicated lead levels across the site from low parts per million to in excess of 13 percent (130,000 mg/kg). It is this heterogeneity of concentrations and the physical form of the lead present, i.e. complexed and fine metallic particles, which most likely account for differences seen in lead levels determined in TCLP leachate from these mixes. It is this key factor and recognition of treatability sample representativeness which afforded a clearer picture of the potential for remedial failure.

Mix Soil:Cement:$CaPO_4$	TCLP Lead mg/L
75:15:10	ND, 8.7
70:15:15	ND, 0.6
65:15:20	ND, ND
70:20:10	0.75, 5.7
65:20:15	ND, 0.52
60:20:20	ND, 0.52

Bulk densities indicated an increase of 15 to 20 percent in material after stabilization, calculated on a dry weight basis. The material or site soils used in this treatability study, although representative of soil type, was found to contain varying amounts of debris including battery casing fragments of all sizes, battery components, and stone cobbles, all of which were sieved out. Also, it was determined that moisture played a significant role in the mixing process with respect to the availability of lead to reactants. Therefore, it was determined that various material handling considerations must be addressed prior to treatment such as particle sizing, drying, and the sequence and residence time in which reactants are combined, i.e. better results were obtained when samples were dried and mixed thoroughly with reactants such as calcium phosphate prior to the addition of Portland cement and finally water. One final factor which was not addressed and may contribute significantly to the effectiveness of the mixes, particularly the last six mixes containing calcium phosphate, was the curing time of the stabilized mix. There was evidence during the study that curing beyond seven days appeared to improve the containment efficiency (stabilization), but these results were not conclusive.

SUMMARY

This treatability study began initially as a simple confirmatory effort. It was through the recognition of the need for representativeness and a clear focus on the remedial objectives that variables were uncovered which could have contributed to a faulty or unacceptable design. Additionally, this study has alluded to the importance of the data quality objective process. The representativeness is, at best, a very difficult concept to evaluate and without a clear understanding of the limitations involved, serious and costly consequences can result.

TABLE 1

PHYSICAL CLASSIFICATION AND MOISTURE CONTENT

Test Pit/ Soil Boring	Description/ Classification	Particle Size			Atterberg Limits		Moisture Content[1] (%)
		Gravel (%)	Sand (%)	Silt & Clay (%)	Liquid Limit (%)	Plasticity Index (%)	
TP-1	Sandy lean clay, CL	0	33	67	33	15	23.2
TP-2	Sandy lean clay, CL	1	21	78	43	20	22.9
TP-3	Sandy lean clay, CL	1	34	65	30	10	21.3
TP-4	Sandy lean clay, CL	0	38	62	25	10	14.2
TP-5	Sandy lean clay, CL	1	37	62	28	11	11.8
TP-6	Sandy lean clay, CL	0	27	73	26	10	15.7
TP-7	Sandy silty clay, CL-ML	1	31	68	25	7	16.1
GR-TP2-2.5[2]	Sandy lean clay, CL	0	20	80[3]	NA	NA	NA
TP-456	Sandy silt, ML	1	47	52	23	3	13.4
SB91-20	Sandy lean clay, CL	0	18	82	28	12	17.5
SB91-21	Sandy lean clay, CL	0	40	60	32	14	18.7
SB91-22	Sandy lean clay, CL	0	36	64	41	21	21.7
SB91-23	Sandy lean clay, CL	0	25	75	36	20	21.7
SB91-24	Sandy lean clay, CL	0	34	66	33	17	19.6
SB91-25	Sandy lean clay, CL	0	32	68	27	12	21.3
TP-4A (at 0.5' depth)[4]	Sandy lean clay, CL	0	22	78	NA	NA	NA
TP-4A (at 1.5' depth)[4]	Sandy lean clay, CL	0	24	76	NA	NA	NA
TP-5A (at 0.5' depth)[4]	Sandy lean clay, CL	0	26	74	NA	NA	NA
TP-5A (at 1.5' depth)[4]	Sandy lean clay, CL	0	32	68	NA	NA	NA
TP-6A (at 0.5' depth)[4]	Sandy lean clay, CL	0	19	81	NA	NA	NA
TP-6A (at 1.5' depth)[4]	Sandy lean clay, CL	0	16	84	NA	NA	NA
TP-9 (at 0.5' depth)[4]	Sandy lean clay, CL	0	25	75	32	16	NA
TP-9 (at 1.5' depth)[4]	Sandy lean clay, CL	0	28	72	35	18	NA
TP-10 (at 0.5' depth)[4]	Sandy lean clay, CL	0	23	77	37	19	NA
TP-10 (at 1.5' depth)[4]	Sandy lean clay, CL	0	28	72	32	15	NA

1 As received
2 Grab sample of undisturbed clay layer at TP-2
3 43% silt, 37% clay
4 Composite samples taken from discrete horizons at depths below the upper disturbed layer

NA = Not analyzed
TP = Test pit
SB = Soil boring

TABLE 2a

MOISTURE-DENSITY RELATIONSHIP OF COMPACTED SOIL-CEMENT MIXTURES

Mix		TP-1[1]		TP-2	
		Maximum Dry Density (pcf)	Optimum Moisture (%)	Maximum Dry Density (pcf)	Optimum Moisture (%)
20% Cement		106.8	19.0	108.3	18.8
"	+ 1% lime	105.8	19.9	107.2	19.3
"	+ 5% lime	104.3	20.3	106.3	19.9
"	+ 5% NaPO4	102.5	22.2	103.8	22.3
30% Cement		106.8	17.5	109.6	19.4
"	+ 1% lime	106.3	19.5	107.8	19.1
"	+ 5% lime	104.2	20.7	105.7	21.3
"	+ 5% NaPO4	103.9	21.0	105.6	22.0
40% Cement		108.2	18.3	109.2	19.2
"	+ 1% lime	107.4	19.9	108.0	18.6
"	+ 5% lime	105.3	20.1	106.2	19.9
"	+ 5% NaPO4	104.8	21.2	105.5	21.1

Note: Values determined by ASTM D 558-82

[1] Drainage ditch

TABLE 2b

MOISTURE-DENSITY RELATIONSHIP OF COMPACTED SOIL-CEMENT MIXTURES (SAMPLE TP-456)[1]

Cement (%)	Lime (%)	Calcium Phosphate (%)	Maximum Dry Density (pcf)	Optimum Moisture Content (%)
30	10	–	116.0	16.9
30	–	10	114.8	17.1
30	10	10	109.3	17.3
30	–	5	116.7	15.8
30	–	–	122.0	14.0
40	5	–	111.7	17.7
50	–	–	120.9	15.1
50	10	–	117.1	15.8
50	–	10	114.9	16.9
50	10	10	111.3	17.8
15	–	–	120.3	13.3
15	10	–	115.5	15.4
15	–	10	112.7	14.3
15	10	10	108.7	19.8
40	–	–	121.3	14.5
40	10	–	117.2	15.6
40	–	10	119.3	15.8
40	10	10	109.9	18.5
15	–	15	111.2	17.5
15	–	20	110.7	17.5
20	–	10	114.2	17.5
20	–	15	112.6	17.2
20	–	20	109.8	17.7

Note: Values determined by ASTM D 558-82

[1] Composited surface material from Test Pits TP-4A, TP-5A, and TP-6A.

TABLE 3

TOTAL AND TCLP LEAD OF UNTREATED MATERIAL

Test Pit	Total Lead[1] (mg/kg)	Total Lead Upper[2]	0.5' Horizon[3]	1.5' Horizon[3]	TCLP Lead (mg/L)
TP-1	10,100				56.4
TP-2	24,300				132
TP-3	48,700				111
TP-4	30,000				345
TP-4A	40,300	142,000	61.8 (75.3)	91.6	
TP-5	45,400				238
TP-5A	17,800	74,700	38.4	43.8	
TP-6	35,700				296
TP-6A	32,600	118,200	42.2	106.0	
TP-456		134,000[4]			
TP-7	7,220				111
TP-9			37.6	35.2	
TP-10			18.1 (14.5)	12.6	

( )Duplicate sample analysis

[1] Lead levels in sieved and composited materials
[2] Lead levels in composite of upper materials only
[3] Lead levels in composite samples of discrete horizons in the underlying clay at depths below the disturbed upper material
[4] Lead levels in composite of upper materials from TP-4A, TP-5A, and TP-6A

TABLE 4

TCLP LEAD, pH, AND ALKALINITY OF SOIL-CEMENT-LIME-SODIUM PHOSPHATE MIXTURES

Test Pit	Soil (%)	Type II Portland Cement (%)[1]	Lime (%)	Sodium Phosphate (%)	TCLP Lead (mg/L)	TCLP pH	TCLP Alkalinity (mg/L)
TP-1	80	20	–	–	56.9	4.8	1,620
	79	20	1	–	54.9	4.8	1,840
	75	20	5	–	51.7	5.0	2,680
	75	20	–	5	10.3	4.7	1,060
	70	30	–	–	28.3	5.2	3,200
	69	30	1	–	29.6	5.4	3,620
	65	30	5	–	25.1	5.4	4,220
	65	30	–	5	8.3	4.9	2,380
	60	40	–	–	24.2	5.5	4,180
	59	40	1	–	13.0	6.0	4,330
	55	40	5	–	3.3	6.7	4,700
	55	40	–	5	3.3	5.3	3,920
TP-2	80	20	–	–	254	4.9	2,500
	79	20	1	–	316	4.9	2,580
	75	20	5	–	267	5.2	3,670
	75	20	–	5	170	4.7	1,630
	70	30	–	–	197	5.3	3,980
	69	30	1	–	198	5.8	4,410
	65	30	5	–	125	6.0	4,560
	65	30	–	5	90	5.1	3,430
	60	40	–	–	176	5.9	4,900
	59	40	1	–	163	6.1	5,020
	55	40	5	–	52.8	6.6	4,760
	55	40	–	5	56.5	5.9	4,500

[1] Mix percentages calculated on a dry weight basis

TABLE 5

TCLP LEAD, pH, AND ALKALINITY OF SOIL-CEMENT-LIME-CALCIUM PHOSPHATE MIXTURES[1]

Soil (%)[2]	Type II Portland Cement (%)[2]	Lime (%)[2]	Calcium Phosphate (%)[2]	TCLP Lead (mg/L)	TCLP pH	TCLP Alkalinity (mg/L)
85	15	0	0	57.4	11.3	2,450
75	15	10	0	46.4	11.5	2,760
75	15	0	10	ND (8.7)	9.3 (5.1)	1,940 (1,440)
65	15	10	10	32.2	10.9	2,380
70	15	0	15	ND (0.6)	5.7 (8.0)	2,360 (2,500)
65	15	0	20	ND (ND)	6.3 (6.9)	2,380 (2,550)
70	20	0	10	0.75 (5.7)	11.0 (6.3)	2,340 (2,290)
65	20	0	15	ND (0.52)	8.2 (9.6)	2,180 (2,580)
60	20	0	20	ND (0.52)	7.2 (8.3)	2,280 (2,620)
70[3]	30	0	0	83.9	11.7	2,620
60	30	10	0	36.7	11	2,860
60	30	0	10	12.6	11.5	2,480
50	30	10	10	50.2	11.6	2,540
65	30	0	5	49.0	11.6	2,540
60	40	0	0	103	11.2	2,620
50	40	10	0	153	11.2	2,800
50	40	0	10	34.0	10.9	2,720
40	40	10	10	61.4	11.5	2,580
55	40	5	0	102	12	2,680
50	50	0	0	ND	6.4	4,400
40	50	10	0	33.7	11.6	2,820
40	50	0	10	47.0	11.5	2,660
30	50	10	10	55.3	11.5	2,640

[1] Composited sample from TP-4A, TP-5A, and TP-6A
[2] Mix percentages calculated on a dry weight basis
[3] Sample tested at moisture content 5% above optimum

ND = Not detected
( ) Parentheses indicate reanalysis

18

METHOD MODIFICATION... OR DEVIATION?
Addressing Data Comparability and Defensibility

Richard G. Mealy, Quality Assurance Manager,
Warzyn Inc., 1 Science Court, Madison, Wisconsin 53711

ABSTRACT
In the wake of federal investigations regarding fraudulent environmental testing, modifications made to published method by individual laboratories is a rapidly growing cause for concern. The ability to achieve Data Quality Objectives (DQO) for comparability is compromised when these modifications impact inter-laboratory precision and accuracy.

Although the rationale for these modifications is comprehensible in specific situations, there is a need for more formal mechanisms to control this process. In the absence of regulatory guidance and enforcement on this issue, the ability to make correct environmental decisions is endangered.

The issue of method modifications is highlighted in order to:

- understand the rationale behind modifications
- determine the impact of modified methods on environmental decision-making
- make the distinction between modifications and deviations
- review techniques used to validate modified methods
- guard against adverse impacts of invalid modifications on projects

INTRODUCTION
The environmental testing business is a rapidly expanding market with total annual revenues estimated from 0.5 to 1.4 billion dollars. This boom has resulted in a population explosion of smaller laboratories, each attempting to cash in on a piece of this lucrative market. This has, in turn, placed an undue burden on both federal and state agencies responsible for regulatory oversight of environmental testing operations.

In addition, a recession economy, such as that endured over the last 12-18 months, serves only to further augment the problem as regulatory agencies tend to conserve budget dollars and laboratories are forced to increasingly cut operational costs. The result of the former is that all activities, including enforcement, are limited, while that of the latter is to continually seek "short-cuts" to all stages of the analytical testing process.

In the absence of adequate enforcement, method modifications can evolve into distinct deviations, resulting in substantial changes to method accuracy and precision limits published in referenced methods. Thus far, the emphasis of Quality Assurance (QA) has been on the validity of laboratory data, while the comparability of data generated by one laboratory versus another has been largely overlooked. Upon closer examination of the method modification issue, it is apparent that there is a need for additional guidance from the regulatory community as well as a need to better educate our clients on this and other relevant issues.

RATIONALE BEHIND METHOD MODIFICATIONS

Modifications are made to published methodology for a wide range of reasons invalid. It is important to emphasize that there are cases in which modifications are necessary and/or appropriate, such as cases in which:

- published performance criteria cannot be duplicated using similar apparatus and operating conditions
- the intent is to combine multiple, similar methods into a single method
- the modification is technically sound and yields equivalent performance data
- the modification arises from interpretation of nebulous issues

All too often, however, modifications represent shortcuts to obtain a competitive edge within the laboratory community through decreased labor and/or materials costs. This type of modification usually involves the softening or complete elimination of method requirements.

The number of testing labs has grown to more than 1600, many of which are collecting multiple state certifications in order to expand their revenue base. In general the laboratory community recognizes that individual regulatory agencies are simply too understaffed to serve as an effective monitoring body to screen out those laboratories who have crossed the line between modification and deviation. In many cases, even the resources that are available to serve in an enforcement role lack the level of training necessary to provide an accurate assessment of a laboratory's ability to consistently generate quality data.

This issue is not nearly as black and white as one would prefer. Data Quality Objectives vary considerable between projects, and there will always be situations in which the use of even grossly modified analytical methods would be acceptable, based on the needs of the project.

IMPACT ON DATA COMPARABILITY/DEFENSIBILITY

Comparability, one of the five DQOs identified by the EPA, refers to the confidence with which one data set can be compared to another. The goal of this aspect of data quality is to procure samples which are representative of the site during the field sampling activities, subsamples for analysis which are representative of the entire sample collected, and consistent, standard protocols for sample analysis and reporting the data. All of this, however, is dependent upon the ability to achieve equivalent precision and accuracy between testing laboratories.

Defensibility refers to the extent to which the data are able to withstand the scrutiny of the court. The general rule is that the most reliable data are those data that are generated following published analytical methods, and are further supported by extensive documentation that provides a complete audit trail of the analytical process.

For the client, perhaps the single greatest fear is the liability incurred when decisions are made that later prove to be based on invalid data. Erroneous decisions span the range between spending more than necessary for remedial activity to making inaccurate health risk assessments. Complicating this issue even further, under the current level of enforcement, invalid data is typically not discovered for months, or even years, after the data is generated.

The most obvious example of the effects of modifications occurs in cases where multiple laboratories are involved in testing for the same parameters at different locations within a large-scale site investigation. Frequently, samples will be "split" between two laboratories as a quality control check on the data being generated. Discrepancies between split samples are often related to minor differences in method protocols. Even the most seemingly obscure modification to a method can produce significantly different results from those generated using the standard technique. This makes it difficult to evaluate data, and re-sampling/analysis is often required. The question of who should bear the burden of these expenses becomes another issue. If it cannot be proved which results are in error, the client inevitably absorbs the costs.

In the event that analytical data are subpoenaed as part of the litigation process, the possibility exists that any modification can be raised as a factor which reduces the reliability of the data. If the reliability of the data is in question, the data may be rejected from inclusion in the record, and any subsequent decisions made based on these data be summarily dismissed as well. The intensity associated with legal depositions and expert testimony may well present one of the best mechanisms to reveal the detail associated with deviations from published method protocols.

MODIFICATION VS. DEVIATION

From a strict quality assurance perspective, even discussions about making modifications to methods is cause for concern. The grim reality, however, is that many of the published methods in use today have not been updated (save for minor typographical revisions) since their original promulgation many years ago. This remains the case despite the degree of technological advancement that has occurred over the same span of time. The laboratory community (and hopefully the regulatory community as well) recognizes the fact that few, if any, laboratories adhere to method protocols exactly as published. Consequently, we must learn to live with the fact that modifications are a necessary part of environmental testing, and focus on making the distinction between modifications and true deviations.

For the purposes of this discussion, a deviation is distinguished from a modification by virtue of meeting any one of the following qualifications:

- the modified method results in significantly different results as compared to data generated using the published method
- there is insufficient documentation to support the contention that the first statement is false
- the modification is not deemed valid by the governing regulatory agency

The first of these qualifiers is designed to evaluate the overall method in terms of the results produced. The term "significantly different results" can be interpreted as changes to precision and accuracy, the ability to achieve specific detection limits, the differential susceptibility to interferences, or even the interpretation of the resultant data. An example of a modification which fails to meet this criterion is the analysis of base/neutral and acid extractables using a single, neutral extraction. The ability to recover the acid components would be minimal at best, which in turn affects precision, accuracy, and detection limits. The second qualifier focuses on the documentation associated with the modification.

Using the example above, the value of performing a method validation study is to demonstrate the ability to effectively extract the compounds of interest. An inexperienced analyst, making this modification without the necessary documentation, may be unaware of the impact of the modification. The final qualifier is included because of the number of differences between state and federal as well as inter-state regulations. For example, the state of Wisconsin has recently enacted a suite of unique methods associated with the analysis of petroleum-related contamination, while many states remain receptive only to EPA method 418.1 (freon extraction/infra-red [IR] spectrophotometry). While GC fingerprinting techniques are valuable in that they provide qualitative identification of petroleum product types in addition to semi-quantitative estimates of concentration, these techniques are useless when regulatory action criteria are based on analysis using the IR technique.

Table 1 represents a summary of analytical method modifications, some of which are routinely employed, as well as the impact that they can have on the reliability and interpretation of results. It is important to emphasize the relevance of project DQOs in any discussion of the validity of specific modifications. If the purpose of the analytical testing is merely to provide field screening of samples to identify grossly contaminated areas, then those modifications that result in low bias and higher detection limits have no significance to the nature of the operation. Consequently, these modifications would be valid considerations for this level of DQOs.

As with most issues of similar stature, the line between modification and deviation is gray at best. Only after careful consideration of a number of factors can the distinction be determined. Unfortunately, there is no set of rules to adhere to, merely guidelines to follow.

VALIDATION OF METHOD MODIFICATIONS

If it is determined that modification to a specific method is either advantageous or necessary, the first step is to outline a plan to validate the technique and document the results obtained. While this process may seem labor intensive, (considering the intent of the modification is most likely to impart a measure of efficiency to the process) the quality and depth of the validation process can be vital if the data are eventually involved in litigation. It is also recommended that the laboratory or chemist attempt to obtain an opinion or approval from the regulatory agency involved. Resources such as the RCRA Hotline (800-424-9346) or the Method Information and Communication Exchange (703-821-4789) should also be consulted.

The validation program should be designed to evaluate precision, accuracy and detection limits both in the presence and absence of known or suspected interferences. In the first method modification listed in Table 1, the silica gel cleanup step is designed to eliminate co-extracted interferences from oils of a mineral or vegetable nature. Consequently, if the modification were only validated without evaluating the effects of interferences, method precision accuracy and detection limits would be equivalent to those appearing in the published method. If this same validation was performed in the presence of these interferences, significant bias would be observed.

In this case, if the validation process were sufficiently detailed, it is possible that a more specific process of filtration through silica gel could be identified with an interferent removal efficiency equivalent to that of the referenced method technique. The published method indicates that stirring 3.0 grams of silica gel in 100 mLs of freon for 5 minutes will effectively remove 100 milligrams of interfering hydrocarbons. An experiment could be designed which would determine the mass of silica gel which could consistently remove 100 milligrams of interfering hydrocarbons using only gravity filtration.

The determination of detection limits should be performed according to the EPA protocol outlined in Appendix B to 40 CFR Part 136. The determination of accuracy and precision is typically performed by spiking the parameters of interest at a level of approximately 10 times the nominal detection limit, but at a concentration that falls within the range of the calibration standards without dilution. For this process, most methods require the analysis of a minimum of 4 replicates, but the more replicates analyzed, the greater the confidence that the resultant accuracy and precision estimates are representative of the analysis.

Finally, one of the most important aspects of documentation is to include a summary of the modifications made to the published method within the standard operating procedure (SOP) for the method. This level of written documentation serves primarily to indicate the willingness to identify the modifications, and prompts the reviewer to evaluate (or inquire) whether or not the modification poses any conflicts to the Data Quality Objectives of interest. If a regulatory agency spokesperson or one of the resources mentioned previously was consulted, the advice received could be noted in this section as well.

SAFEGUARDING AGAINST THE CONSEQUENCES OF DEVIATIONS

Safeguarding against the consequences of significant deviations from referenced methodology is of interest to both the client and the testing laboratories. There is a broad spectrum of quality when the entire population of testing labs is considered. While there is certainly a niche for those labs whose operations are not firmly founded in quality control and quality assurance (QC/QA), there must be mechanisms which will ensure that these laboratories are viewed based on their ability to meet the DQOs rather than on the price of analytical services alone.

The enforcement branches of the various regulatory agencies have been actively pursuing litigation of labs performing fraudulent testing, yet the level of enforcement simply cannot manage the sheer numbers of laboratories. There are also a number of schemes in use which allow a laboratory to perform testing in a state without having to undergo a site audit. As an example, the state of South Carolina currently does not perform site audits outside the state. Consequently, a laboratory can obtain certification in a state such as Wisconsin, apply for reciprocal certification in the state of South Carolina, and perform work in that state without the trouble of an audit. This type of loophole would be eliminated by the initiation of a national accreditation program, which is currently under discussion by the EPA and several independent lobby groups. Such a program, however, would need to provide a means to distinguish between laboratories capable of producing only data of field screening quality and those capable of producing legally defensible data.

From the perspective of our clients, the main concern is that the laboratory they choose to contract with is capable of meeting the DQOs of interest. Most clients currently rely on the federal and state agencies to provide an evaluation of laboratory capability - in the form of state certification. More intensive educational programs are required to ensure that the clients are aware of the lack of detail associated with the audit process (in most cases) in order that they may consider a supplemental audit program of their own.

Our clients must learn that good results from the analysis of the WS and WP performance evaluation (PE) programs administered by the EPA is not in itself a testament of laboratory quality. Clients should be encouraged to request and review SOPs associated with analytical methods. They should further be encouraged to audit the laboratory to verify that the analytical and QC/QA procedures are performed as they are written in the SOPs and the QC manual. All too frequently, after an SOP is written, analytical training is passed from analyst to analyst, each generation providing a more dilute version of the SOP.

The role of the regulatory agencies must be to provide clear guidance regarding protocols. Efforts must be made to combine similar methods or identify equivalent techniques, in order that laboratories are discouraged from independently creating third generation methods. In addition, there is a need for a forum to identify and rapidly resolve ambiguities in the published methods. These ambiguities are the source of many unintentionally "modified" methods as laboratories attempt to interpret the method guidance.

Finally, there must be mechanisms to ensure that method performance criteria are achievable using the apparatus and conditions described in the method. A common complaint among laboratories is that method performance criteria cannot be duplicated, only to find upon thorough investigation that one or more aspects of the method was altered between the time it was written and the validation process.

SUMMARY

The issue of method modifications has far reaching consequences. The possible outcomes from the use of modified methods can ultimately include rejection of analytical data, should the modification(s) cross the line from modification to deviation. Unfortunately, this line cannot be drawn in black and white, which requires careful evaluation of any modification before incorporation into methods used for regulatory compliance.

Most modifications result from interpretations of ambiguous regulatory guidance, intent to incorporate advancements in technology, or attempts to perform analytical testing more efficiently in order to be more competitive in the price arena. The environmental community must be able to rely on the enforcement arm of the regulatory agencies to provide independent assessment of the suitability of these modifications. In order to achieve this, there is a need for more formal guidance from the regulatory side, more technical training for our clients, and better documentation from the laboratory community.

The need for modifications to published methods can never be eliminated, but we can generate a common set of guidelines to be followed in the event that modifications are required. Controls can also be established to ensure that only successfully validated modifications be employed, and that modified methods be consistent with the DQOs of concern.

Table 1: Some possible method modifications and resultant impact on the data generated.

Method	Modification	Impact
EPA 418.1	Modify removal of non-petroleum hydrocarbons by filtering extract through silica gel.	Insufficient contact time for removal of these interferences. Results may be biased high.
EPA 601/602 8010/8020 624 8240	Decrease purge time from 11 minutes to 4-5 minutes.	Purge efficiency will be proportional to volatility. Little or no effect on gases, or lighter volatiles, but higher molecular weight compounds (dichlorobenzenes, xylenes) may have lower purge efficiencies. This will result in low bias, higher detection limits, and increased carryover.
TCLP Organics	Reporting results when an MS/MSD is performed rather than a single MS. Recovery from MS = 10%, MSD= 90%.	Some labs will bias correct the data for 10%, others for 90%, and yet others based on an average of the two recoveries (50%). Depending on the specific analyte, some laboratories may report results as failing TCLP criteria, while others will not.
Test methods for Reactive Cyanide (7.3.3.2) and Reactive Sulfide (7.3.4.2). Chapter 7, SW-846	Modification of purge gas flow rate to improve analyte recovery/method performance.	These methods are recognized for typical recoveries in the 0-10% range. While modifying the method to improve performance would seem logical, quantitation is based on a specific flow rate. Making this modification will increase the potential for a given waste to either pass or fail reactivity criteria.
Trace metals-digestion techniques	Modifying initial sample size and final digestate volume to meet state-specific (e.g. Michigan) detection limits.	Beyond certain limits, the sample size to acid volume ratio may impact the digestion efficiency, leading to low bias. In addition, this modification, while effectively concentrating the analyte, also concentrates any interferences, rendering typical matrix modifier techniques less effective.
GC or GC/MS organic analyses	Substitution of capillary or megabore columns for packed columns.	In theory, capillary columns provide improved resolution and precision, and thus should produce data at least equivalent to data generated using capillary columns. Some states may not allow.
EPA method 418.1 (method 9073)	Perform extraction from solid samples using 5 minute sonication vs. 4 hour Soxhlet extraction.	Eliminates labor intensive step, reducing cost of analysis. Results may be biased low.
Organic methods	Allowance of one or more compounds to fail QC criteria in matrix spikes, or continuing calibration standards.	Data for analytes failing to meet method criteria may be associated with high or low bias. Ability to detect the analytes at specific levels may be in question.

19

LABORATORY AUDITING AS A QUALITY CONTROL PROCEDURE TO EVALUATE ACHIEVEMENT OF DATA QUALITY OBJECTIVES

Ian Phillips, Senior Environmental Chemist, GEI Consultants, Inc., 1021 Main Street Winchester, Massachusetts 01890

ABSTRACT:

On-site audits of environmental testing laboratories have been found to be an effective tool to assess the level of quality that a laboratory routinely produces as well as evaluate whether a laboratory can meet project or program data quality objectives. This paper will present the procedures and considerations that should be employed when defining the scope, contents, methodologies, and conclusions of an on-site laboratory audit.

On-site laboratory audits involve the review of the systems a laboratory employs to control the quality of the data reported. Laboratories frequently evaluate the quality of their data through the measurements of accuracy and precision. However, accuracy and precision alone are not adequate to evaluate the quality of the data generated. An audit allows the laboratory user to evaluate the quality of the data from the perspectives of reproducibility, comparability, traceability, and authenticity. Reproducibility and comparability are, theoretically, controlled by the employment of standardized methodologies. However, internally, individual laboratory employees may be performing test procedures in significantly different ways. In addition, the procedures and data acceptability criteria used by individuals may differ not only between employees but from published procedures and/or laboratory Standard Operating Procedures (SOPs). Traceability of the complete testing procedure employed, including the standards used, is critical to the future defensibility of data. Without the proper documentation, data may be rendered useless in litigation proceedings. Finally, an audit of a laboratory will aid in the overall evaluation of whether a laboratory is capable and committed to the production of data of sufficient quality to meet the data quality objectives of individual projects or programs.

Environmental testing laboratories provide critical data to industry, regulators, and environmental consultants. These data are used to make decisions relative to the nature and extent of contamination, regulatory compliance, risk assessment, and remedial alternative selection. Without proper quality controls by the data user, including the establishment of data quality objectives, the data generated may be found to be inadequate or unusable. The use of on-site audits is a very effective quality control technique to help assure that data are of sufficient quality to meet the data quality objectives of a project or overall program.

INTRODUCTION

To many end users of chemical testing data, the laboratory is a black box. Samples are sent and, three weeks later, a stack of paper comes back with

numbers printed next to a list of compounds of interest. The end user then compares these numbers to a Maximum Concentration Level or a clean-up goal, writes a report, and sends it off to the regulators. The question remains, however, "Is the quality of the data adequate for its end use?"

The US Environmental Protection Agency's document Data Quality Objectives for Remedial Response Activities (EPA, 1987) defines five levels of analytical quality for remedial investigations/feasibility studies (RI/FS). Levels IV and V are data of sufficient quality and documentation that the data may, without additional support, be used for litigation support, risk assessment, and regulatory compliance. Contract Laboratory Program (CLP) data are an example of Levels IV and V. The test methods and quality control (QC) procedures used to produce Level III data are generally similar to Levels IV and V without the supporting data that accompany a CLP package. Level III data are frequently combined with other data generated during a project to evaluate overall conditions and remedial options at a site. Levels I and II are for data generated in the field for screening or health and safety purposes.

The Data Quality Objectives (DQOs) of a project or a program should be defined and an appropriate level of analytical quality should be selected. However, as has been become increasingly apparent, simply requesting a level of quality does not assure that a laboratory will produce, or is even capable of producing, at that level. Without QC measures, such as laboratory audits, the data may be found to be found to be inadequate, unusable, or fraudulent.

This paper will present the procedures and considerations that should be employed when defining the scope, contents, methodologies, and conclusions of an on-site laboratory audit.

PRE-AUDIT PLANNING

There are three components to designing an effective laboratory audit:

- Define the audit objectives;
- Review the laboratory's Quality Assurance Program Plan (QAPP); and
- Prepare an audit checklist which incorporates the audit objectives and evaluates the laboratory's quality control procedures.

As stated previously, the audit's objectives may be specific to a project or general to a wide range of programs. The scope of the audit should reflect those objectives. For project specific audits, the auditor must carefully review the end use of the analytical data and what decisions will rely upon that data. In addition, project specific audits may allow the auditor to focus on a smaller portion of a laboratory's operations. For example, if a project objective is to determine the extent of volatile organics in the ground water at a site, a detailed audit of the inorganics laboratory would serve little purpose. Program audits are broader in

scope and are generally used to evaluate a laboratory's level of data quality.

Once the objectives and scope of the audit have been defined, it is critical to review a laboratory's QAPP. The information obtained from the QAPP will be the basis of some of the key questions posed to laboratory personnel during the audit. The critical points to identify in the QAPP are: 1) the quality control procedures employed, 2) the data tracking and review procedures, and 3) the data acceptance criteria.

The QAPP should state the quality control (QC) measures that are employed and documented for the routine testing procedures performed. The QC measures include holding times, preservatives, blanks, matrix spikes, duplicates, blank spikes, and/or surrogates. The QAPP should also state the frequency for each QC measurement. The frequency and QC acceptance criteria should be reviewed during the audit.

The procedures used to track and review the data should be clearly presented in the QAPP. It is important to determine if a laboratory documents the traceability of standards, instrument maintenance, instrument performance, and employee training. This information may be critical in later demonstrating that the personnel and equipment were operating under the proper conditions. In addition, the QAPP should identify how and by whom all data are reviewed. The levels, criteria, and frequency of the reviews should also be presented.

The documentation retained by a laboratory should be evaluated for completeness, both on the project level and the overall laboratory level. On the laboratory level, a laboratory's QAPP should state the criteria by which data are judged to be acceptable for release to the client. For example, data validators have CLP's Data Validation Guidelines to determine whether data are acceptable. A laboratory should have similar criteria established for all of the tests they perform. If this information is not presented in the QAPP, the SOPs for each test should be reviewed either prior to or during the audit. The absence of this criteria indicates that data acceptance is subject to each analyst's interpretation, and therefore, data generated may not be comparable or reproducible.

In addition, if it is available in the QAPP, the qualifications of the laboratory personnel should be reviewed.

After defining the scope of the audit and reviewing the laboratory's QAPP, a checklist should be prepared to reflect the issues that are critical to meeting the audit objectives. The checklist should be composed of questions that: 1) Verify the information presented in the QAPP, 2) Determine whether the laboratory personnel are following the QAPP and the SOPs, and 3) Evaluate the qualifications of the personnel performing the testing. In addition, the checklist should contain the questions that are included on a CLP audit checklist.

THE AUDIT

The audit involves the physical visit to the laboratory. The visit may be on an announced or an unannounced basis. Unannounced audits have the advantage of seeing a laboratory "under real conditions." However, "real conditions" may mean that key personnel may not be present or available. Generally, an announced audit is best for evaluating the overall quality of a laboratory. Unannounced audits are best used on a project-specific basis to verify that the data quality objectives of that project are being met. Unannounced audits are also extremely helpful in verifying that special modifications to methods, if required, are being performed.

The audit will verify the information provided by the laboratory and help evaluate whether the laboratory routinely performs testing of adequate quality to meet the objectives of a project or program. The contents of the audit will likely include a combination of the following:

- Observation of the facilities and equipment;
- Review of the laboratory files;
- Evaluation of the Standard Operating Procedures; and
- Personnel interviews.

Depending on the objectives of the audit, the contents of the audit may focus more heavily on one or more of the subjects presented above.

In observing the facilities and equipment of a laboratory, the auditor should consider the amount of work space available, the duplication of instrumentation, the maintenance records of the equipment, and the overall cleanliness and organization of the laboratory areas. The available space and the duplication of instrumentation are particularly important as they control, along with the experience of the personnel, the volume and efficiency of the laboratory.

The quality assurance (QA), individual laboratory area, and the project files should be reviewed during an audit. The QA files should be reviewed to verify that the quality control measures specified in the laboratory's QAPP are being performed and meeting the laboratory's criteria. For example, any control charts, method detection limit studies, corrective actions and anomalies should be reviewed. In addition, many QAPPs state that reports to management are made. The auditor should request to review these reports as they will provide an internal picture of the laboratory's commitment to its own QA program.

The files from each laboratory area should be reviewed in order to evaluate the traceability of the data generated. Each laboratory area should have, at a minimum, files tracing the preparation and sources of all standards and spiking solutions, the daily temperature logs of all sample storage refrigerators, and balance calibration logs.

The project files should be reviewed for their contents and completeness. Project files should contain all of the information relevant to the testing performed. The relevant information should include copies of the chain of custody, the final data report, the sample preparation data, and any instrument output. Project files may also contain calibration and method blank information. If calibration is not included in the file, the location of this information should be referenced.

An effective method to evaluate the files is to select a final sample extract and request all of the documentation used to generate the final report for that sample. The laboratory should be able to generate the information referenced above, the standards used to generate the calibration, the stocks or neat material used to make those standards, and any other information used by the laboratory to meet their data acceptance criteria. All data should be traceable back to the original standards. If the quality of the standards cannot be confirmed, the basis for all quantitation is undermined.

The details of the methods performed in each laboratory should be documented and available for review. During the audit the presence of the SOPs should be verified, and laboratory personnel should be questioned about their contents. The use of SOPs is a critical component of a laboratory's ability to generate reproducible and comparable data. If possible, more than one employee from each area should be asked similar questions concerning the SOP for that area.

Throughout all of the steps of the audit, the auditor is interviewing laboratory personnel in an attempt to evaluate their knowledge and experience, their understanding of the SOPs and the QAPP, their understanding of the methods, and their commitment to the quality of the data. The nature of their responses gives a good indication of the DQO level of the data routinely generated.

As stated previously, the personnel from each laboratory area should be asked about the contents of the SOP. In addition, where applicable, personnel should be asked what makes the data acceptable. If different answers are received from two employees in the same area, then the SOP and/or QAPP is not being followed by at least one of the employees and perhaps both.

Personnel should also be asked hypothetical questions due to the data interpretation problems often presented by environmental samples. While no "right" answer may be available, the auditor will get an excellent indication of how decisions are made and the level of experience of the personnel. This type of question is particularly important for tests that involve significant analyst interpretation, such as pesticide and PCBs as well as many inorganic tests.

CONCLUSION

In evaluating the overall quality of the laboratory, an auditor should review the contents of the completed checklist with the DQO of the project or program in mind. Based on the audit, the auditor should be able to answer the following questions:

- At what EPA DQO level is the laboratory routinely performing?
- Is the quality of the data traceable, well documented, and defensible?
- Do the personnel have the right types of experience for the project or program?
- Can they meet the data quality objectives of the project or program?

SUMMARY

Laboratory audits can be a very powerful quality control tool to evaluate whether the data are of sufficient quality to meet the objectives of a project or program. Auditing can help prevent the data generated from being found inadequate or unusable.

REFERENCES

U.S. Environmental Protection Agency (1987). Data Quality Objectives for Remedial Response Activities, EPA 540/G-87/003, March.

U.S. Environmental Protection Agency (1988). Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, February.

U.S. Environmental Protection Agency (1989). Preparing Perfect Project Plans, EPA/600/9-89/087, October.

20 TOTAL QUALITY MANAGEMENT IN THE ENVIRONMENTAL LABORATORY

F. Joseph Unangst, Vice President, Galson Laboratories, A Division of Galson Corporation, 6601 Kirkville Road, East Syracuse, New York 13057

Abstract: Environmental service laboratories are under extreme pressure to improve performance, but many forces militate against such improvements. For example, the industry requirements for holding times and report turnaround, marked with excessive penalties, place managers in a position that threatens them to compromise ethical practices. Seasonal fluctuations in workload and increased competition provide an unstable pricing scheme. Multiple certification programs and regulatory requirements make standards variable and often confusing. Knowing all this, environmental professionals face special challenges in choosing a laboratory that invokes confidence.

One way to facilitate such a choice is to investigate a laboratory whose principles include Total Quality Management. Total quality begins with sound ethical practices. Ethics are defined through guiding principles that can be used to evaluate the laboratory's performance. Next, management personnel must commit to the Total Quality Management (TQM) process. The "cost of quality," as well as its returns, must be demonstrated to top management to get this commitment.

A TQM program begins with organizing a quality improvement team. This team works to design and implement the program. The program typically consists of quality awareness training, supervisor training, quality teams, and employee recognition. The process requires a new behavior that stresses constant improvement, ends the dependence on mass inspection, continually improves service and production, emphasizes training, replaces management with leadership, and elicits total employee involvement.

The Total Quality Management system works in the environmental laboratory industry just as it demonstrably has in numerous other industries. It may be the only philosophy that will assure a company of succeeding in this difficult business. The stresses encountered become opportunities to improve. This paper describes the application of a quality improvement process to a service laboratory. The paper outlines how changing a way of doing business is the only way to remain competitive and cost-efficient.

INTRODUCTION

The environmental laboratory industry is under extreme pressures to provide service to its customers. The industry is subject to a significant number of competing demands that may have caused a few laboratories to compromise their integrity. The most pronounced pressures include:

- **Sample Holding Time.** This is undoubtedly the most pressing time constraint, where failure to meet the holding times results in suspect or lost data, with potential resampling required.

- **Report Turnaround Time.** This is a frequently neglected yet critical customer requirement.

- **Regulatory Requirements.** These include data report formats that often change, variable QC requirements that depend on which regulation the samples fall under, and variable QA requirements that depend on both regulations and specific customer requirements.

- **Workload Fluctuations.** Included in this are decreases in work due to the winter in several regions, the loss of work to competition, or the termination of periodic contracts. Also, work may increase dramatically because of any of the following factors: project delays that later cause project overlap, the use of sales persons who are paid on a commission basis, management overbooking work, and uncontrolled change of project scope.

- **Competition.** Increases in competition occur during slow winter periods, when large laboratories attempt to use price to maintain base workloads, and during recessionary times.

- **Staffing.** The environmental laboratory business is a young industry with typically younger management and staff with less than 10 years' experience. The rapid growth of the business has caused a shortage of people trained in performing the work. Younger people are usually more mobile and more difficult to retain.

- **Penalties.** The penalties associated with missed holding times or late reports have the unfortunate side effect of potentially undermining ethical

practices, which has been widely publicized in our industry. The penalties may be tied to lateness of the final report, which promotes poor report quality.

These demands placed on the environmental laboratory make it an excellent proving ground for Total Quality Management. The reasons for implementing a TQM process are very clear. It is very profitable due to the ability to demand higher prices for quality services in a free market and because it is less expensive to do things right the first time. It also creates and preserves jobs through increasing business and making the laboratory financially stronger. Lastly, it's the right thing to do - the customer deserves this as a covenant of ethical business practice.

The TQM process begins with the highest level of management being committed to sound operational principles, or guiding principles.

SETTING THE GROUNDWORK

Management Commitment. The TQM process cannot be delegated from the top. This is not something the CEO or President can give to the Quality Assurance group to implement. If the person at the top echelon in your organization is not involved and committed to providing quality laboratory services and you are not one of those two people, do not waste your time attempting to implement total quality. It will not work. It is capable of working in somewhat autonomous divisions or groups, as long as the head of the group or division is committed and not pressured to do otherwise by the next higher level of management. Otherwise, you must abandon any efforts until you get the commitment from the top.

This commitment can often be attained by presenting to top management the cost of not implementing a TQM program. According to a 1989 American Society of Quality Control survey, this cost averages 35 percent of gross sales lost in the service industry.

Individuals in top management must understand this is a business proposal with unequaled return on investment. Their commitment must be visible, relentless, and educated. They must know and accept that the quality process will involve a change in corporate culture.

Quality Service Principles. Roy Disney once said "decisions are easy when values are clear." When every employee

understands the principles under which the laboratory operates, they become capable of making decisions on their own. In developing guiding principles, the people in the laboratory gain the responsibility to perform according to the principles. However, they must also be given the authority to do so.

As an example of responsibility being equal to authority, in a laboratory where the customer service policy states a service objective of a satisfied customer at the end of every transaction, management must allow the customer service person to take any step necessary to solve customer problems, arrange a quick satisfactory resolution, or a prompt refund or credit.

The principles must be clearly understood and accepted by everyone.

The principles should stress the basic fundamentals of total quality service: focus on the customer, put quality first, show continuous improvement and innovation, consider people our greatest asset, encourage total employee participation, foster training and education, communicate clearly, demonstrate integrity, employ teamwork, and be profitable.

These principles set the rules for becoming a world-class quality operation. The principles should be reviewed periodically to determine their continued relevance, allowing for amending them, deleting some, or supplementing them, as circumstances warrant.

The Mission. When the principles are in place, the laboratory can embark on its mission. This is an area that requires a lot of soul-searching to determine what you want to be as a laboratory. For example, you may want to become the largest laboratory network in the United States, you may want to be most renowned for quality, you may want to be the most expeditious, you may want to be the best RCRA laboratory. You must define what you are in clear and precise terms so that **everyone** in the laboratory unmistakably understands the mission.

If the mission statement will not fit on a business card, it is too long. Everyone must be able to recite and accept the mission as his or her own.

The mission and principles can be developed through committees made up of employees from all levels and divisions. The principles and mission lay the groundwork for implementing a Total Quality Management.

IMPLEMENTATION

Implementing a TQM laboratory system is not as difficult, as expensive, or as slow as many consultants or opponents may lead you to believe. The initial step is to develop a Quality Improvement Team (or any other name you may want to call it.) The make-up of this committee must include high-level managers from all divisions, or sections, who are committed to the process. Again, this is not something that can be delegated. This committee will have been involved in setting the groundwork through its involvement in developing the principles and mission.

These team members must fill themselves with knowledge of the quality processes. They must educate themselves on the available resources for accomplishing the goal of integrating the new philosophy into the business culture. Much of the knowledge can be learned quickly through networking with others who have implemented similar systems. Consultants are an expensive alternative that should be used only if the initial level of understanding is minimal or if urgent implementation is required.

The Quality Improvement Team determines how to implement the quality concepts. The program has these basic components: total participation (including top management), leadership training, making authority equal to responsibility, quality system structure, communication, training, measurement, and recognition. More components may be necessary, depending on the individual circumstances.

RECOMMENDED STEPS

The implementation should not be a volunteer program; **everyone** must be involved in a quality team. In order to get everyone involved, a series of steps should be taken to allow rapid, effective implementation. If the following approach is taken, the benefits of implementation will be realized almost immediately.

Communication to all employees is vital during initial and all subsequent stages of TQM implementation. There will be a lot of ambitious employees who will want everything to be in place immediately. The implementation team must manage the emotions of the cultural change by keeping everyone informed. The team must tell people the steps to be taken and the approximate time to implement them (this time frame should be realistic, allowing extra time so that people do not get discouraged).

The initial presentation to the company is critical and demands special care and excellence. Explain the move toward quality; prove that quality will preserve jobs through improved profits and increased market share. It must be stressed that a quality process is not being undertaken to fix the errors the nonmanagement people have been causing in the past. Management must take responsibility for past errors and realize people have known how to do things right all along; management just hasn't allowed them to fix it. Finish with a statement that describes the quality process as an opportunity for the laboratory to improve together as a team.

Whatever you do, keep the plan simple. The entire implementation can be accomplished using just four steps. The concepts are simple and the approach is simple; keep it that way.

Step One: Provide Quality Awareness and Leadership Training to Top Management and Supervisors. The people most affected by the new cultural change will be the supervisors. The supervisors will be required to change the way they have done business to date. They will be asked to make decisions based on input from everyone who works for them rather than being the person who makes all the decisions. This is the most difficult cultural change. Supervisors who have worked for years as nonsupervisors under the old system of being told what to do are now not allowed to tell their subordinates what to do. In their eyes, they have lost out on a good thing. The fact is it wasn't a good thing when their supervisors did not listen to them and they will now be part of the new culture of participative management.

Because of this significant change in responsibility, supervisors must be a vital part of the process of implementation from the very beginning. We must remember that the supervisors are usually the most experienced people, they must be protected, and nurtured into the new system. A laboratory cannot afford to lose these people. This radical change may frighten supervisors; consequently, their involvement will help to allay those fears.

The quality awareness training can be as little as four hours or as many as twelve hours. In the environmental laboratory business, most people are well educated and already familiar with the scientific method, which is a significant portion of the awareness training. The awareness training should touch on the various tools of problem solving, the quality improvement process, statistical process control, and the history and success of TQM. Awareness should also stress that this is the

new way of doing business; everyone will be responsible for making it happen.

The supervisors and top management will also require leadership training. Since everyone in the company will be required to be on a quality team, team leaders will be needed. The team leader role is most easily and best filled by current supervisors. In order to prepare the supervisors for their new roles as team leaders, a training session on how to conduct participatory meetings will be required. This can be done out of house (check your local community college for an economical alternative to consultants) or developed as an in-house course.

The awareness training for supervisors will teach them in-depth, as team leaders, to take their teams through the systematic problem-solving process. This includes analysis of problems, brainstorming, reaching consensus on solutions, planning and implementing solutions, and evaluating results. By teaching supervisors in-depth techniques for quality improvement through teams, they will be able to disseminate the process to all people in the lab.

The leadership training is extremely important for both top management and supervisors to assure the long-term success of the laboratory as well as their own personal success. Leadership training shows the new team leaders they must move from "management," where people are controlled, to "leadership," where people are motivated and inspired to participate. The managers must learn to respect their employees, listen, solicit ideas, and realize everyone can think as an adult. The managers must trust employees in order to gain their trust.

Once the proper training for team leaders and top management is in place, begin to train everyone in quality awareness.

Step Two: Quality Awareness Training for Everyone. If the leadership training has been successful, nonsupervisory employees will have realized some differences in their managers and will be very eager to participate in the training. Many will begin to orient themselves to the quality process once they realize management is serious about implementing it.

The quality awareness training for nonsupervisors can be as little as four hours per employee if sufficient materials are available for them to refer to when they begin functioning in their team.

Awareness training will be similar to (but less detailed than) the supervisors' awareness training. This is possible if you are using your previous supervisors as team leaders. The team leaders will use team meetings to do more in-depth training on problem solving with real laboratory situations.

The approach of in-depth problem-solving training by the team leaders provides an excellent, cost-effective way to train a large number of individuals while gaining benefit from their experience.

Step Three: Assign Everyone to a Quality Team. The teams should have eight to twelve people. Everyone is required to be on a team, even the CEO. There may be more supervisors than you need team leaders. That will be all right; use extra supervisors as facilitators of slightly larger teams (maybe 13 or 14 people). Everyone on the team at first should have a common interest in the assignment (e.g., for GC/MS volatiles, make the whole group a team). This is the least disruptive way to implement the process.

Teams will realize they need input from other areas to solve their problems (e.g., sample management, sales or report generation for the GC/MS volatiles team) and people will trade positions on teams in order to get the diverse input they need. The composition of teams will develop over time into multidisciplinary, multilevel units.

The teams are now given the responsibility to improve the operation of the group by use of the quality improvement process. Since they are given the responsibility, the rules of the quality system provide them the authority to make the changes to improve the processes. Decisions of teams should be presented to management if the team feels it is making a recommendation to expend resources or money beyond its level of responsibility. Typically, in this case, the financial officer has already been brought into the team for cost decisions.

Keep in mind the entire quality improvement process and all of its tools are not needed in every case. If someone suggests we stop doing something that is obviously serving no purpose, and nobody that still works here knows why we are doing this, then just stop doing it. Typically, these things we were doing that served no purpose will have no identifiable customer. There is no need in these cases to use the six-step problem-solving process; in some other cases, an abbreviated problem-solving process may be used.

The quality team meetings should be totally focused on quality. The team should have a top priority for everyone, and the decisions that result from the teams must affect the members. At the meetings, promote ideas that save time or money or that reduce stress.

Benchmarking is an important tool for problem solving. Benchmarking can be done elaborately, which will pinpoint where the laboratory is with respect to a problem or service. On the other hand, benchmarking can be done less formally, as a communicative tool that obtains information from your peers and competition on how to solve problems or improve performance. People are often generous in **sharing** data (this means you also must share some insight). This can be a very quick and inexpensive problem-solving tool and should become a mandatory part of quality improvement teams.

Step Four: Support the Program. The ultimate support of the program has to come from the top. The ways in which the program is supported include recognition, maintaining a high-level overseer, communication, measurement, and making it permanent through a documented quality system. The highest levels of management must be involved with the support of the program.

Recognition can take many forms, formally and informally, publicly and privately. Forms of recognition can be simple thank-you's, buying having doughnuts, gift certificates, providing plaques, parties, monetary rewards. The system of recognition needs to be imaginative and sincere. The recognition, reward, and gratitude must be ongoing and reach the person in a way that he or she appreciates. Different people have different ways in which they feel appreciated, so it is best to use many different methods or to ask the individual what they like. The recognition or reward should not be an incentive; it should be a thank you.

The support of the team process should be overseen by a quality chief, the highest level person possible. This person is solely responsible for making the quality process work. The person needs to understand the quality concepts and assist the team leaders. The chief is required to monitor the progress of the teams and report to the President or CEO.

Communication is one of the guiding principles and should be used to support the quality team concept. All employees should be aware of the progress of the teams' and laboratory's performance based on some simple, consistent indicators. An internal newsletter, a "quality" bulletin board, a "quality"

voice-mail box (for all to listen to), or periodic whole-lab meetings can be used us avenues of TQM communication. These allow the teams to share ideas and to be reinforced that the process is working.

Measurement supports the process. But only measure things that will help generate more ideas or show progress. Initially look at the number of ideas generated and implemented and the dollar savings of the implemented ideas. You may also look at the time savings generated. The quality chief should be ultimately responsible for communicating the measurement results to everyone.

The most important step in maintaining the program is to document the quality system. This documentation (the Quality Manual) should state your policies with respect to quality and customer service as well as your mission and principles. It should clearly state the connections between the quality program, the quality teams, the quality assurance functions, the quality control functions, quality training, and responsibilities for quality. This document becomes the standard operating procedure of the TQM process. It is used to audit your performance with respect to the quality process and to orient new employees to the process.

A Final Note on Implementation: Keep it simple, keep it exciting, keep reviewing the process for improvement, and keep in mind you will all make mistakes in the transition. Say you're sorry when you make a mistake, accept other's apologies. If you're upset with someone, allow them the benefit of the doubt and believe they made a mistake. Ask them. Communicate.

SUMMARY

Total Quality Management will work to help control the competing demands faced by the environmental laboratory business. The answers to the problems will come from within, from the people who perform the work day in and day out.

TQM will require a cultural change that must originate from a highly committed and actively supportive top-level management team. From this process will come guiding principles that address all of the concepts required for a totally participative, customer-focused, improvement-oriented, highly motivated team of employees.

The implementation of TQM can be very simple and inexpensive, wherein benefits are realized almost immediately. Getting

supervisors involved in the implementation is critical for success. Assuring 100 percent participation throughout the laboratory is also a vital component.

After initial planning, implementation involves these steps:

Step One: Provide Quality Awareness and Leadership Training to Top Management and Supervisors.

Step Two: Quality Awareness Training for Everyone.

Step Three: Assign Everyone to a Quality Team.

Step Four: Support the Program.

TQM is a dynamic process that will remain a part of the laboratory forever. As long as the process is communicated well to everyone and the team leaders are held accountable for the progress of their teams, the results will be phenomenal.

The new business arena is demanding total quality. To simply **survive** in this demanding business will require the use of TQM. To master the philosophy will earn the laboratory competitive dominance.

21

DESIGNING AND IMPLEMENTING A REPRESENTATIVE SAMPLING AND ANALYSIS PLAN FOR PCBS IN NON-HOMOGENEOUS INDUSTRIAL SCRAP.

A FIELD SAMPLING AND LABORATORY ANALYSIS CASE STUDY

David N. Speis, Vice President and Director, Quality Assurance and Technology, ETC Corp. 284 Raritan Center Parkway, Edison, NJ 08818-7808; Marilyn P. Hoyt, Principal Technical Consultant, ENSR Consulting and Engineering, 35 Nagog Park, Acton, MA 01720

ABSTRACT: Characterizing non-homogeneous industrial scrap originating from recycling operations for chemical compounds of environmental concern typically poses many difficult field and laboratory challenges. Foremost among these are defining the entity to be characterized, developing representative sampling techniques, and selecting appropriate analytical methodology.

These challenges were the central issues of a recent dispute between the United States Environmental Protection Agency and a scrap metal recycling firm. The firm's business activities involved the purchase of obsolete electronic components and scrapped computers from the primary equipment manufacturer. The purchased material was shredded, incinerated to remove organic material, and smelted to reclaim gold and other precious metals.

An investigation by EPA into the environmental implications of the operation indicated the presence of high concentrations of polychlorinated biphenyls (PCB). The company disputed the findings of the PCB investigation, citing the sampling and analytical techniques used for the investigation as non-representative and subject to false positives caused by interferences. In the firm's estimation, these procedures provided a distorted view of the PCB content of the various industrial scrap piles.

At the request of the company and with the agreement of EPA, a unique field sampling and analytical scheme was designed to address these issues. Specific quality control procedures were employed during sampling which enabled the investigators to determine field precision and accuracy. Routine laboratory QC procedures enabled the investigators to assess laboratory precision and accuracy. Overall method performance was evaluated through the use of performance spikes that were also analyzed by an EPA selected referee laboratory using traditional analytical techniques.

The use of these procedures provided data that enabled the company and the government to obtain an accurate and representative assessment of the PCB content of the scrap. The data was then used to make confident decisions on the ultimate fate of the scrap material.

INTRODUCTION AND BACKGROUND: Appropriate field sampling and laboratory procedures are key to providing representative analytical data on chemical compounds of environmental concern in non-homogeneous solid matrices. These procedures were the central issues in determining if polychlorinated biphenyls (PCB) in electronic scrap posed a hazard to human health and the environment as defined under terms of the Toxic Substances Control Act (TSCA).

A scrap metal recycling firm had purchased obsolete electronic components and scrapped computers from primary manufacturers for precious metal reclamation. This discarded material was transported to a shredding and storage facility owned by the firm for processing.

The firms shredding and storage facility occupies a 6.5 acre site adjacent to a tidal river. All scrap material arriving at the site was shredded using an industrial automobile shredder and stored on site in discrete piles, organized according to source, until its precious metal content could be determined. Once an assay of the shred had been completed, the material was incinerated to remove organic material. The resultant ash was transported to a remote smelter for the reclamation of gold and other precious metals.

In December 1986, the USEPA conducted a field inspection of the facility. Samples were collected and analyzed using CLP methodology for pesticides and PCBs. Non-representative grab sampling procedures were employed for sample collection. The analysis performed by the USEPA indicated that PCB concentrations in the scrap exceeded the 50 parts per million (PPM) standard established by USEPA regulations. At the time the field inspection was initiated, there were twelve (12) piles of shredded material on the site ranging in size from 100 tons to 1500 tons.

The results of the USEPA analysis were not accepted by the metal recycling firm which contended that the scrap was not representatively sampled and the PCB values were biased by positive interferences. A consent decree regarding the dispute was eventually negotiated between the firm and the USEPA. As part of the consent decree agreement, the firm agreed to perform a remedial investigation which was designed to overcome the sampling and analysis limitations of the initial USEPA study.

The overall objective of the investigation was to determine the PCB content of the twelve (12) electronic scrap piles and the underlying ground cover (consisting primarily of scrap pile residues and some soil) at the site. The analytical objectives of the investigation were to 1) develop and apply a scheme for representatively sampling the non-homogeneous electronic scrap and 2) determine the PCB content of the scrap using GC/MS methods which would not be affected by positive interferences. The data from the investigation was to provide the basis for determining the remedial solution to be applied to the electronic scrap as dictated by the terms of the consent agreement.

ESTABLISHING DATA QUALITY OBJECTIVES (DQOs): Establishing DQOs were essential to the planning process for this investigation. The remedial investigation objective focused on obtaining an accurate PCB value for each scrap pile which was representative of its true PCB content. This value would be used to determine if specific scrap piles exceeded the 50ppm TSCA limit. All field sampling, sample analysis, data collection, reporting and validation activities were designed to be consistent with this objective.

Several sampling and analysis concerns were identified by EPA and the recycling firm which would impact the ability to achieve these objectives:

* The scrap piles ranged in weight from 100 to 1,500 tons. Development of an adequate, representative sub-sampling approach for this size scrap pile was required.

* The scrap material consisted of particle sizes which ranged from dust sized organic polymers particles to grapefruit sized chunks of steel. Procedures had to be identified which assured homogeneity of laboratory sample aliquots.

* Effective cleanup procedures had to be identified and incorporated into the sample preparation scheme which eliminated interferences from polymeric material likely to be co-extracted along with PCBs.

* Previous PCB analysis used pattern recognition techniques for qualitative and quantitative identification. This may have resulted in elevated concentrations because of interferences calculated into the final results. Confirmatory techniques had to be incorporated into the final analysis to ensure that false positives did not occur.

Specific control parameters were incorporated into the project plan that would enable EPA and the recycling firm to determine if the sampling and analysis objectives had been achieved and the data was satisfactory for addressing the objectives of the remedial investigation.

FIELD SAMPLING: The sampling procedures used for this investigation were designed to obtain a representative sample of each scrap pile which could be analyzed to determine the true PCB content and distribution. The sample protocol used for the electronic scrap piles was based on a hexagonal sampling design which has been developed by the USEPA for PCB site cleanup[1]. The objective of this design is to obtain a representative characterization of the scrap pile by collecting and analyzing a large number of samples. A hexagonal grid is projected onto a sampling circle which is centered on the scrap pile, has a radius which extends to the pile boundary and encompasses the entire pile. A site map (Figure 1) depicts the position of each scrap pile.

For this project, each scrap pile was flattened to a depth of four (4) feet. The diameter of the scrap pile was measured and a scaled diagram of the pile was plotted on graph paper. The actual radius of the sampling circle which encompassed the scrap pile was measured. The number of samples to be collected from the sampling grid was determined based on the radius of the scrap pile as indicated in Table 1.

Table 1

Scrap Pile Radius, r(ft)	Number of Samples
≤ 4	7
> 4 - 11	19
> 11	37

The radius of all flattened scrap piles exceeded eleven feet in this investigation. A sample grid for the scrap pile was constructed. The center point of the grid is the center of the sampling circle. The distance between sampling points becomes a function of the circle radius. The distance between sampling rows is also a function of the circle radius. These distances were determined using Table 2.

Table 2

Number of Samples	Distance Between Adjacent Points	Distance Between Adjacent Rows
7	0.87r	0.75r
19	0.48r	0.42r
37	0.30r	0.26r

The sampling points were initially plotted on the scrap pile diagram before being transferred onto the scrap pile. Each grid location was marked with a wooden stake and labeled with a unique sample point code. The sample points for each row were staggered midway between the points of the adjacent row. Core samples were collected at each of the designated points on the sampling grid using a power auger and composited in pre-cleaned 55 gallon drums.

The power auger and shovel were steam cleaned prior to collecting any samples and between different scrap piles. The condensate from the equipment steam cleaning step was collected in separate sample bottles and extracted for PCBs. The condensate extracts were stored at 4°C until the PCB content of the previous sample and the next sample had been determined. If the PCB value for the previous sample contained PCBs and the next sample contained PCBs at concentrations >50ppm, the condensate extract was analyzed to determine if PCB cross contamination occurred during the sample collection step.

SAMPLE PROCESSING AND HOMOGENIZATION: The composited sample borings from each scrap pile were processed through a Hammer Mill and a Rotary Shear for homogenization and particle size reduction using continuous flow-trough processing procedures. This process was performed separately for each pile to ensure that its integrity was maintained during this process.

The collected samples from all grid locations in a specific scrap pile were composited and weighed. These composited samples were processed through the Hammer Mill for further size reduction (approximately 2000 lbs of material).

Occasionally, large un-millable metal chunks were found in the shredded scrap sample. These chunks were manually removed from the granulated scrap sample prior to Hammer Mill processing. The weight of this material and its PCB content was accounted for in the final PCB concentration calculation.

The un-millable scrap was placed into a previously weighed, wide mouth, 2.5 gallon glass jars. The jars containing the scrap were re-weighed and the weight recorded. These jars were transferred to the laboratory for extraction and analysis.

The entire sample from the Hammer Mill was continuously transferred to a Rotary Shear for final particle size reduction. A ten percent sub-sample of the granulated material was withdrawn from the Rotary Shear using a built-in continuous sampler. This sub-sample represented ten percent of the original sample (approximately 200 lbs.). The scrap sample at this point was reduced to small particles with a maximum particle size of 1/4 inch which had a consistency resembling potting soil.

The sub-sample was coned and split into two equal portions. Each sub-section was coned and quartered until the remaining sample was sufficient to fill two eight ounce jars. Duplicate sub-samples were collected to determine the precision of the homogenization technique.

Residual contamination of the shredding and milling equipment was possible during the sample homogenization process. Conventional decontamination procedures could not be employed between samples for this equipment because of equipment's size and the difficulty accessing the contact surfaces.
To decontaminate the milling and granulating equipment between processing of each sample pile, all sample material was removed from the Hammer Mill and approximately two mill volumes (7-8 cubic feet/volume) of previously analyzed cleansing sand was processed through the machine. A ten percent aliquot of the processed cleansing sand was collected using the continuous sampler. Eight (8) ounce sampling jars were filled with aliquots of the cleansing sand. Each sample aliquot was labeled and retained for PCB analysis to verify the absence of cross contamination between processing episodes if needed.

FIELD QUALITY CONTROL: A field sampling quality control program was employed to insure that all field samples collected for analysis adequately represented each scrap pile. Table 3 defines each of the field QC checks which was employed for this investigation. The duplicate aliquot precision criteria is detailed in Table 4.

Table 3
Field Quality Control Checks

Field Blanks: PCB free reagent water was provided to the field technicians by the laboratory and was transferred to an additional clean sample container while at the field sampling location. Field blanks were used to evaluate environmental and procedural effects of the sampling event and to determine if cross contamination occurred during sampling. These blanks were analyzed for PCBs only if PCB cross contamination was suspected to have occurred during the sampling event.

Equipment Rinse Condensates: Prior to collecting samples from any scrap pile, the field sampling shovel and the auger were steam cleaned. After sampling each scrap pile, the shovel and auger were steam cleaned again. The condensate from the steam cleaning was collected and analyzed for PCBs to ensure that cross contamination of equipment did not occur between scrap pile samplings.

Field Duplicates: Duplicate samples were collected from all scrap piles by rotating the 37-point sampling grid to permit sampling of points adjacent to those points used for the first collection. The sample collection process was repeated on the adjacent points. These samples were homogenized, analyzed and evaluated to determine the precision of the sampling procedure.

Duplicate Aliquots: Duplicate aliquots of each scrap pile sample were collected in the field following the coning and quartering step. The duplicate aliquots were analyzed as separate samples and evaluated to determine the precision of the homogenization procedure.

Table 4
Precision Criteria for Field Quality Parameters

Duplicate Aliquot Precision:

Parameter		Relative % Difference
Total X PCBs (Aroclors)	> 40ppm	≤ 50
Total X PCBs (Aroclors)	10 – 40ppm	≤ 100
Total X PCBs (Aroclors)	< 10 ppm	Detected*

Field Duplicate Precision:

Parameter		Relative % Difference
Total X PCBs (Aroclors)	> 40ppm	≤ 50
Total X PCBs (Aroclors)	10 – 40ppm	≤ 100
Total X PCBs (Aroclors)	< 10 ppm	Detected*

* Detected PCBs apply to concentrations below the quantitation limit that are capable of being qualitatively identified. Less accurate quantitative values can be assigned to these PCBs based on extrapolation of the calibration curve. Detected PCBs must be present in each sample of the duplicate pair.

ANALYTICAL METHODOLOGY: The analytical method used for this investigation is based on USEPA Method 680.[2] The method provides procedures for the determination of polychlorinated biphenyls in electronic scrap samples by gas chromatography/mass spectrometry (GC/MS) using full mass range scanning or selected ion monitoring (SIM) for additional sensitivity. The method is applicable to PCBs that occur as Aroclor mixtures or as single congeners. Identified PCBs were measured and reported as the commercial Aroclor mixtures 1242 or 1254 when sample congener patterns match those established for these two specific products. PCB concentrations were also identified by isomer group depending upon the level of chlorination.

A 100 gram aliquot of homogenized electronic scrap was soxhlet extracted using hexane:acetone. An aliquot of the solvent extract was concentrated to 10ml. The sample extract was washed repeatedly with Sulfuric Acid to remove non-aromatic hydrocarbon interferences. PCB mixtures and other extract components were separated by capillary column gas chromatography and identified by low resolution, electron ionization, mass spectrometry (GC/MS). The GC/MS was operated in the full scan mode for this investigation. The GC/MS can also be operated in the selected ion monitoring mode (SIM) if lower detection limits are desired.

Three surrogate compounds were added to the sample before sample preparation to monitor method performance. Three internal standards were added to each sample extract prior to GC/MS analysis and used to calibrate MS response and serve as retention time markers.

PCBs were identified and measured as Aroclor mixes 1242 or 1254 when the pattern observed matched that for standards of the commercial mix. Selected peaks for individual congeners in the sample were compared to those peaks in standards of the commercial mixes. The polychlorinated biphenyl content of the samples was also calculated as isomer groups (i.e. total dichlorobiphenyls, total trichlorobiphenyls, etc). PCB concentrations were calculated for each level of chlorination and summed together to obtain the total polychlorinated biphenyl concentration. These values were compared to The Aroclor results data to determine whether a concentration bias occurred at the detection limit and at the upper concentration limit of the calibration range.

ANALYTICAL QUALITY CONTROL: Quality control systems were incorporated into the analytical method to ensure that valid qualitative and quantitative data was produced during the analysis of field samples. Ongoing internal QC checks were routinely performed during sample analysis to assure that method systems were in control.

Table 5 details the laboratory QC checks used for this project. The data from these checks were used by the analyst to fine tune the analytical process and take corrective action where required. They were also employed by the QA staff to monitor data for systematic analytical problems. The criteria for these QC parameters are detailed in Table 5.

Table 5
Laboratory Quality Control Parameters

Method Blank: Method blanks were analyzed with each batch of samples (up to a maximum of 20 samples/batch) to check "reagent" or "process" introduced PCB contamination.

Laboratory Check Standard (LCS or Spiked Blank): A PCB free solid matrix (fired sand) was spiked with a PCB congener standard and analyzed with each batch of samples (up to a maximum of 20 samples/batch) to verify method performance. Recovery criteria were established for the LCS based on data generated during method validation.

Spiked Duplicate Samples: Duplicate aliquots of the same field sample were spiked with a mixture of PCB congeners and analyzed to determine if the accuracy criteria had been achieved and to assure that the method was functioning properly for electronic scrap. The relative percent difference (RPD) between the two values was used to check analytical precision.

Internal Standards: Chrysene-d^{12}, Phenanthrene-d^{10}, and Perylene-d^{12} were added to the sample extract in known concentrations and used as references to calculate concentrations of targeted compounds present in the sample. The internal standards were also used to asses instrument sensitivity for each sample analysis.

Surrogate: Tetrachloro-m-xylene, octachloronaphthalene and decachlorobiphenyl were spiked into an aliquot of each sample prior to extraction. The recoveries of surrogate compounds was used to monitor method performance for each sample.

Single Blind Performance Evaluation Checks: A single blind performance evaluation (PE) sample was prepared by EPA and introduced into the laboratory with every batch of 20 samples. This PE sample consisted of homogenized non-ferrous "white goods" (appliances) scrap that was previously analyzed during the validation of the analytical method. The PE was used to monitor the performance of the analytical system on a known concentration sample.

Table 6
Precision and Accuracy Criteria: Method Quality Parameters

LCS/Blank Spike Accuracy:

Parameter	Control Interval
2,4,4' Trichlorobiphenyl	82 – 113%
2,2',3,3',4,4' Hexachlorobiphenyl	87 – 119%

Matrix Spike Accuracy:

Parameter	Control Interval
2,4,4' Trichlorobiphenyl	61 – 134%
2,2',3,3',4,4' Hexachlorobiphenyl	63 – 143%

Matrix Spike Precision:

Parameter	Relative % Difference
2,4,4' Trichlorobiphenyl	30
2,2',3,3',4,4' Hexachlorobiphenyl	30

Surrogate Accuracy:

Parameter	Control Interval
Tetrachloro-m-xylene	68 – 104%
Octachloronapthalene	62 – 99%
Decachlorobiphenyl	57 – 88%

Performance Evaluation Accuracy:

Parameter	Recovery Criteria**
Total Aroclor (1242 + 1254)	+/– 30%

** Determined by USEPA review of performance evaluation data.

RESULTS:

Field Duplicates. Duplicate field aliquots from the non-ferrous bulk (NFB) scrap pile (261005-01,02) were analyzed to establish the precision of the field sampling technique. The precision criteria for the field duplicates was achieved indicating representative field sampling. Additional analysis of field duplicates from the remaining scrap piles was therefore not required or performed by prior agreement.

Table 7
Field Duplicate Results

Field Sample No.	EA Lab No.	PCB (ppm)	x PCB (ppm)	RPD
261005-01A	83670	121	129	9.8
261005-01D	83673	137	–	–
261005-02A	83699	107	117	16.3
261005-02D	83702	126	–	–

Criteria = $\leq$50% RPD for samples containing >40ppm PCB

Duplicate Aliquots. Field duplicates of each sample were analyzed to determine the effectiveness of the homogenization technique. The precision data (RPD) of the data pair indicated the method in which the PCB data was to be reported. The RPD criteria for duplicates was achieved for all samples in the field study indicating that the homogenization procedures were adequate for producing representative samples.

All scrap piles which contained an average PCB content >65ppm for the duplicate aliquots were reported as the average of the pair. Sample 261489-01A, 01D and sample 261491-01A, 01D contained an average PCB content between 35 and 50 ppm. The standard deviation of the replicate pair for each of these samples is less than the average. Based on the data reporting rules previously established (average greater than standard deviation) the PCB value for this scrap pile was reported as the average of the pair.

Table 8
Duplicate Aliquot Results

Field Sample No.	ENSR Sample No.	RPD Aroclor
261005-01A	83670	12
261005-01D	83673	–
261005-02A	83699	16
261005-02D	83702	–
261486-01D	83686	4
261486-01D	83689	–
261478-01A	83790	22
261478-01D	83793	–
261454-01A	83782	18
261454-01D	83785	–
261492-01A	84142	47
261492-01D	84145	–
261510-01A	84133	35
261510-01D	84136	–
261491-01A	84159	22
261491-01A	84162	–
261479-01A	84185	34
261479-01D	84188	–
261013-01A	84172	17
261013-01D	84175	–
261489-01A	84247	19
261489-01D	84250	–
261500-01A	84239	30
261500-01C	84241	–
261005-03A	84259	22
261005-03D	84262	–
200000-01A	84451	–
200000-01D	84454	14

Criteria; ≤50% RPD for samples containing >40ppm PCBs.
≤100% RPD for samples containing 10 – 40ppm PCBs.

Laboratory Control Sample. The laboratory control sample (LCS) or spiked blank was analyzed to ensure that the method was being properly executed in the laboratory. The recovery of the LCS achieved the established criteria for the majority of the spiked chlorinated biphenyls. A high bias was observed for two LCS samples. Three spiked chlorinated biphenyls in these two samples exceeded the established recovery criteria. The surrogate recovery for these two samples parallelled the spiked chlorinated biphenyl recovery.

Table 9
Laboratory Control Sample Results

Lab Control Sample No.	% R Cl_3	% R Cl_6
LCS910076	*	*
LCS910095	110*	70*
LCS910099	83	88
LCS910119	112	138
LCS910160	127	134
LCS910093a	89	86
LCS910073a	96	95

a – Aqueous steam condensate samples
* – Analyzed as screen to verify recoveries. Values reported are estimates. Sample subsequently confirmed during clean up attempts.

Criteria:

Trichlorobiphenyl (Cl_3) – 82–113%
Hexachlorobiphenyl (Cl_6) – 87–119%

Matrix Spike/Matrix Spike Duplicate (MS/MSD): The results of the MS/MSD indicated that a general high recovery bias existed for spiked samples. In general the high bias paralleled the surrogate recovery for these samples. The recovery criteria was exceeded for trichlorobiphenyl on three occasions. The criteria for hexachlorobiphenyl was achieved for all MS/MSDs. The precision criteria was achieved for all spiked duplicates with the exception of one hexachlorobiphenyl replicate pair.

Table 10
Matrix Spike/Matrix Spike Duplicate Results

Sample No.	%R Cl_3	RPD	%R Cl_6	RPD
83699MS	168	11	129	26
83702MSD	129	–	99	–
84185MS	131	20	96	36
84188MSD	160	–	138	–
84239MS	e	–	e	–
84241MSD	n			
84451MS	128	7	72	7
84454MSD	137	–	77	–

e – Spiking error invalidated data.
n – High concentrations of native trichlorobiphenyl in sample invalidated data.

Accuracy Criteria:		Precision Criteria:	
Trichlorobiphenyl;	61 – 134%	Trichlorobiphenyl;	≤ 30
Hexachlorobiphenyl;	63 – 143%	Hexachlorobiphenyl;	≤ 30

Field Sample Data. Results of the analyses indicated that two shred piles contained polychlorinated biphenyls as Aroclors and as congeners below 50 ppm. The remaining ten piles of electronic shred and the ground cover contained PCBs above 50 ppm measured both as Aroclors and as individual congeners.

The Aroclor results demonstrated that the PCB content of most piles were distributed between Aroclor 1242 and 1254. Pile 261486-01 was significantly different from the other piles; PCBs in the shred were over 95% Aroclor 1254. The Aroclor 1242 content of the shred pile was almost entirely associated with the unmillable portion of the pile.

Concentrations as measured from congener analysis were generally lower (up to 50%) than those determined from the Aroclor analysis. Most of the analyses were performed at high dilution factors because of the significant organic matrix present in the shred extracts. It is likely that a significant portion of the individual congeners present fell below the concentration level required for detection and ion ratio confirmation. Congener/Aroclor agreement between analyses performed at lower dilution factors was better than noted for analyses performed at high dilutions.

Significant weathering effects were not observed in the data for electronic shred; the congener patterns observed in samples closely resembled those of the Aroclor standards. Concentration results for each sample were calculated separately using five individual peaks for each Aroclor; these individual peak values, averaged for the reported sample results, generally demonstrated low variance.

Significantly greater variances were evident in the observed patterns of PCBs in the unmillable fraction than were evident in the Aroclor standards. Variance among the Aroclor concentration of individual peaks exceeded 100% in some cases, indicating selective losses of some isomers from the mix.

The steam condensate samples did not contain PCBs above the program-specified reporting limit of 10 ppm. Detectable Aroclors were, however, present in the steam condensates associated with shred pile 261500-01. With the exception of the first shred pile sample, 261005, Pile 261500-01 had the highest Aroclor content associated with the unmillable fraction on a weight basis.

The PCB data for the scrap samples are listed in Table 12. PCB congener data for a single sample from the duplicate aliquot pair of each scrap pile and one PE sample have also been included in Table 12.

Table 12
Electronic Scrap - PCB Results

Scrap Pile No.	Field Sample No.	EA Lab No.	Aroclor Conc. PPM	Total PCB Congener PPM
1	261005-01A	83670	121	158
1	261005-01D	83673	137	–
1	261005-02A	83699	107	159
1	261005-02D	83702	126	–
2	261486-01D	83686	542	540
2	261486-01D	83689	523	–
3	261478-01A	83790	198	189
3	261478-01D	83793	158	–
4	261454-01A	83782	109	60
4	261454-01D	83785	91	–
5	261492-01A	84142	53	55
5	261492-01D	84145	86	–
6	261510-01A	84133	87	–
6	261510-01D	84136	61	65
7	261491-01A	84159	33	39
7	261491-01A	84162	41	–
8	261479-01A	84185	135	103
8	261479-01D	84188	96	–
9	261013-01A	84172	357	352
9	261013-01D	84175	302	–
10	261489-01A	84247	38	39
10	261489-01D	84250	46	–
11	261500-01A	84239	616	–
11	261500-01C	84241	453	546
12	261005-03A	84259	125	90
12	261005-03D	84262	156	–
13	200000-01A	84451	122	–
13	200000-01D	84454	140	79

SUMMARY: The PCB data obtained from the analysis of the electronic scrap samples collected from the metal recycling firm's scrap shredding facility indicated that ten (10) of twelve (12) scrap piles and the ground cover exceeded the consent decree limit of 50 ppm for PCBs. The sampling and analysis objectives that had been established for the study were achieved. Quality control deficiencies observed during sample analysis did not impact data useability. Consequently, the data provided an accurate depiction of the PCB content of each scrap pile.

The precision data for the analysis of duplicate field samples indicated that the field sampling techniques used in this study were adequate for obtaining representative samples of each scrap pile. The precision data for the analysis of duplicate sample aliqouts indicated that the sample homogenization techniques were also adequate for generating uniform sub-samples from the scrap pile composites.

The criteria established for the quality control parameters in this study, in general were achieved. High concentrations of background organic compounds and high concentrations of PCBs present in the scrap resulted in multiple dilutions of the sample extracts. The dilution process increased data variability.

The recovery of spiked analytes and surrogates were closely related which demonstrated that the surrogate data could be used as an indicator of data bias. In general, a low bias was observed in the PCB data which may have been caused by the substitution of a more rigorous extract cleanup technique than the technique used during method validation.

ENDNOTES:

1. USEPA Field Manual for Grid Sampling of PCB Spill Sites to Verify Cleanup, EPA Contract No. 68-02-3938, G. Kelso, M Erickson, D. Cox, USEPA, Office of Toxic Substances, Field Studies Branch (TS-798), Washington, D.C. 20460

2. USEPA Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry, A. Stevens, T Bellar, J. Eichelberger, W. Budde, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio 45268, November, 1985.

ADDITIONAL REFERENCES:

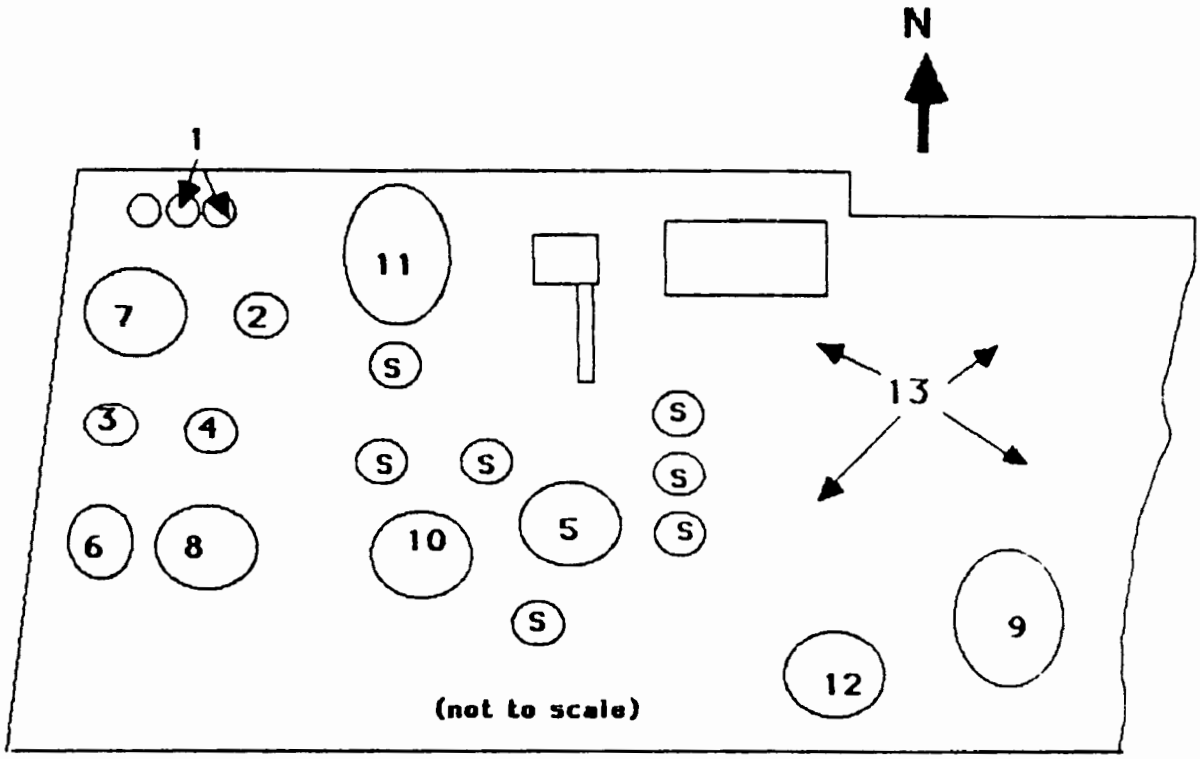
1. USEPA Contract Laboratory Program, Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, 2/88,

2. SOP For Determination of Percent Moisture In Solid Samples, ETC Corp., Edison, New Jersey, December 11, 1989.

3. 40 CFR Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11, Office of the Federal Register, National Archives and Records Administration, Washington, D.C., page 510.

FIGURE 1

ELECTRONIC SCRAP SHREDDING FACILITY



Inventory List. Weights and Order of Sampling.

Pile No.	ID No.	Description	Weight - Lbs.
1	261486-01	Client A	478,000
2	261478-01	Client B	261,760
3	261454-01	Client C	226,480
4	261492-01	Client D	290,140
5	261510-01	Client E	413,560
6	261491-01	Client C	609,340
7	261492-01	Client D	290,140
8	261013-01	Client F	800,440
9	261489-01	Client C	1,479,660
10	261500-01	Client E	1,197,460
11	261005-81	NFB 1989	1,068,290
12	261005-01	NFB Old	3,266,540
13	200000-00	Product Layer (Ground)	TBD

22 ADVANCES IN DATA QUALITY OBJECTIVE GUIDANCE FOR SUPERFUND REMEDIAL INVESTIGATION

for technical focus session -- Design of Cost-effective Monitoring Programs

Dean Neptune, PhD., Senior Environmental Chemist, Quality Assurance Management. U.S. Environmental Protection Agency, 401 M St., SW, Washington, DC 20460

Abstract

The US Environmental Protection Agency spends close to a billion dollars each year collecting environmental data crucial to credible decision-making. Too often in these monitoring operations, the data users (or decision makers) merely tell the data collectors to obtain data and after collection, the data users decide on what data they require. As in any large program, there are opportunities to do the job more effectively. In early 1983, Quality Assurance Mangement group in EPA began a major effort in applying Total Quality Management (TQM) to the design of expensive environmental monitoring programs. This TQM effort was labelled Data Quality Objectives, which simply requires the data user and supporting technical staff to answer three easy to state questions:

- What environmental data do you require to answer the question concerning the data users?

- How will the environmental data be used to answer the question of concern?

- How good does the data need to be for this use?

Much progress has been made in developing the technical elements of the data quality objective process. It has been applied to several Superfund cleanups with impressive results in time and money savings. One very clear result has been to balance the need for sampling and analysis with the cost of remediation. In some cases, less samples and analyses are required and in others more samples are taken to reduce the amount of media requiring remediation.

Over the last year, there has been much effort on improving the DQO process. Although the DQO process is a powerful tool for designing cost-effective monitoring systems, it has required significant commitment on the part of data users to establish their clear objectives early in planning. This has not been easy to do. The new guidance issued in FY 1992, is simplifying the demands required of the data users by relying more on the technical staff early in the planning process. The technical staff is now presenting alternative scenarios of concern based on problem priorities established by risk evaluation. This empowers the data users to select that problem and solution scenario that reflects their real concerns and do it in an efficient manner.

This presentation will describe the customization of the Agency's programmatic DQO process guidance for use by RPM/technical staff in Superfund site remediation.

23

PERFORMANCE EVALUATION SAMPLES--WHAT DO THEY TELL US?

Gary L. Robertson, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89193 and Joyce Lee, Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119.

ABSTRACT

One of the more important parts of most quality assurance (QA) programs for environmental data is the use of performance evaluation (PE) samples. The analytical results from PE samples are used to make judgements regarding the useability of the data from environmental samples. While PE samples provide important information on the capabilities of the laboratory there are limits to the extrapolation of PE sample results to environmental sample results. Factors which affect this are the quality of the PE sample, the type of PE sample and how closely the matrix of the PE sample approximates that of the field samples. The analytical result of the PE sample should be used in conjunction with the other available quality control information for both the PE sample and the field samples to evaluate the quality of the data. This presentation will discuss these issues and provide a perspective on the application of PE sample results to environmental data.

24 DATABASE TRENDS IN PROBLEMS OBSERVED IN CONTRACT LABORATORY PROGRAM (CLP) INORGANIC DATA REVIEWS

Keith A. Aleckson, Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119, and Edward J. Kantor, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada 89193

ABSTRACT:

Inorganic data audits are performed to assess the technical quality of analytical data and to evaluate overall laboratory performance. Technical data quality is assessed based on the total number of problems observed in each data package. The processes used to identify problems in inorganic analytical data range from a check of the quality control to a thorough investigation of the raw data submitted with the case. In addition to providing the basis for determining technical data quality, the number and type of problems provide a mechanism to track data quality for the Contract Laboratory Program (CLP), or for an individual laboratory, over time. Long-term tracking is accomplished by using a data base of standardized audit comments, which explain common problems found within the data submitted by CLP laboratories. Each comment represents an individual problem, and the frequency of these comments is tabulated by the data base. Common problems observed during the past year in CLP data packages include calibration errors, failure to submit deliverables, instrument contamination, and the use of incorrect quality control solutions.

NOTICE: Although the research described in this article has been supported by the United States Environmental Protection Agency through contract 68-C0-0049 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

25 USE OF ORGANIC TAPE AND DATA REVIEWS IN TECHNICAL AND QUALITY ASSURANCE OVERSIGHT OF SUPERFUND CONTRACT LABORATORIES

Janice Armour, Vijaya Dandge, David Hewetson, Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119, and Edward Kantor, U.S. EPA, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada 89119

ABSTRACT:

Organic tape and data reviews are performed to assess the technical quality of the data, adherence to relevant quality control criteria and overall laboratory performance. The processes used to identify problems range from a thorough review of quality control information submitted, to a review of the raw data and forms associated with the case. The number and type of problems will be discussed, as well as how overall laboratory performance is determined and subsequently tracked over a period of time. A tool in charting overall laboratory performance, is the CLP Laboratory Performance Scoring, which is used to assess laboratories based on Quarterly Blind scores, Audits scores, CCS scores, and Timeliness scores. Long-term tracking is accomplished by using the Organic Audit Data Base that contains all of the Standard Operating Procedure (SOPs) and Quality Assurance Plan (QAPs) reviews, tape/data review scores, On-site Recommendations, and tape submissions (both timeliness and complete data file submissions). An additional long term tracking tool, and a possible tool in forecasting, performed by the Laboratory Performance Data Base and Scout, utilizes multivariate data to assess overall laboratory and program quality. Data from the tracking tools, as well as problems observed during reviews of CLP laboratory data over the past year will be presented.

Notice:

Although the research described in this article has been supported by the United States Environmental Protection Agency through contract 68-C0-0049 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN DATA

Lester J. Dupes, Quality Assurance Scientist, BCM Engineers Inc., One Plymouth Meeting, Plymouth Meeting, Pennsylvania 19462

ABSTRACT

Although data validation guidelines for organic and inorganic parameters have been used since the early 1980s to evaluate and determine data usability, few guidelines exist for the validation for analytical data for polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs). The recent U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) Statement of Work for Analysis of PCDDs/PCDFs and the EPA Test Methods for Evaluating Solid Waste (SW-846 Methods 8280 and 8290) provide consistent guidance for laboratory analyses but few exist for data validation scientists. To remedy this situation, BCM has developed a company standard operating procedures manual for data validation scientists for evaluating and validating PCDD/PCDF data deliverables that is based on a review of multi-laboratory supplied analytical data reported under EPA methods.

This paper provides general information on understanding laboratory analytical data deliverables and their format. It covers quality assurance objectives, validation criteria, evaluation procedures, and specific actions applied to the results. It provides specific information on reviewing PCDD/PCDF data completeness, holding times, gas chromatography resolution, initial and continuing calibrations, blanks, duplicate and matrix spike criteria, internal standards performance, interferences, identification criteria for PCDDs/PCDFs, and toxicity equivalence calculations. These criteria and procedures will help the data validation scientists ensure consistent validation of PCDD/PCDF data packages from laboratories.

INTRODUCTION

Data validation of polychlorinated dibenzo-p-dioxin and dibenzofuran data deliverables provides the data user with data of known quality, and valid and legally defensible results and supporting data. The validation process determines the validity and correctness of the analytical data provided by the laboratory. The laboratory-reported positive results and detection limits are evaluated and qualified based on the Quality Assurance/Quality Control (QA/QC) measures employed by the analytical methodology. The exceedance of QA/QC limits may indicate the necessity for estimating or rejecting results, based on the severity of the problem.

The following sections explain the major elements of data validation for PCDD/PCDF data deliverables submitted under Contract Laboratory Program (CLP)[1] and Test Methods for Evaluating Solid Waste (SW-846) Methods 8280 and 8290[2,3] methodologies. Quality Assurance objectives, validation criteria, evaluation procedures, and actions applied to the results will be outlined in each section. Technical details have been taken from the specific methodologies and guidance documents listed as references.

PRELIMINARY REVIEW

For data validation scientists, the objective of the preliminary review is to confirm that the analytical procedures followed by the laboratory and that the production of the deliverables required were performed in compliance with the methodology requested. The data validator should first check to determine if all raw sample data and QC data has been provided according to CLP or other methodology. Any non-CLP method should include a level of data deliverables similar to the CLP. Then, the validation scientist should review the laboratory case narrative and make note of any problems mentioned and any resolutions made. If the data deliverables are incomplete, the validation scientist should issue a written data validation inquiry to the laboratory requesting that the missing data be supplied.

CHAIN-OF-CUSTODY

Samples collected during any sampling event may be used as evidence in litigation. Therefore, possession of the samples must be traceable from the time each sample is collected until it is introduced as evidence in legal proceedings. Chain-of-custody procedures are followed to document proper custody of samples, to verify collection times and dates, and to identify the sample location, matrix, and preservation techniques. Step-by-step details of custody procedures are included in the project Quality Assurance Project Plan (QAPjP). If these are not available, the scientist should reference the NEIC Polices and Procedures Manual[4] when reviewing the documentation for proper custody.

Using professional judgment, the validation scientist should note and report all deviations from proper custody procedures to determine any impact on the data. Severe problems such as broken custody seals or loss of sample custody may invalidate all reported results.

HOLDING TIMES

Currently, the method-specific holding time for PCDDs/PCDFs indicates that all samples must be extracted (date procedure started) within 30 days and completely analyzed within 45 days of sample collection. The data validation and qualification procedures for review of analytical holding times for volatiles, semivolatiles, and pesticides/PCBs have been well established in the EPA's Laboratory Data Validation Functional Guidelines for Evaluating Organics Analysis.[5] These procedures should be applied by the validation scientist to dioxin/furan analyses to provide for consistent validation procedures. The validity of results is based on the time period from the date of sample collection to the date of the laboratory's preparation and analysis of each site sample. If samples exceed the specified holding times, the validation scientist qualifies all positive results and sample detection limits as estimated. Gross exceedance of holding times may indicate that the non-detect data are unusable.

MASS SPECTROMETER CALIBRATION

The mass spectrometer calibration at the laboratory is conducted using the compound FC-43 prior to performing any analysis using CLP 12/90 methodology. This calibration ensures that mass resolution and identification are acceptable. It is similar in nature to bromofluorobenzene (BFB) and decafluorotriphenylphosphine (DFTPP) tunes for volatile and semivolatile analyses. Acceptable mass spectrometer calibration is based on ion abundance ratios. The ion abundances of M/Z 414 and M/Z 502 should be 30 to 50 percent of M/Z 264 base peak.

SW-846 Methods 8280 and 8290 also mention mass spectrometer calibration to verify resolution. Method 8290 requires use of perfluorokerosene (PFK) for calibration. Since mass spectrometer calibration is a preliminary analytical method criteria and is only a recommended procedure, data deliverables are not required and, therefore, no data should be qualified by the scientist.

CHROMATOGRAPHIC RESOLUTION

The objective is to determine that adequate peak resolution exists for selected analytes prior to the analysis of samples for PCDD/PCDF compounds. Resolution is performed for the primary and confirmatory columns by evaluating resolution of 2,3,7,8-TCDD from other closely eluting isomers: 1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair. The peak resolution is measured from a column performance mixture or calibration analysis. CLP 12/90 also requires that resolution for 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD be evaluated. Acceptable resolution criteria for the TCDD isomers is a valley between peaks of $\leq$ 25 percent and $\leq$ 50 percent for the HxCDD isomers. Laboratory analysis should not proceed if GC resolution criteria are exceeded.

The validation scientist should reference the individual methodologies to determine that the proper analytical frequency for measuring resolution criteria is maintained and evaluated. A validation review of all initial and continuing calibrations and/or performance mixtures to ensure that continuing resolution of the TCDD and HxCDD isomer is within the criteria must be completed. If the samples are analyzed after exceeded resolution criteria, then poor resolution of 2,3,7,8-compounds present in the samples may occur. Therefore, the validation scientist should qualify sample results for 2,3,7,8-TCDD and/or 1,2,3,4,7,8 and 1,2,3,6,7,8-HxCDD as estimated.

WINDOW DEFINING MIX DATA

The window defining mix is analyzed prior to the initial calibration and continuing calibration, depending on the methodology employed. The laboratory uses this data to establish GC/MS switching times for each ion monitored. This analysis creates a retention time window because the mix contains the first and last eluting isomer for each dioxin and furan homologue. The established retention time windows are used in evaluating peaks present in the samples as potential dioxins and furans. The peaks outside each homologue retention time window can be eliminated as dioxin or furan isomers.

The window defining mix may also contain the chromatographic resolution compounds as a single solution and both criteria can be evaluated during a single analysis. The window defining mix also monitors potential retention time shifts by comparing the recovery standard retention times to the retention times in the most recent continuing calibration. A maximum shift of $\pm$10 seconds is allowed.

The validation scientist must evaluate all sample peaks to determine if the retention time of the peaks is within the retention time window established for each homologue. The peaks outside each homologue retention time window can be eliminated as dioxin or furan isomers. Chromatographic resolution is validated as previously discussed. The retention times of the recovery standards are compared to the continuing calibration to verify a retention time shift of less than $\pm$ 10 seconds. If the shift is greater than the criteria, the sample data must be closely evaluated to look for false positive or negative results.

INITIAL AND CONTINUING CALIBRATIONS

An initial calibration of five increasing concentration standards containing all native dioxins and furans and related isotopically labeled internal standards are analyzed to demonstrate the GC/MS capability of producing acceptable quantitative data. The initial calibration determines the linear range and measures the individual response of all compounds. The continuing calibrations document instrument stability, acceptable compound response, and deviation from curve linearity on a daily basis. All methodologies have slightly different calibration procedures and specific methods must be used to verify method compliance. However, the review of initial and continuing calibration data includes validation of the following criteria: chromatographic resolution of TCDD and HxCDD isomers, retention times, relative response factors, mass spectrometer (MS) sensitivity, and relative ion abundance criteria for PCDD/PCDF peaks. Chromatographic resolution and retention times criteria have been previously discussed. The relative response factors calculated for the 5-point initial calibration must not exceed 15 to 30 percent relative standard deviation, depending on the analytical method. Additionally, the percent difference between the initial and continuing calibration response factors must not exceed 20-30 percent. MS sensitivity is laboratory-determined by measuring the signal-to-noise ratio (S/N) of each ion. The S/N must be verified by the laboratory to be greater than 2.5:1 for the unlabeled PCDD/PCDF ions and greater than the 10:1 for the internal and recovery standards to show acceptable detection of each compound.

The validation scientist must continue to evaluate and qualify data based on the chromatographic resolution and retention times. The relative response factors, relative standard deviations, and percent differences should be recalculated by the validation scientist to verify accuracy in calculation and reporting. Positive results and detection limits associated with calibrations exceeding percent difference criteria are estimated. All peaks for the unlabeled PCDD/PCDF ions and internal standard compounds must meet the S/N criteria. A low S/N could result in a problem of actual detection of the compounds and results or detection limits should be estimated.

BLANK CRITERIA

The analysis of blanks and evaluation of the resultant data determines the potential existence and magnitude of laboratory, field, or sample cross-contamination. Method and rinse blanks are used to isolate the source of sample contamination. Method blanks monitor potential lab contamination and are carried through all preparation and analytical procedures. A minimum of one method blank per matrix must be analyzed with each sample analysis batch. According to CLP 12/90 criteria, method blanks cannot contain any chemical interferences or electronic noise for the specific ion monitored which is greater than five percent of the appropriate internal standard. Any peak positively identified as a PCDD or PCDF present in the method blank must not be greater than two percent of the internal standard used for quantitation. Rinse blanks of approved solvents are important in monitoring the effectiveness of decontamination procedures during field sampling

Positive sample results for 2,3,7,8-substituted isomers should be qualitatively questioned by the data validation scientist if the results are similar in concentration to the concentrations present in the rinse or method blank(s). Since the total homologue concentrations reported in the blanks and samples may consist of many isomers, the results should be validated on a peak-by-peak basis by requantitating the individual non-2,3,7,8-peaks in the samples and blanks. These concentration can then be compared to the blank results on an individual basis.

MATRIX SPIKE ANALYSIS

A selected site sample is divided into two portions: one is analyzed unspiked and the other portion is spiked with several target compounds prior to being extracted and analyzed. Spike recoveries are evaluated to determine sample matrix effects. The data provides information on the precision and accuracy of the analytical preparation and analysis on various matrices. One spike sample is analyzed for each matrix type (i.e., water, soil/sediment, chemical wastes, and ash) present in a sample analysis batch.

The CLP requires a matrix spike analysis, Method 8280 does not require a matrix spike analysis, and Method 8290 requires a matrix spike and a matrix spike duplicate analysis. CLP recoveries of each spiked compound must be within 50 to 150 percent. Method 8290 specifies a 20 percent relative difference between matrix spike/matrix spike results. The validation scientist must use professional judgment to determine the impact of matrix spike recoveries outside criteria on the unspiked sample results. Spike recoveries should be recalculated to determine accuracy in reporting.

DUPLICATE SAMPLE ANALYSIS

Laboratory duplicates and field duplicates are evaluated as an indication of overall precision. Field duplicate analyses measure both field and lab precision; therefore, the results may have more variability than lab duplicates that measure only lab performance. It is also expected that soil or solid matrix duplicate results generally have a greater variance than water matrices due to difficulties associated with collecting identical, homogeneous field samples.

CLP criteria indicate that a duplicate of one sample for each matrix is to be analyzed. Most environmental investigations require that field duplicates be analyzed at some specified frequency. According to CLP 12/90, a $\pm$ 50 relative percent difference criteria ($\pm$ 25 percent for Method 8290) is used for laboratory duplicates. The validation scientist should estimated positive results for the original and duplicate samples outside the $\pm$ 50 percent criteria. The field duplicates should be evaluated using professional judgment. Concentrations near the detection limits should be carefully evaluated during validation to determine if qualification is necessary.

INTERNAL AND RECOVERY STANDARD PERFORMANCE

Internal and recovery standards are spiked into all calibration standards, samples, and blanks. These spikes consist of a number of isotopically labeled compounds added prior to sample extraction and preparation, based on analytical method requirements. The internal standards recoveries measure method efficiency and are used in quantitating native analyte concentrations present in the samples. Recovery standards are added after sample preparation and extraction, but prior to instrument injection. Recovery standards are used for calculating internal standard recoveries.

The recovery criteria for each method varies; however, recovery criteria range from 25 to 140 percent. Since dioxin/furan methods use isotopic dilution techniques, positive results and detection limits are corrected for internal standards recoveries, only very low recoveries indicate a potential problem. More importantly a minimum S/N of 10:1 is required to verify an acceptable level of instrument detection; isotope ratios are used to identify the compounds and check for possible interferences.

The validation scientist must evaluate all internal standards recoveries to the method-specific recovery criteria. Note in the validation report all recoveries outside criteria, but do not qualify data quantitated using the internal standards, unless the S/N ratio or isotope ratio is not within criteria. Results quantitated using an internal standard that exhibits a low S/N ratio or incorrect isotope ratio may be estimated due to potential sample matrix effects.

IDENTIFICATION CRITERIA AND QUANTITATION OF PCDD/PCDFs

The identification of a detected peak must meet all of the following criteria to be considered a PCDD or PCDF: retention time, peak identification, and both signal-to-noise and isotope ratios.

If more than one of the following criteria is exceeded, the peak is not identified as a dioxin or furan. The scientist must evaluate all peaks to verify the laboratory reported results. If the validation determines that peaks have not met criteria, the result for the peak is qualified as rejected.

Retention Time Criteria

The positive identification of a 2,3,7,8-substituted dioxin or furan isomer is determined by comparing the retention time of the peak to the isotopically labeled internal or recovery standard added during extraction. The retention time must be within -1 to +3 seconds to be considered a 2,3,7,8-isomer. If the labeled 2,3,7,8-standard is not present in the extract, a relative retention time (RRT) is calculated from the analyte's retention time and the corresponding internal standard. The RRT of the analyte must be within 0.05 RRT units (0.005 units for Method 8290) of the RRT calculated from the continuing calibration. Retention time windows defined during the window defining mix are used to identify the non-2,3,7,8-isomers for each dioxin or furan homologue. Additionally, the recovery standard previously discussed in the window defining mix must continue to meet the $\pm$ 10 second retention time criteria from the associated continuing calibration to monitor potential retention time shifts.

The data validation scientist must evaluate all potential sample and blank peaks for the retention time criteria listed above. The peak must be within the established retention time window to be considered a non-2,3,7,8-isomer. The exact retention time or relative retention time must be met for the peak to be considered a 2,3,7,8-isomer. The recovery standards should also be evaluated to determine if retention time shifts are occurring in the samples. Peaks outside the retention time window or not meeting specific criteria should be rejected or identification changed as necessary.

Peak Identification Criteria

The two characteristic mass ions monitored for each dioxin or furan homologue and the confirmation mass ion (M-[COCl]$^+$) for each compound at the specific 2,3,7,8-isomer retention time or detected within the retention time windows must maximize simultaneously within $\pm$ 2 seconds. The M-[COCl]$^+$ ion is monitored because the ion is a confirmation ion for dioxins and furans resulting from a loss of 63 mass units from the dioxin or furan during mass spectrometer ionization.

Method 8290 does not monitor the M-[COCl]$^+$ ion; however, a lock mass ion monitors the stability and sensitivity changes during the entire GC/MS analysis. A positive or negative spike of the lock mass ion at the retention time of a 2,3,7,8-isomer may be potentially enhance or supress the 2,3,7,8-isomer integrated area.

Validation of all sample peaks within the retention time windows, and evaluation of internal and recovery standards must be performed by the scientist to verify simultaneous detection within $\pm$ 2 seconds. Peaks not meeting this criteria should not be considered dioxins/furans. The lock mass ion must be evaluated for positive or negative spikes as part of Method 8290 criteria. Large spikes may indicate that the affected positive results or detection limits should be estimated or rejected based on the magnitude of the spike.

Signal-to-Noise Ratio Criteria

Each potential dioxin/furan peak must meet a minimum of a 2.5:1 signal-to-noise criteria. Internal standards must meet a minimum of 10:1 criteria. These criteria must be met to be considered acceptable signals for quantitation by the laboratory.

Verification by the validation scientist of all sample peaks within the retention time window and internal and recovery standards must meet the specified S/N criteria. If the sample peak does not meet S/N criteria, but all other identification criteria are acceptable, the validation scientist must use professional judgment to determine if the peak should be reported as a dioxin or furan.

Isotope Ratio Criteria

Isotope ratios are used to accurately determine the number of chlorine atoms present in a compound by evaluating the ^{35}Cl and ^{37}Cl atoms present in a chlorinated compound. Isotope ratios are based on the probability that a ^{35}Cl and/or ^{37}Cl atom is present in the chlorinated compound. These probabilities change as the amount of chlorination increases or decreases. Evaluation of specific ratios allows the identification of tetra through octa chlorination of dioxin and furans. The isotope ratio corresponds to the integrated areas of peaks for the m, m+2, and m+4 mass ions. By division of these areas (e.g., m/m+2), a ratio of the two ions is produced. These ratios are physical constants and both slight errors in area integration or potential interferences may occur. Therefore, a $\pm$ 15 percent difference criteria from the theoretical ratio is used for evaluation.

If a compound does not meet an isotope ratio criteria, the compound is not reported by the laboratory as a PCDD/PCDF. However, the peak is quantitated and reported as an Estimated Maximum Possible Concentration (EMPC).

The validation scientist must evaluate all isotope ratios reported for positive sample results, internal standards, and recovery standards by comparing the reported ratio with the list of isotope ratio ranges (± 15 percent from the theoretical ratio) found in each method. Several ratios should be recalculated to verify accuracy in laboratory reporting. The scientist must verify that peaks not meeting isotope ratio criteria are calculated as EMPC by the laboratory.

QUANTITATIONS OF PCDDs/PCDFs

The quantitation of positive results and detection limits provide the data user with values for each site sample. Total concentrations are also calculated by summing the individual 2,3,7,8-and non-2,3,7,8-isomer concentrations within the retention time window. The detection limit for a compound is individually calculated to provide an estimated concentration of the analyte needed to produce a peak at a S/N ratio of 2.5:1.

Validation is performed by recalculating the results to ensure accuracy. Each analytical method must be referenced by the scientist to determine the correct quantitation method. Recalculation is performed to verify that the correct sample peak area, internal standard area, response factor, sample volume or weight, and quantity of the appropriate internal standard is used. Errors found in quantitations should be checked by the laboratory through a data validation inquiry made by the scientist, and affected forms and results should be resubmitted.

POLYCHLORINATED DIPHENYL ETHER (PCDPE) INTERFERENCES

The objective of evaluating PCDPEs is to determine if these interferences are affecting PCDF quantitations. A (M + 72) mass ion is monitored in conjunction with the compound-specific mass ions for hexa through deca chlorinated diphenylether which interfere with dibenzo furans.

CLP criteria states that the positive identification of a PCDF cannot be made if a PCDPE peak of greater than 2.5 S/N is detected at the same retention time as the corresponding furan. If a PCDPE is detected, an EMPC is calculated and reported for the PCDF isomer. This quantitated result provides a reference to the maximum concentration possible if the peak had met all of the identification criteria as a furan.

The PCDPE mass ion must be evaluated by the scientist to identify peaks above a S/N of 2.5:1. The retention time of the PCDPE is compared to the retention time of peaks present in the corresponding furan. Furan peaks which are interfered with by PCDPE should be reported as EMPC by the laboratory for CLP.

TOXICITY EQUIVALENCE

The methodology requires the calculation of the 2,3,7,8-TCDD toxicity equivalence according to the procedures given in the EPA's "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risk Associated with Exposure to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016).[6] Of the possible chlorinated PCDDs/PCDFs, the 17 isomers that bear chlorine atoms in 2,3,7, and 8 positions are the greatest concern in the assessment of risk to human health and the environment.

A factor is assigned to each of the seventeen 2,3,7,8-substituted PCDDs and PCDFs that relates the toxicity of that isomer to a concentration of the most toxic isomer 2,3,7,8-TCDD. These factors are

called toxicity equivalence factors (TEFs). The concentrations of any of the 17 isomers that are detected in an environmental sample can then be adjusted by the TEF and summed yielding a concentration of 2,3,7,8-TCDD with an equivalent toxicity. The "Total" concentrations are not assigned TEF values in the March 1989 TEF procedure and, therefore, are not included in the toxicity equivalence calculations.

If the toxicity equivalence exceeds CLP criteria, then analysis on a second column capable of resolving 2,3,7,8-TCDD/2,3,7,8-TCDF and as many other isomers from coeluting peaks is required. Method 8290 requires a two-column analysis to provide a more accurate value for 2,3,7,8-TCDF due to coelutions. All values except 2,3,7,8-TCDF are used from the original column analysis, while the 2,3,7,8-TCDF result from the second column is used in calculating TEFs. Since a quantitative and qualitative uncertainty is associated with EMPC values, they are not included in the TEF calculation performed in the methods according to CLP 12/90. Some EPA regional criteria indicates that EMPC values for 2,3,7,8-isomer be used to obtain the worst-case scenario.[7]

The validation scientist should verify that the correct TEF factors and sample concentrations are reported by the laboratory. The scientist must also verify that the correct EPA regional or state criteria is used and recalculation of TEF concentrations are accurate.

SUMMARY

Data validation of deliverables produced from PCDD/PCDF analyses provides the end data user with valid and legally defensible results and supporting data. The complexities of the various methodologies require the data scientist to have a thorough understanding of the analytical techniques, quality control procedures, and quality control criteria for these deliverables. The development of a Standard Operating Procedure has provided BCM data validation scientists with guidance in validation. As with the analytical methodologies that provide the analyst with a consistent protocol for performing the analyses, the validation guidance provides for a consistent review of dioxin/furan data deliverables.

REFERENCES

1. United States Environmental Protection Agency, Contract Laboratory Program Statement of Work for Analysis of Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF), Document Number DFLMO1.0, December 1990, revised September 1991.

2. United States Environmental Protection Agency, The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans, Test Methods for Evaluating Solid Waste, SW-846, Method 8280, September 1986.

3. United States Environmental Protection Agency, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Test Methods for Evaluating Solid Waste, SW-846, Method 8290, November 1990.

4. United States Environmental Protection Agency, NEIC Policies and Procedures, EPA-330/9-78-001-R, May 1978, revised May 1986.

5. United States Environmental Protection Agency, Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, February 1988.

6. EPA's "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risk Associated with Exposure to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016).

7. EPA Region III QA Directives, Dioxin's International Toxicity Equivalency Factors (I-TEF/89), QAD 016, February 1990.

27 COST EFFECTIVENESS OF DATA QUALITY OBJECTIVES IN ENVIRONMENTAL MONITORING

PERFORMANCE-BASED METHODOLOGY

Mark Dymerski-Technical Manager, Steven Malecha-Technical Manager, and Maureen McDevitt-Technical Director, Enseco-Rocky Mountain Analytical Laboratory, Arvada, Colorado 80002.

ABSTRACT

Because of limited resources available for investigation and remediation of contaminated sites, there is a pressing need to produce quality data in a cost effective manner. The development of the Environmental Protection Agency - Contract Laboratory Program (EPA-CLP) addressed project specifications by requiring laboratories to follow to specific methodologies. While this conformity was necessary in the infancy of the Environmental Testing Industry, laboratories today can meet client needs with techniques and methodology that differ from the strict guidelines of the CLP. The performance based process allows the laboratory to tailor its techniques around the specific requirements of a project and site. The flexibility of this process means that the laboratory is far more dynamic in its analytical approach. New techniques and improvements in laboratory efficiencies can be utilized to greatly reduce costs which benefit both the customer and laboratory. The performance based approach involves a process of shared information between client and laboratory. This partnership between client and laboratory instituted from a project's beginning provides the necessary communication to meet data and budgetary objectives. With no official national laboratory certification program, the CLP has functioned as such. A laboratory that participates in the CLP is given preferential treatment in the industry, even if it does not follow the CLP protocol for Industrial clients. As a result of this bias in industry, maintaining CLP status is a cost of doing business. It has become far more competitive to participate as winning bids for CLP sample lots continue to decrease below most laboratories' cost structure. The problems between performance based methodology and CLP can be seen in recent requests for proposal from the Department of Energy. Some parts of proposals state that the technical approach to clean up of these sites would utilize the technical expertise of lab personnel in solving analytical problems. Other sections call for a program similar to the CLP. Both techniques cannot successfully function in the same program. Other issues that affect the Environmental Testing Industry pose additional problems. Laboratory capacity is a key issue that must be addressed in the DOE plan. The private sector needs to know the true scope of the program, so that it can properly prepare itself. Another issue that has risen involves the clear discrepancy emerging between the acceptable levels of radioactive materials a facility can accept. Presently, there are two different regulatory definitions of radioactive material licensing. The Nuclear Regulatory Commission (NRC) grants licenses to laboratories in states that do not have their own policies while "agreement" states grant their own licenses based on their own criteria. The discrepancies between state and federal regulations can vary greatly. Definitions of safe levels greatly affect the functionality of laboratories that analyze mixed wastes. These differences between a centrally regulated industry and one that allows individual judgement create many questions about how the Environmental Testing Industry functions.

28 ENSR's AUTOMATED DATA VALIDATION SYSTEM

Mary Fenci and Marilyn Hoyt, ENSR, Acton, Massachusetts, 01720, and Joel Karnofsky, Berkeley, California, 94702.

ENSR has recently developed an automated data validation (ADV) system for volatile, semivolatile, pesticide/PCB, and inorganic data. This system is used for large data sets where the analytical protocols specified follow the CLP protocol.

For selected projects, ENSR receives laboratory data deliverables both as hardcopy and on diskette. The diskette data are read into the ADV system, while the basic screening-level checks are performed. A variety of reports are available through the system; these reports are used to highlight data problems and deficiencies.

Once the data has been validated, it is exported to ENSR's Project Database Management System. This system is used to manage both field and laboratory data, as well as facilitating more graphical and statistical presentations of data.

This presentation will provide an overview of the system and present a detailed view of the ADV reports used to detect data problems and deficiencies.

29 USING HANDHELD COMPUTERS TO IMPROVE THE QUALITY OF FIELD DATA DOCUMENTATION AND TRANSMITAL

BARBARA R. HILL, MANAGER CLIENT SERVICES, JEAN K. HOLLEY, MANAGER COMPUTER SERVICES, WASTE MANAGEMENT INC.; ENVIRONMENT MONITORING LABORATORIES 2100 CLEANWATER DRIVE GENEVA, IL 60134

ABSTRACT

Waste Management's Environmental Monitoring Laboratories (EML) receives over 200,000 pieces of field data information a year from groundwater wells at our solid waste and hazardous waste facilities across the United States. The accurate transmittal of this data to our company's central environmental groundwater database at the EML is vital for regulatory reporting and groundwater monitoring program analysis. Examination of the sampling and field data documentation process revealed significant time and accuracy advantages would be gained by inserting handheld computers into the sampling procedures.

Handheld computers were programmed to accept all information on the EML Chain-of-Custody and Field Information Forms. All data input was password protected to accept data for a particular sampling event only from authorized samplers who were trained and identified as the designated samplers for the event. Barcoding capabilities were added to enable the samplers to barcode well and sample bottle identifications. The system was developed to utilize a modem to our centralized VAX computer system at Geneva, Illinois. All field data and comments were electronically loaded into the appropriate sections of our groundwater database. Data range specifications were built into the system to prevent gross transcription errors such as transposing pH and conductivity readings.

The system was programmed to print a copy of all field data information from a portable field printer for final sampler quality checks, review and signatures prior to transmittal to the EML database. Future application enhancements include obtaining direct readings from on-site or "down the hole" instrumentation into the handheld computer unit for electronic transmital to the laboratory.

INTRODUCTION

Waste Management's Environmental Monitoring Laboratories track sampler error rates on all incoming samples to the Geneva facility. Because the lab is responsible for company wide sampler training and sampler auditing, this information is useful to track sampling team

performance improvement and is part of the total quality improvement effort. Although the error rate is low (0-3% at most sites), every error has the potential to cause invalidation of the data . There is also significant time and cost associated with the resampling of the event.

Several units were evaluated to automate as much of the sample collection process as possible. Programming was completed on two units which were identified as most useful for our companies' purposes. Pilot studies were completed at the EML and in the field. Error rate improvement was particularly sought in the following areas:

Documentation

Filtering Information

Correlation of Signatures/Dates/Sample Points/Bottles Sets

Miscellaneous

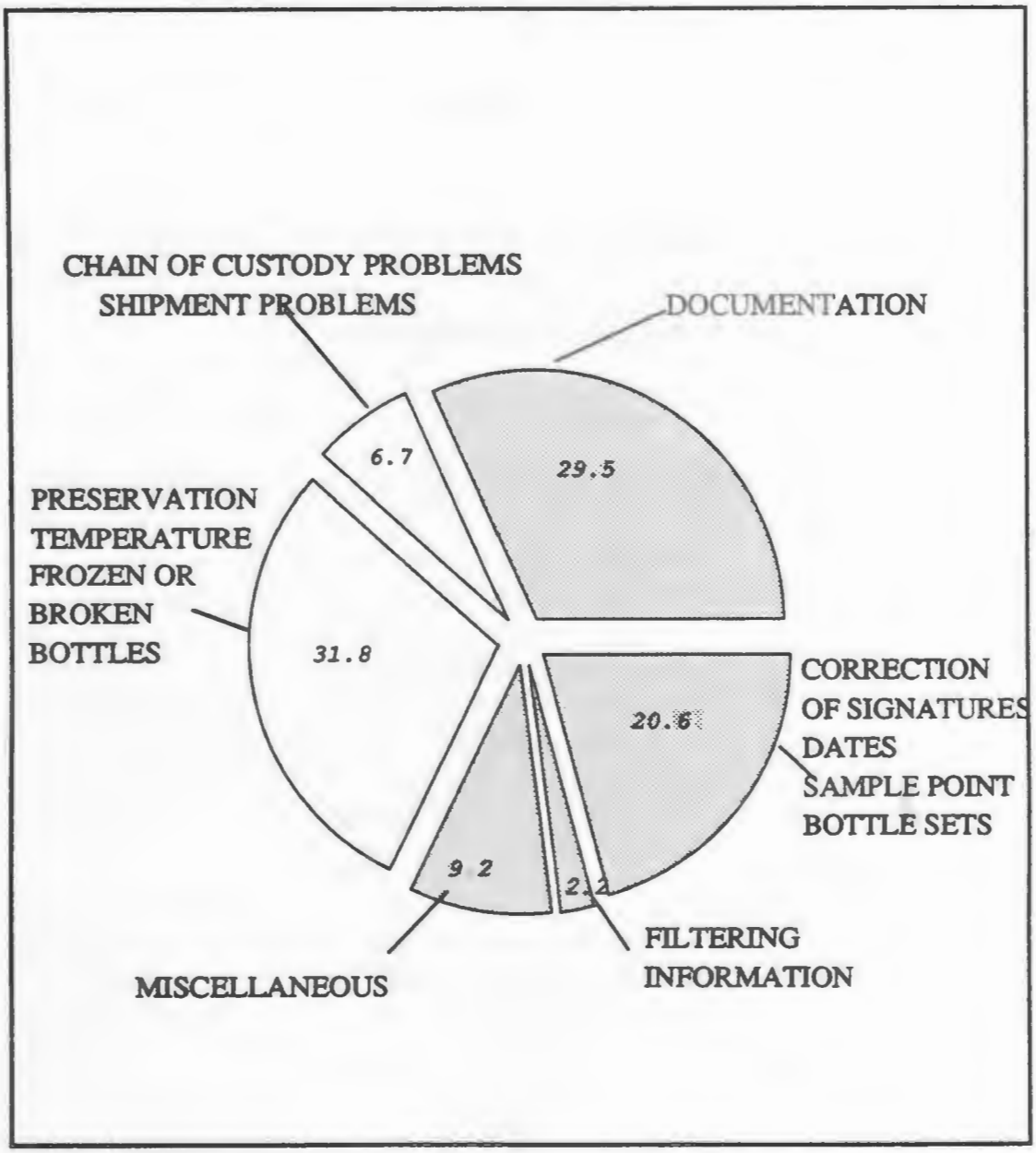
These categories related to the total error rate as follows:

CATEGORIES OF SAMPLER ERRORS SLATED FOR QUALITY IMPROVEMENT BY USE OF A DATALOGGER

Catagory	% of Total Errors
Documentation	29.5%
Filtering Information	2.2%
Correlation of Signatures/ Dates/Sample Points/ Bottle Set	20.6%
Miscellaneous	3.0%
Total Errors Affected	55.3%

CATEGORIES OF SAMPLERS' ERRORS

TOTAL % ERROR POSITIVELY IMPACTED BY DATA LOGGER = 55%
(SHADED AREAS)



Potential cost savings from elimnating these errors were as follows:

Resampling (184) events @1750	$322,000
Analytical Costs (184 events @2500)	$460,000
Rescheduling/error tracking	$ 38,825
Total Potential Savings	**$820,825**

SUMMARY

Several handheld computers were evaluated during the pilot testing phase; ITRON T3000 handheld computer was selected as the unit that provided the most features that met list of requirements. The following is a list of requirements (both hardware and software) :

HARDWARE REQUIREMENTS:

1. Rugged unit - Unit required to withstand extreme weather conditions; water and dust resistant, shock-absorbent and light in weight.
2. Screen Display - Unit required to display and collect data in a easy-to-read manner.
3. Bar code - Required to integrate with barcode reader.
4. Power Supply - Rechargeable hicad batteries or alkaline batteries.
5. Unit reliability - Unit required to have an excellent reliability and lifespan.
6. RAM Memory - 128K with expansion capablility to 1MB

SOFTWARE REQUIREMENTS:

1. Standard Operating System - MS DOS like operating system .
2. Programming capability - Ability to easily program a customized system.

Custom software for the ITRON unit was developed to provide specific funtions .

These features include:

1. SECURITY

The user is required to enter a user name and PIN number before accessing any data on the unit or functions.

2 DATA VALIDATION

Data can be uploaded or downloaded electronically. This allows sampling data to be verified and checked for errors.

3 BARCODES

The unit supports a barcode reader to read labels on bottles and sampling points.

4. DATE AND TIME IDENTIFICATION

The unit has an internal clock that allows automatic date and time identification for all data entered.

5. DATA CALCULATIONS

The unit collects the data entered by the user and performs calculations on the data entered (i.e. purge times, volumes, flow rates)

6. PRINT CAPABILITIES

A printer can be attached to the unit which provides the user the ability to print key forms or data.

7. FILE TRANSFER

The unit includes a built-in modem which can be used to transfer data to and from the unit.

Our pilot studies have pointed to the following advantages of incorporating handheld computers into our groundwater sampling programs:

1. Documentation and Security -the validation of all data entries insures review by sampling teams and prevents gross data entry errors. Only trained samplers are granted access to the Field Data Collection System (FDCS)

2. Barcoding prevents bottle set mix-up and positively identifies sampling points prior to actual sampling.

3. Calculations programmed into the FDCS system prevent human error on field information forms.

4. Time Savings- field data entry time is cut in half, error tracking and subsequent rescheduling of events is minimized.

5. Cost savings-the cost savings realized is substantial.

6. Data uploading and downloading-automated data transfer via modem prevents manual data entry errors and saves significant time.

Pilot studies are complete and we are looking forward to the quality improvements and complete company wide savings that will be realized as we phase in the FDCS system.

30 LABORATORY AUTOMATION SYSTEM FOR STANDARD AND REAGENT PREPARATION

Marjorie Hummel, Lars Lindquist, Robert Dovi, Frank Dias, Bruce Warden, WMI-Environmental Monitoring Laboratories, Inc., 2100 Cleanwater Drive, Geneva, IL 60134

ABSTRACT

Reagent and standard preparation is necessary for almost every technique used in the chemical laboratory. This is a laborious task and little effort has been made to automate this process. In 1989, our laboratory initiated a project to automate the preparation of 27 standards and 22 reagents for EPA approved methods. This automated system was developed using a custom-designed robot built by Bohdan Automation(Mundelin,IL 60060). The system provides the following benefits:

- Labor savings by unattended operation
- Better utilization of analyst time
- Efficiency gains due to increased sample throughput and improved turn-around time
- High quality of standards and reagents maintained while reducing preparation and documentation time
- Gravimetric verification of all preparations
- An electronic audit trail
- Safer chemical handling.

This automated system is a PC menu-driven, 3-axis overhead gantry arm, operational robot. The system prepares standards and reagents gravimetrically using two different size pipets and an electronic balance. Tests, to date, show the system is equivalent to manual preparation using ASTM Class A glassware.

INTRODUCTION

Standard and reagent preparation is necessary with most methods and can be quite laborious and tedious. Accurately prepared standards and reagents are essential in obtaining the high quality of data needed. The safe handling of chemicals by analysts is another consideration - handling chemicals by an automated system is safer.

With these objectives in mind, our laboratory decided to automate this process. The product of this project is a custom-built laboratory automated system, known as the Reagents and Standards Preparation Robot (RASP). The RASP is capable of preparing up to 49 standards and reagents. It is also capable of working with both liquid and dry chemicals.

Solutions and chemicals are weighed out manually and the diluents and additional liquid chemicals are then added proportionately by the RASP. Liquid chemicals are pipetted by the RASP into the bottles and amounts are determined gravimetrically. At the end of each reagent and/or standard preparation, a label and a report are generated and the pertinent data archived on the PC's hard drive.

RASP DESIGN

The RASP is 102 inches in height and sits on a 32x60 tabletop. The interior of the system is enclosed behind Plexiglass access doors. On the exterior is an air compressor to run the pneumatics,a backup power supply for the robotic portion of the system in the event of a power failure, and a PC with two printers for label and report generation.

The overhead gantry arm moves throughout the whole work area in the three axes (X,Y,Z). The arm is equipped with a gripper hand to pick up bottles or a 1ml pipet hand or a 10ml pipet hand. The arm is controlled by three SAC-560 Smart Axis Controllers. These controllers are microstepper-motor controllers which " will interface to any step motor driver requiring step and direction inputs".[1]

The automated system also includes a top-load balance which is used for all the gravimetric determinations.The robot gravimetrically determines the weights of all standards and reagents made. The balance is used to determine the fluid levels in the bottles prior to pipeting.

The RASP has two polyurethane pipet heads which are connected to automatic microstepper-controlled syringes. These heads allow the use of either 1ml or 10ml pipets. Underneath the heads is a drawer to receive spent pipet tips.

A pump dispenser is connected to four peristaltic pumps. These pumps deliver four diluents which are used for both standards and reagents.

Finally, the last component is a stir plate used to stir the prepared solutions - reagents are stirred for five minutes and standards for 30 seconds.

DISCUSSION

An equivalency study was performed to determine the precision and accuracy of standards prepared by the robot against ASTM Class A glassware.

Standards prepared by the RASP were used for Inductively Coupled Plasma (ICP) and Graphite Furnace Atomic Absorption (GFAA) analyses.

Three separate calibration standards were prepared by the RASP for each of the two analytical systems. Using the calibration curves derived from these calibration standards, certified standards were analyzed by the two techniques. Criteria for equivalency corresponds to results within the acceptance ranges of the certified standards.

To test for precision, ten-element samples and standards were prepared ten times by the RASP and manually using ASTM Class A glassware for ICP analysis. Ten replicate copper samples and standards were prepared for GFAA. These were analyzed using working standards previously prepared manually by the analysts. Criteria for equivalence was for the averages of the set of ten determinations to fall within the current specifications for percent recovery (%R) ± 15% for GFAA and ± 10% for ICP. See Tables 1, 2, and 3 for results. Only sodium for the ten standards prepared for ICP analysis was out of specification (87.8% recovery); recoveries for copper in the robot and manually prepared samples ranged from 99.5% to 106.3%.

Further testing was performed using the RASP by preparing six calibration standards for six point calibration curves for a combined chloride/sulfate analysis and for chemical oxygen demand analysis. Certified quality control standards (three for each analyte) were analyzed to test for accuracy of standard preparation of the calibration standards. Acceptance is based on the ± 2 sigma of the true value established by the manufacturer of the certified quality control standard.The results are summarized in Table 4 below:

Table 4. Recoveries for Standards

	Concentration (ppm)		
Analyte	True	Determined	%Recovery
Cl^-	63.9	63.9	100
Cl^-	35.4	38.4	108
Cl^-	63.9	63.9	100
SO_4	24.3	22.4	92
SO_4	30.4	28.1	93
SO_4	24.3	21.7	89
COD	200	237	94
COD	200	228	90
COD	200	229	90

Table 1. ICP PRECISION DATA

ICP CCV (Robot)

	Ag (500)	Ba (500)	Cd (250)	Cr (500)	Cu (500)	Mn (500)	Fe (2500)	Ca (50000)	Mg (50000)	Na (50000)
	474	483	249	509	469	480	2499	47440	45540	46730
	470	469	248	496	468	462	2342	45110	44170	45100
	486	476	261	520	477	484	2510	48060	46400	47140
	482	473	254	506	476	476	2464	49190	46640	46070
	479	482	251	516	487	477	2476	47750	45290	46710
	486	492	265	528	498	496	2557	49130	47010	47530
	489	490	264	528	480	489	2555	49100	46710	46810
	491	481	260	531	485	497	2556	49130	45610	46520
	489	493	262	534	481	498	2568	48090	46730	47130
	493	491	267	528	504	509	2598	49120	46900	46730
$\bar{X}$	484	483	258	520	484	487	2513	48212	46100	46647
ave %R	96.8	96.6	103.2	103.9	96.7	97.4	100.3	96.4	92.2	93.3

ICP CCV (Manual)

	Ag (500)	Ba (500)	Cd (250)	Cr (500)	Cu (500)	Mn (500)	Fe (2500)	Ca (50000)	Mg (50000)	Na (50000)
	483	493	262	506	491	486	2450	48590	47340	48210
	492	498	265	512	491	503	2504	47250	47170	47690
	475	496	270	501	488	496	2487	46880	45780	48890
	479	492	255	497	489	484	2432	48050	47250	48550
	479	493	260	495	489	481	2420	47940	47510	49810
	476	494	259	500	495	482	2417	48530	48150	49470
	485	488	258	499	497	474	2396	48130	46900	48630
	479	488	252	490	480	476	2399	47120	47060	48050
	486	505	264	501	499	489	2442	47470	47380	47590
	477	498	259	496	486	479	2447	46790	46620	47810
$\bar{X}$	481	495	260	500	491	485	2439	47675	47116	48470
ave %R	96.2	98.9	104.2	99.9	98.1	97.0	97.6	95.4	94.2	96.9

( ) = Conc in ppb.

Table 2. ICP PRECISION DATA

ICP STANDARD (ROBOT)

	Ag (1000)	Ba (1000)	Cd (500)	Cr (1000)	Cu (1000)	Mn (1000)	Fe (5000)	Ca (100000)	Mg (100000)	Na (100000)
	990.2	948.3	559.0	1057	950.8	1047	5249	104000	96510	93620
	918.7	851.2	509.4	956.9	865.6	956.9	4776.5	86970	80180	80925
	926.5	878.3	527.8	985.2	895.4	986.2	4909	94880	86440	85105
	936.6	886.1	521.1	975.0	892.2	989.8	4914.0	88910	84075	82570
	970.4	956.2	517.1	955.2	988.7	965.3	4814.5	97120	96920	92110
	935.3	915.8	508.1	942.5	934.6	966.2	4819.1	96075	96190	88765
	937.3	921.2	531.9	946.3	954.8	977.9	4939.8	98620	97055	89200
	908.3	879.4	491.3	887.6	904.6	933.3	4651.5	86620	86445	82210
	924.8	901.3	514.5	917.8	936.6	956.8	4763.0	93405	94145	86355
	1036.5	1001.1	507.9	957.8	1046	989.5	4956.5	98510	95425	96670
$\bar{X}$	948.5	913.9	518.8	958.1	936.9	976.9	4879.3	94516	91338	87753
Ave %R	94.8	91.3	103.8	95.8	93.7	97.7	97.6	94.5	91.3	87.8

ICP Standard (Manual)

	Ag (1000)	Ba (1000)	Cd (500)	Cr (1000)	Cu (1000)	Mn (1000)	Fe (5000)	Ca (100000)	Mg (100000)	Na (100000)
	964	985	490	958	947	944	4846	96910	93880	98180
	964	994	492	969	952	955	4844	97090	94390	97340
	964	966	490	958	943	956	4796	95540	93760	97970
	971	978	487	970	946	942	4803	95460	94160	96650
	953	981	491	955	954	955	4741	97250	93900	95120
	948	984	491	961	945	946	4805	96400	94260	95040
	966	975	493	961	963	958	4835	96890	95710	98330
	952	968	493	976	959	956	4854	96330	94640	97720
	952	998	490	966	949	965	4851	96500	93240	97690
	957	978	486	977	945	962	4859	95080	94200	94620
$\bar{X}$	959	981	490	965	950	954	4823	96345	94214	96856
ave %R	95.9	98.1	98.1	96.5	95.0	95.4	96.5	96.3	94.2	96.9

( ) = conc. in ppb.

All means fell within ±10% recovery criteria.

Table 3. GFAA PRECISION DATA (for THE ELEMENT Cu)

	Standard Samples (30.0 ppb)		CCV (20.0 ppb)	
	Robotics	Manual	Robotics	Manual
1.	30.2	34.3	19.3	19.1
2.	30.9	31.7	19.1	20.2
3.	30.7	31.4	19.9	20.5
4.	30.3	31.4	18.9	18.6
5.	30.3	32.1	19.8	20.3
6.	34.3	31.4	19.2	20.1
7.	30.8	31.5	25.8	20.2
8.	29.1	31.7	19.1	19.7
9.	30.7	32.0	19.5	19.9
10.	30.8	31.7	19.3	20.5
MEAN	30.8	31.9	20.0	19.9
AVER %R	102.7	106.3	100.0	99.5

The RASP was considered validated for the preparation of standards for these analytes.

The precision of the RASP was also checked by analyzing ten standards each prepared at two concentration levels for the three analytes(Cl^-,SO_4, and COD).The relative standard deviations for the tests are tabulated in the following Table 5.

Table 5. Precision for Cl^-, SO_4 , COD analytes

	Concentration (mg/l)	%RSD* Manual	RASP
Cl^-	2.5	4.6	12.2
Cl^-	100	0.4	2.2
SO_4	40	0.9	2.1
SO_4	400	0.4	1.0
COD	20	18.9	24.9
COD	600	0.8	1.2

*(n=10)

These results were considered acceptable even for the low levels of Cl^- and COD. (Analytical error may have increased the %RSD for these low levels.)

The RASP is now being used to prepare the following reagents for the analytes listed in Table 6.

Table 6. RASP Prepared Reagents

Reagent	Analyte
Mercuric Thiocyanate	Chloride
Ferric Nitrate	Chloride
Barium Chloride	Sulfate
Barium Methlythimalblue Color	Sulfate
Automated Buffer	Cyanide
Chloramine-T	Cyanide
Pyridine Barbituric Acid	Cyanide
Magnesium Chloride	Cyanide
Buffer pH 3.1	Alkalinity Methyl Orange
Methyl Orange	Alkalinity Methyl Orange
Sodium Persulfate	Total Organic Carbon
Phosphoric Acid	Total Organic Carbon

CONCLUSIONS

Our laboratory has automated the process of preparing standards and reagents using a robotic system. Based on the equivalency studies conducted comparing the automated process verses a manual process, the validity of the RASP to prepare standards and reagents has been demonstrated. The robot has been preparing standards as needed on a daily basis for GFAA and ICP and on a weekly basis for the COD, Cl^-, and SO_4 analytes.

REFERENCES

1.SAC-560 Manual Software Version 2.7A; Motion Control Group, American Precision Controls: Buffalo, New York; p.2.

DESIGNING COST-EFFECTIVE MONITORING PROGRAMS

Kim D. Johnson, Account Executive, Environmental Testing and Certification Corp. (ETC)-Midwest, 3025 Hgwy. N78, Mt. Horeb, Wisconsin 53572.

ABSTRACT

In the environmental field, the design of monitoring programs is a daily occurrence. As our field matures, the need for a cost-effective approach to monitoring programs is gaining attention.

The Program Management group worked hand-in-hand with the engineering group in the development of a monitoring program for an industrial client. During the characterization phase of the project, we chose to perform all analyses using the full list of parameters (i.e., EPTOX or TCLP) using Level III Data Quality Objectives. Based on the test results, we met with the engineering staff to discuss a recommendation to the state agency that a reduced parameter list be considered. Agreement with the agency was reached and we developed Level II data quality objectives for the next phase of the project. For this investigation phase, Pb was identified as a tracer analyte.

The purpose of the investigation phase was to determine the perimeter of the contamination at this site. To cost-effectively support the project needs, we developed a modified analytical procedure for Pb which consisted of an abbreviated digestion procedure, limited QC, and shortened ICP run time. The modification was an attempt to lower initial project costs, and shorten the analytical turnaround time. After the analysis of a large number of individual soil samples, we developed a correlation between the EPTOX (Level III data) and the total analysis (Level II data). This correlation data was presented to the state agencies as our basis to justify clean-up levels at this site. Using the site specific data, we reached an agreement with the agency. The analytical results and the support of the analytical laboratory senior staff played an intricate role in the negotiation with the agency.

Many agencies take the position that clean-up must be to background levels. Determining the background level for a specific site, however, can be difficult: How are natural occurring elements factored into this equation? What are potential alternate sources for non-natural occurring elements? How do background levels compare to realistic detection limits? Our strategy of working with the agency and justifying the background levels based on site specific data has been very successful. With concentrated efforts, we have developed a positive image with the agency; based on our determination to be:

- Responsive
- Cooperative
- Responsible

The success of tying the analytical needs to the project needs was a true test of teamwork. The success of the partnership has resulted in:

- Cost-effective program
- Saving of $100,000 for our client
- Accelerated project schedule
- Decreased remediation scope

The need for further cost-effective alternatives for monitoring program development is increasing. In the future, analytical guidance must be closely tied to the development of the project objectives and engineering firms need to work closely with regulatory agencies to develop "customized" site-specific solutions. The support from the analytical laboratory staff is critical to assist clients in chemistry options which can help in development of appropriate DQO. As a laboratory community, we develop strong working relationships which can be very beneficial to our clients. Also, as chemists and scientists, this evaluation of testing options and interpretation of data are strengths. We are hopeful that such actions will offer cost-effective savings to our clients and ultimately, the agency programs.

32 WASTE MINIMIZATION PROGRAM AT ENVIRONMENTAL LABORATORIES

ENVIRONMENTAL

Harish Mehra, Laboratory Director, Chemical Waste Management, Inc., Western Region Laboratory, P.O. Box 4249, Modesto, CA 95352

ABSTRACT

In this paper several methods of controlling the amount of hazardous waste generated at environmental laboratories are discussed. Waste minimization is an important element of current hazardous waste regulations, and developing a "less is better" philosophy can help you meet your objectives in this area. In the body of this paper we will outline how you can achieve waste reductions leading to cost of disposal savings of up to 70%.

All approaches discussed in this report comply with existing health and safety programs, QA/QC concerns, and prescribed EPA laboratory methods. Fourteen specific guidelines are discussed concerning chemical inventory control, waste segregation and treatment, standardized sample sizes, and more conservative subsampling that increase overall efficiency and waste reduction, while ensuring high standards of quality control and rapid turnaround time. Management practices are suggested which can help to achieve goals of waste reduction. The obvious advantages of a waste minimization program are outlined such as reducing costs, saving time and protecting human health and the environment. Therefore, ensuring that environmental laboratories are part of the solution and do not become part of the problem.

33 LABORATORY COMPLIANCE THROUGH SELF AUDIT

Gloria L. Poling, Quality Assurance Manager, Robert A. Thompson, WET Chemistry Supervisor, Chemical Waste Management, Inc., Western Region Laboratory, 1430 Carpenter Lane, Modesto California 95351

ABSTRACT

When analyzing hazardous waste samples, accurate analytical results are critical in determining waste disposal decisions and complying with federal and state regulations. The environmental and financial implications of inaccurate analytical data are detrimental to companies dedicated to protecting the environment and servicing customers. This poster session displays a pro-active, comprehensive Self-Audit program of data review and method adherence which is designed to detect, in a timely manner, analytical problems and compliance issues that could affect waste decisions.

The Western Region Laboratory self-audit program began with the development of formalized checklists for the Lab Director, QA Manager, and supervisors to complete over a prescribed time frame. These audits are performed on a daily, weekly, monthly, quarterly, and semi-annual basis. The frequency is dependent upon the severity of non-compliance for a particular issue. As the program has matured, the frequency of self audits, the items covered, and the level of staff participation have been modified to allow for new problems which occur from time to time.

The Laboratory Director and QA Manager conduct self-audits for compliance with controlled document policies; training performance, documentation, and organization; MDL policies; QC procedures; proper documentation of discrepancies; archiving procedures; facility adequacy; and a review of past action items. In addition, the laboratory group self-audits and laboratory quality assurance group activities are monitored.

Laboratory supervisors self-audits are extremely detailed and include review of data calculations; frequency of QC samples and calculation of control limits; proper documentation techniques; reagent tracking and compatibility of storage; control chart trends; personnel adherence to analytical methods; tracking of samples from receipt to report generation; proper sub-sampling techniques; instrument maintenance and calibration; and effective trouble-shooting for out-of-control situations. Sample processing coordinators perform self-audits that include issues regarding sample storage, paperwork discrepancies, submission of QC samples, and laboratory turn-around time.

The quality assurance group monitors documentation of corrective action for out-of-control situations, errors in the monthly QC statistics report, develops trend analysis charts for blind duplicate discrepancy resolution, and compares results of other QC performance samples.

INTRODUCTION

With the myriad of regulatory, compliance, and health and safety issues currently facing environmental laboratories, a well-structured program to monitor the laboratory's compliance is highly beneficial. The Western Region Laboratory's Self-Audit Program is an extensive system of checklists and other mechanisms designed to measure Quality Assurance, Health and Safety, and Environmental compliance. The success of this program has been it's comprehensiveness, timeliness, and the involvement of personnel at all levels.

Daily, the Laboratory Director performs a laboratory safety/housekeeping inspection. At the end of each month, the Laboratory Director awards points that are applied to each group's safety performance scoring. Likewise, the QA Manager performs a similar inspection of administrative areas.

Monthly, quarterly, and semi-annually, self-audits are performed by the Laboratory Director and QA Manager in accordance with a frequency table located in the Laboratory Director/QA Manager Self-Audit Module. The topics of these self-audits range from ensuring compliance with corporate policies, procedures, and SOP's to review of instrument maintenance and calibration and parameter MDL studies. In addition, the supervisors' self-audits are reviewed with regards to comprehensiveness and seriousness of the discrepancies. The Quality Assurance Manager utilizes a parameter checklist to monitor compliance of Standard Reference Material submission, parallel data input, MDL requirements, or any other activities which are parameter specific.

Upon completion of the self-audit during a given month, the Laboratory Director/QA Manager generate a written summary of the audit results. Corrective action is assigned to the appropriate supervisor for those items which have discrepancies. Due dates for the corrective actions are designated. Correction to action items are followed up by the Laboratory Director/QA Manager on a monthly basis.

The Supervisor's Self-Audit Module is designed to monitor compliance with the Corporate Quality Control Policy and Procedures and with Good Laboratory Practices. On a daily basis, the supervisor has the responsibility of monitoring department productivity, ensuring that samples are analyzed by sample priority, and reviewing raw data and benchsheets.

Using the Supervisor's Quality Assurance Self-Audit Checklist, the supervisors perform weekly, monthly, quarterly, and semi-annual self-audits. The frequency of the items covered is based on the potential and severity of non-compliance. At the end of each month, the results of the audit are summarized with copies of the summary routed to the Laboratory Director and QA Manager, The supervisor assigns responsibilities and due dates for any corrective action. Monthly, the supervisor follows up the action items to ensure completion.

The supervisors' self-audit checklists are extremely detailed. Weekly, at least 10% of the raw data is checked for correctness and completeness. Instrument maintenance, calibration, and daily instrument performance checks are reviewed for compliance. Laboratory contamination is monitored by means of the method blank data. Quality control check sample data is scrutinized to ensure that the QC check samples are plotted, in control, and documented. In addition, duplicate and fortification date are checked for frequency, percent error and recovery calculation, and proper corrective action to out of control situations. Documentation techniques are then reviewed to ensure that the data is defensible, comprehensive, and can "stand alone". Reagents, standards, and sample storage/compatibility are checked for compliance. Monthly, supervisors ensure that personnel are sub-sampling according to corporate SOP; instruments are calibrated and linearity criteria is acceptable and documented; standards and reagents are prepared and disposed of when necessary; and control limit trends and biases are being reviewed. Quarterly, the supervisors are required to perform self-audits on all Standard Division Practices (SDP's). A new checklist is developed for any new or updated SDP. In addition, sample tracking from receipt/Chain-of-Custody to raw data to report generation is audited to ensure sample traceability. On a semi-annual basis supervisors observe analysts performing procedures and document the recertification of analysis.

Many of the self-audit tasks are performed by front-line chemists, technicians, and administrative personnel. Laboratory chemists and technicians are responsible for supply inventory, housekeeping, and ensuring that daily QC samples are within the acceptable range. Immediate action and documentation of out-of-control situations is expected. Also, on a monthly basis, the chemists and technicians within a department cross review each other's logbooks for discrepancies. A summary of this review is forwarded to the department supervisor, who the assigns responsibility to the appropriate analyst as necessary.

Field Support Technicians conduct weekly self-audits of waste containers and waste storage areas. This ensures that waste containers are properly labeled and stored in secondary containment. The results are reviewed by the Waste

Approval Supervisor who delegates and distributes corrective actions and target completion dates. As with all self-audit materials. once corrective action is complete the documentation is filed.

Sample Receipt Technicians perform sample processing self-audits. When a sample is processed, a pre-acceptance checklist is completed. If a serious discrepancy is noted, the sample is put on "hard hold" and the information is provided to the appropriate Customer Service Representative. No analysis can be performed on these samples until the discrepancy is resolved. There are other less serious discrepancies that must be resolved by a Customer Service Representative, but the sample can be processed by the laboratory. In addition, compliance for submission of blind duplicate and parallel samples is monitored utilizing a parameter checklist. Sample Receiving Technicians perform a secondary containment self-audit weekly to ensure that samples are stored by compatible classes and are in secondary or tertiary containment.

Quality Assurance Administrative Support personnel perform self-audits to ensure the laboratory's quest for quality and compliance is meet. By using the "Final Report QC Check" checklist, commercial date packages are reviewed with regards to the customer's request versus the quality of the final product. Utilizing this process, discrepancies are resolved before submission of the data to the customer. Monthly, at least 10% of all out-of-control QC data for a particular lab group is evaluated for proper corrective action and documentation. The results are forwarded to the Group Supervisor, Laboratory Director, and QA Manager. In addition, the QA group graphs Standard Reference Materials, Parallels. and Blind Duplicate results to monitor for trends and frequent discrepancies. Quarterly, the QA group monitors performance of fume hoods and local exhaust systems, documenting all results. Also quarterly, working "Class P" weights are verified against NIST traceable "Class S" weights and the results and correction factors are documented. Semi-annually, the temperature reading of all working thermometers is verified against a NIST traceable thermometer and the results and correction factors recorded.

Waste disposal decisions are especially critical to the entire organization. Any analytical error found during a self-audit is immediately reported to the Waste Decision Group and appropriate corrective action taken. As a secondary check, each waste disposal decision requires the consensus of two Approvals Chemists who have reviewed the analytical date independently of the other. Any errors that occur on the profile or at the point of disposal decision are tracked by the Waste Approval Manager. Re-occurring errors require a corrective action plan approved by the Waste Approval Manager.

SUMMARY

The success of the self-audit program is evident in many instances. Calculation errors that would have affected waste disposal decisions have been found and corrected before any environmental damage or financial expense to the company could occur. On several occasions method adherence issues were noted and corrected to achieve method compliance and better comparability of data. Most importantly, items which carry a higher severity for non-compliance have been noted and are more frequently reviewed. As the self-audit program has developed, the number of discrepancies has immensely decreased in number and severity. Another benefit of the self-audit program has been the involvement of all employees. It has created an "esprit de corps" among the staff in that they are allowed and encouraged to locate discrepancies and to be creative with new, innovative self-audit techniques. Compliance with company QA/QC policies has consistently been achieved through the self-audit process. To ensure the continued success of the program, each Self-Audit Module is reviewed annually.

34

DATA VALIDATION GUIDANCE FOR EPA ORGANIC AND INORGANIC ANALYTICAL METHODS

Ann Rosecrance, Core Laboratories, 10205 Westheimer, Houston, TX 77042

Abstract: The validation of analytical data is important in all environmental measurement activities to assess the quality of the data generated and verify that method quality control requirements and project data quality objectives are met. Data validation is the process of determining the compliance of analytical data with established method criteria and project specifications. This paper provides guidance for the validation of data from the most frequently used EPA organic and inorganic analysis methods for ambient air, drinking water, wastewater, solid waste, and hazardous waste. Comparisons of the quality control criteria for organic analysis methods and inorganic analysis methods are presented in order to identify common elements and differences in the quality control requirements between similar methods. A uniform approach to data validation is presented that can be used for validating data from samples of different matrices analyzed by the various available analytical methods.

INTRODUCTION

The U.S. EPA has developed numerous analytical methods for the determination of organic and inorganic chemicals in a variety of sample matrices by GC, GC/MS, ICP, and AA techniques. Each method defines specific requirements associated with application of the method; additional requirements may be further defined in the associated quality assurance project plan. Laboratory analysts and data reviewers need to be familiar with the requirements of all of the analytical methods that are routinely used in order to ensure that the appropriate procedures are followed. With the large number of analytical methods that are available, it is easy to become confused on the specific requirements of each method. Further, since environmental sample data may be used as legal evidence, and data can be rejected if not in compliance with the applicable requirements, it is critical that sample analyses and associated data are in accordance with the method requirements and project specifications.

Data validation activities determine if analytical data are in compliance with the method requirements and project specifications. Data validation procedures developed by the U.S. EPA and other state agencies for specific programs are used as standards for data validation.[1,2,3,4] Previous studies have provided method comparisons and data validation guidance for multiple organic analysis methods for GC and GC/MS analysis of volatiles, semivolatiles, and pesticides/PCBs in drinking water, wastewater, solid waste, and hazardous waste.[5,6] Additional method comparisons and data validation guidance have been provided for organic methods of analysis for ambient air.[7] This paper provides an overview of the quality control requirements for several EPA organic and inorganic analytical methods. Presented are guidance for the validation of data from similar analytical methods and a uniform approach that can be used to validate data from any organic or inorganic analysis method.

The EPA organic analysis methods for GC/MS analysis of volatiles included in this study are: 524 for drinking water[8], 624 for wastewater[9], 8240 for solid waste[10], the Contract Laboratory Program (CLP) Statement of Work (SOW) OLM01.0 for hazardous waste[11], and Method T014 for ambient air[12]. The EPA organic analysis methods for GC/MS analysis of semivolatiles included in this study are: 525 for drinking water[8], 625 for wastewater[9], 8270 for solid waste[10], the CLP SOW OLM01.0 for hazardous waste[11], and Method T013 for ambient air[12]. The EPA organic analysis methods for GC analysis of pesticides/PCBs included in this study are: 508 for drinking water[8], 608 for wastewater[9], 8080 for solid waste[10], and the CLP SOW OLM01.0 for hazardous waste[11]. The EPA inorganic analysis methods included for metals analysis by ICP and AA are the following: Methods of Chemical Analysis of Water and Wastewater 200 series methods[13]; SW-846 Solid Waste Methods 6010 and 7000[10]; and the EPA CLP SOW for Inorganics Analysis, Multi-Media, Multi-Concentration[14].

DATA VALIDATION DEFINITION

Data validation has been defined by EPA as a systematic process, consisting of data editing, screening, checking, auditing, verification, certification, and review for comparing data to established criteria in order to provide assurance that data are adequate for their intended use.[15] Data validation is essentially a question and answer process to determine if data meet both the analytical method requirements and the associated project specifications. The three major questions to assess in validating data are the following: were the required quality control (QC) elements included, were they included at the required frequency, and were the required acceptance criteria met.

DATA VALIDATION APPROACH

The recommended approach for validating data from multiple (or single) analysis methods involves the preparation and use of summaries of the required QC and other criteria for each similar method in use. For example, comparisons of the quality control and other technical requirements of the volatile methods are prepared for use in validating data for volatile organic analyses. The major requirements of each of the analytical methods of interest are then readily available and are compared to other similar methods in an easy to reference format. Revisions or additional methods can be included as needed. This approach is straightforward because it is based on the common elements between methods. The method documents are used for reference when needed to clarify specific requirements. The data validation process proceeds by following closely to the sequence of the analysis and the procedures established by EPA for data validation. Data generated from any of the methods are compared for compliance with the applicable criteria. Using summary charts that provide the required criteria and checklists that record compliance with the applicable criteria, the data validation process can be performed effectively and efficiently for multiple analysis methods.

QUALITY CONTROL ELEMENTS

The quality control elements that are subjected to data validation are comprised of the following types of analyses: method quality control, sample quality control, and other quality control. Method quality control consists of the analyses necessary for setting up for the sample analyses and the analyses that are common to the sample batch. This includes instrument tuning (for GC/MS analyses), calibration standards, blanks, laboratory control standards, spikes, and duplicates. Sample quality control are the criteria that are specific to each sample. For organic analyses, this includes internal standards, surrogate spikes, and the identification and quantitation of target analytes and tentatively identified (library search) compounds. Inorganic sample quality control includes ICP serial dilutions, furnace AA duplicate injections and post-digestion spikes, and the identification and quantitation of target analytes. Other quality control consists of additional analyses that are necessary to assess the field and laboratory procedures and to utilize the data. This includes container certifications, field blanks, field replicates, detection limit determinations, precision and accuracy determinations, and performance evaluation sample analyses. A recommended sequence for data validation that addresses each of these quality control elements is provided in Figure 1.

QUALITY CONTROL FOR ORGANIC ANALYSES

The following section summarizes the major QC requirements for several EPA GC/MS and GC methods for the analysis of volatiles, semivolatiles, and pesticides/PCBs. This information is not a replacement for the reference method documents or the EPA data validation procedures, but it is a management tool to assist laboratory analysts and data reviewers in keeping track of the requirements of multiple analysis methods.

Tuning. Tuning/instrument performance checks ensure that GC/MS mass assignments and relative ion abundances are in accordance with the established method performance criteria. Tuning data are evaluated for analysis of the correct compound, at the required concentration and frequency, and

within the required relative ion abundance criteria. A summary of tuning requirements for volatiles and semivolatiles methods are provided in Tables 1 and 2, respectively. A comparison of the relative ion abundance criteria for BFB and DFTPP for each of the methods are presented in Tables 3 and 4, respectively. Tuning data that do not meet the required relative ion abundance criteria should be evaluated to determine if the deviation is significant and would impact the sample results.

Initial Calibration. Initial calibration checks ensure that acceptable qualitative and quantitative data could be generated at the initiation of the analysis. Initial calibration data are evaluated for analysis of the required analytes, at the required number of levels and concentrations, at the required frequency, and within the required response factor and linearity criteria. Pesticide/PCB data are also evaluated for chromatographic resolution, the acceptability of retention time window determinations, and DDT/endrin breakdown. A summary of initial calibration requirements for volatiles, semivolatiles, and pesticides/PCB methods are provided in Tables 1, 2, and 5, respectively. Initial calibration data that do not meet the required criteria should be evaluated to determine if the deviation is significant and would impact the sample results, and if qualification of the data is needed.

Continuing Calibration. Continuing calibration checks ensure that the qualitative and quantitative measurements established in the initial calibration could be met subsequent to the initial calibration. Continuing calibration data are evaluated for analysis of the required analytes, at the required concentrations, within the required frequency, and within the required response factor and precision criteria. A summary of continuing calibration requirements for volatiles, semivolatiles and pesticides/PCB methods are provided in Tables 1, 2, and 5, respectively. Further details on calibration requirements are provided in the reference methods. Continuing calibration data that do not meet the required criteria should be evaluated to determine if the deviation is significant and would impact the sample results, and if qualification of the data is needed.

Method Blanks. Method blanks measure background contamination to ensure that contamination does not interfere with the analysis and sample data. Method blank data are evaluated for analysis of the correct source of material, at the required frequency, and within the acceptable background level for target analytes. A summary of method blank requirements for volatiles, semivolatiles, and pesticides/PCB methods are provided in Tables 1, 2, and 5, respectively. In general, the contamination in the method blank should be no higher than the detection limit or reporting limit. If unacceptable contamination exists in the method blank, then all associated sample data should be carefully evaluated to determine if the sample data are affected by the background contamination. If affected, the sample data should be qualified appropriately.

Spikes and Duplicates. Spikes and duplicates ensure that the analytical performance in specific samples is within the accuracy and precision specifications that have been established for the method. Blank spikes determine the recovery of analytes in blank matrices and matrix spikes assess the effect of the sample matrix on the analytical results. Duplicates provide a measure of the precision of the sample analysis. Spike data are evaluated for analysis of the required analytes in the required type of spike, at the required concentrations, within the required frequency, and within the required acceptance criteria for % recovery. Duplicate data are evaluated for analysis of the required type of duplicate, within the required frequency, and within the required acceptance criteria for precision (RPD or % RSD). A summary of spike and duplicate requirements for volatiles, semivolatiles, and pesticides/PCB methods are provided in Tables 1, 2, and 5, respectively. Spike and duplicate data that do not meet the required criteria should be evaluated for their impact on the sample results and the data should be qualified appropriately.

Other Quality Control. Other quality control includes additional analyses associated with verification of the acceptability of the sampling and analysis procedures. Sample collection devices should be evaluated for the presence of background contaminants. Field quality control measures should include field blanks and replicate samples to measure field contamination and sample precision. The analytical system should be tested to establish that required method detection limits can be achieved and that

acceptable precision and accuracy data can be obtained. Additional laboratory quality control measures include performance evaluation samples to determine analytical accuracy and method performance. Data for each quality control analysis evaluated to determine if the applicable acceptance criteria were met.

Sample Quality Control. Sample data are evaluated for adherence to a number of criteria in order to determine the acceptability of the sample results. A summary of sample quality control requirements for volatiles, semivolatiles, and pesticides/PCB methods are provided in Tables 1, 2, and 5, respectively. Sample collection, extraction, and analysis times are evaluated to determine if technical holding times were met. Internal standard areas and the retention times in the samples are compared to those in the corresponding calibration standard to ensure that the instrument conditions were stable between the analysis of the calibration standard and each sample. Surrogates are included in samples to determine if the recoveries of non-target analytes were acceptable throughout the preparation and analysis procedure. Surrogate data are evaluated for analysis of the required number and concentrations of surrogates, within the required acceptance criteria for % recovery. A comparison of the acceptance limits for surrogate recovery in volatile, semivolatile, and pesticides/PCB methods are provided in Tables 6, 7, and 8, respectively.

Found target analytes in samples are evaluated against the corresponding analytes in the calibration standard to ensure that the retention times or relative retention times are within the acceptance criteria of the method. Mass spectra for found target analytes are evaluated against the standard mass spectra to ensure that the major ions present in the standard are present in the sample mass spectra within comparable relative ion abundances. Mass spectral library searches for tentatively identified compounds are reviewed to ensure that identifications are acceptable. Quantitative results are checked for correctness of calculations, the use of the appropriate units, and to ensure that found target analytes concentrations are within the calibration range. The reported results are reviewed to ensure that they fully agree with the raw data and that the appropriate quantitation or detection limits were used for reporting the sample values. Sample data are reviewed for adherence to the associated project specifications and reporting requirements. Sample data that do not meet any of the required criteria should be qualified appropriately.

QUALITY CONTROL FOR INORGANIC ANALYSES

The following section provides a brief summary of the major QC requirements for several EPA ICP and AA methods for metals analysis. Further details on method requirements are provided in the reference methods and the EPA data validation procedures.

Initial Calibration. Initial calibration data are evaluated for analysis of the required analytes, at the required number of levels and concentrations, at the required frequency, and within the required acceptance criteria and recommended correlation coefficient (i.e., >0.995). A summary of initial calibration requirements for metals by ICP and AA are provided in Tables 9 and 10, respectively.

Calibration Verification. Initial and continuing calibration verification data are evaluated for analysis of the required analytes, at the required concentrations, within the required frequency, and within the required acceptance criteria for % recovery. A summary of calibration verification requirements for metals by ICP and AA are provided in Tables 9 and 10, respectively.

Blanks. Calibration blanks and preparation blanks are included with metals analyses to check the background from the analysis and preparation procedures, respectively. Blank data are evaluated for analysis of the correct source of material, at the required frequency, and within the acceptable background levels for target analytes. A summary of blank requirements for metals by ICP and AA are provided in Tables 9 and 10, respectively.

ICP Interference Check Sample (ICS). The ICS checks the interelement and background correction factors for the ICP instrument. ICS data are evaluated for analysis of the correct solutions, within the required frequency, and within the required acceptance criteria (% recovery for known analytes and values less than the instrument detection limit for not present analytes). A summary of ICS requirements for metals by ICP analysis is provided in Table 9.

Laboratory Control Standard (LCS). The LCS checks the laboratory performance on the sample preparation and analysis procedures. LCS data are evaluated for analysis of the correct type of LCS, for each matrix and method, at the required frequency, and within the required acceptance criteria for % recovery. A summary of LCS requirements for metals by ICP and AA are provided in Tables 9 and 10, respectively.

Matrix Spikes and Duplicate Samples. Matrix spike and duplicate sample data are evaluated for analysis of the correct type of spike and duplicate, at the required frequency, with the required analytes at the required concentration for spikes, and within the required acceptance criteria (% recovery for spikes and RPD for duplicates). A summary of matrix spike and duplicate sample requirements for metals by ICP and AA are provided in Tables 9 and 10, respectively.

Other Quality Control. Other quality control includes instrument detection limit determinations, linear range analyses, and performance evaluation sample analyses. The EPA CLP SOW for inorganics analysis requires that instrument detection limit determinations and linear range analyses be performed quarterly. Performance evaluation sample analyses are performed at varying frequencies from quarterly to each sample delivery group. Data for each quality control analysis are evaluated to determine if the results were within the required acceptance criteria.

Sample Quality Control. Sample data are evaluated for adherence to sample specific quality control criteria. Sample data are evaluated to ensure that preparation and analysis holding times were met (analysis holding times for metals are generally 6 months from sample collection for samples that are preserved at pH <2, except for mercury which is 28 days), that the target analytes are reported properly, and that reported values are within the calibration range for AA and linear range for ICP. ICP methods require that serial dilutions be performed to determine if there are major chemical or physical interferences in the sample matrix. ICP data are evaluated for analysis of the required sample dilutions and for the agreement of the original sample with the dilution. Furnace AA methods require that duplicate injections and post digestion spikes be performed to measure the precision and accuracy of each sample analysis. Furnace data are evaluated for analysis of the required duplicate injections and post digestion spikes, for each sample, within the required acceptance criteria (% RSD for duplicates and % recovery for spikes). A summary of ICP serial dilution and furnace QC requirements are provided in Tables 9 and 10, respectively.

DATA VALIDATION DOCUMENTATION

Data validation activities should be documented on standardized forms such as the data review checklists provided in Figures 2 and 3 for organic analysis data. The forms should report the adherence or lack of adherence to each of the required quality control criteria. The agreement of the raw data and the data report should be noted. Any major deficiencies identified should be documented in a data validation report describing each deficiency and its potential impact on the sample results. Non-compliant or questionable data should be qualified with appropriate data qualifiers. Examples of qualifiers used in EPA Data Validation Procedures are: (R), the results are rejected due to serious deficiencies in quality control criteria; (J), the associated numerical value is an estimated quantity because certain quality control criteria were not met; (N), presumptive evidence of presence of material; (U) the material was analyzed for but not detected; and (UJ), a combination of U and J.[1,2,3] Finally, the data validation report should include an overall evaluation of the data, in addition to any recommendations for further action.

SUMMARY

Data validation is an integral part of the environmental data generation process and in order to be efficient and effective, the data validation process must be versatile and straightforward. With the large number of analytical methods that are available for sample analyses, the requirements of each method must be readily available. The information presented in this paper summarizes the QC requirements for several EPA organic and inorganic analytical methods and compares those requirements to similar methods. Data validation guidance for multiple methods is provided so that a single approach can be used for validating data from similar analytical methods. This gives laboratory analysts and data reviewers a management technique for addressing the specific requirements of each method utilized and for ensuring that QC requirements of the applicable method are met. This information is not intended as a replacement for the reference methods or EPA data validation procedures, but is a reference on the quality control and data validation requirements of multiple analysis methods.

REFERENCES

1. Quality Assurance/Quality Control Guidance for Removal Activities; Sampling QA/QC Plan and Data Validation Procedures, EPA 540/G-90/004, U.S. EPA, Washington D.C., April 1990.

2. Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, U.S. EPA, 1988.

3. Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses, U.S.EPA, 1988.

4. Standard Operating Procedures for Quality Assurance Data Validation of Analytical Deliverables, New Jersey Department of Environmental Protection and Energy, TCL-Organics SOP No. 5.A.13, October 1991 and TAL-Inorganics SOP No. 5.A.02, February 1992.

5. A.E.Rosecrance, "Data Validation Guidance for Multiple Organic Analysis Methods," in Proceedings of Water Pollution Control Federation's Specialty Conference on Analytical Compliance and Data Objectives, Durham, August 1991.

6. A.E.Rosecrance, "Data Verification Guidance for GC and GC/MS Environmental Analyses," in Proceedings of the 1992 HazTech International Environmental Conference, Houston, February 1992.

7. A.E.Rosecrance, "Data Validation for Guidance for Ambient Air Methods", presented at the Measurement of Toxics and Related Air Pollutants Symposium, cosponsored by U.S. EPA and Air & Waste Management Society, Durham, May 1992.

8. Methods for the Determination of Organic Compounds in Drinking Water, EPA 600/4-88/039, U.S. EPA, Cincinnati, December 1988, Methods 524, 525, and 508.

9. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, U.S. EPA, Appendix A to 40CFR Part 136, Vol. 49, No. 209, October 26, 1984, Methods 624, 625, and 608.

10. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S. EPA, Washington D.C., Third Edition, September 1986, Methods 8240, 8270, 8080, 6010, and 7000.

11. Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, U.S. EPA Contract Laboratory Program OLM01.0, August 1991 Revision.

12. W.T. Winberry, Jr., N.T.Murphy and R.M.Riggin, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA 600/4-89/017, U.S. EPA, Research Triangle Park, June 1988, Methods TO13 and TO14.

13. Methods of Chemical Analysis of Water and Wastewater, EPA 600/4-79/020, U.S. EPA, Cincinnati, Revised March 1983, Section 200.0 and Method 200.7.

14. Statement of Work for Inorganics Analysis, Multi-Media Multi-Concentration, U.S. EPA Contract Laboratory Program, ILM01.0.

15. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, U.S. EPA, Washington D.C., QAMS-005-80, December 1980.

TABLE 1. COMPARISON OF QC REQUIREMENTS FOR VOLATILE ORGANIC ANALYSIS METHODS

PROCEDURE	T014	524	624	8240	CLP
TUNING	BFB	BFB	BFB	BFB	BFB
Frequency	Daily	8 hrs	Daily	12 hrs	12 hrs
Criteria	Table 3	Table 3	Table 3	Table 3	Table 3
IC: Levels	3 + blank	3-5	3	5	5
Criteria (%RSD)	NS	<20%	<35%	<30% (6)	<20.5%
Minimum RRF	NS	NS	NS	0.250-0.300 (5)	0.01-Min value
CC: Frequency	Daily	8 hrs	Daily	12 hrs	12 hrs
Criteria (%D)	NS	±30%	QC Limits	±25% (6)	±25.0%
IS Area	NS	±30% of last CC or ±50% IC	NS	-50 to +100% of last CC	NS
BLK: Frequency	Daily	12 hrs	Daily	12 hrs	12 hrs
Criteria	<0.2ppbv	<MDL	In Control	In Control	<CRQL
SPIKES: Frequency	NS	Daily or 5%	5%	5%	5% or 1/SDG
%Recovery	90-110%	80-120%	Varies	Varies	Varies
REPLICATES: Frequency	NS	Quarterly	NS	5%	5% or 1/SDG
Precision	<5% RSD	<20% RSD	NS	Varies	RPD Varies
HOLDING TIME (days)	30 C*	14 C*	14 C*	14 C*	10 R*
INTERNAL STDS.	NS	1 @ 2-10 ug/L	3 @ 30 ug/L	3 @ 50 ug/L	3 @ 50 ug/L
Criteria	NS	NS	NS	NS	Area: -50 to +100% RT ±30sec
SURROGATES	NS	2 @ 2-10 ug/L	3 @ 30 ug/L	3 @ 50 ug/L	3 @ 50 ug/L
Criteria	NS	80-120%	NS	Table 6	Table 6
ANALYTE ID	RT ±0.10 min 3 ions ±15-25%	RT ±30sec 3 ions ±20%	RT ±30sec 3 ions ±20%	RRT ±0.06 Ions >10% ±20%	RRT ±0.06 Ions >10% ±20%

NS: Not Specified; IC: Initial Calibration; CC: Continuing Calibration;
C: Days from Collection; R: Days from Receipt
Note: For more detailed infomation, refer to the corresponding method document.

TABLE 2. COMPARISON OF QC REQUIREMENTS FOR SEMIVOLATILE ORGANIC ANALYSIS METHODS

PROCEDURE	T013	525	625	8270	CLP
TUNING	50 ng DFTPP	5 ng DFTPP	50 ng DFTPP	50 ng DFTPP	50 ng DFTPP
Frequency	Daily	8 hrs	Daily	12 hrs	12 hrs
Criteria	Table 4	Table 4	Table 4	Table 4	Table 4
IC: Levels	3-5	6	3	5	5
Criteria (%RSD)	<20%	<30%	<35%	<30% (13)	<20.5%
Minimum RRF	NS	NS	NS	0.050 (4)	0.01-Min value
CC: Frequency	Daily	8 hrs	Daily	12 hrs	12 hrs
Criteria (%D)	±20%	±30%	±20%	±30% (13)	±25.0%
IS Area	NS	±30% of last CC or ±50% IC	NS	-50 to +100% of last CC	NS
BLK: Frequency	1/batch	1/batch	1/batch	1/batch	1/group ext.
Criteria	<10 ng/cart.	<MDL	In Control	In Control	<CRQL
SPIKES: Frequency	5%	Daily or 5%	5%	5%	5% or 1/SDG
%Recovery	NS	80-120%	Varies	Varies	Varies
REPLICATES: Frequency	NS	Quarterly	NS	5%	5% or 1/SDG
Precision	NS	<20% RSD	NS	Varies	RPD Varies
HOLDING TIME (days)	Extract: 7*	Extract: 7 C* Analyze: 30 C*	Extract: 7 C* Analyze: 40 E*	Extract: 7-14 C* Analyze: 40 E*	Extract: 5-10 R* Analyze: 35 E*
INTERNAL STDS.	1-5 @ 40 ng/uL	3 @ 5 ng/uL	3	6 @ 40 ng/uL	6 @ 20 ng/uL
Criteria	NS	>70% Recovery	NS	NS	Area -50 to +100% RT ±30sec
SURROGATES	NS	3 @ 5 ug/L	3 @ 100 ug/L	6 @ 100-200 ug/L	8 @ 75-150 ug/L
Criteria	80-120%	80-120%	NS	Table 7	Table 7
ANALYTE ID	RRT ±0.06 3 ions ±15-25%	RT ±30sec 3 ions ±20%	RT ±30sec 3 ions ±20%	RRT ±0.06 Ions >10% ±20%	RRT ±0.06 Ions >10% ±20%

NS: Not Specified; IC: Initial Calibration; CC: Continuing Calibration;
C*: Days from Collection; R*: Days from Receipt; E*: Days from Extraction
Note: For more detailed information, refer to the corresponding method document.

TABLE 3. COMPARISON OF BFB RELATIVE ION ABUNDANCE CRITERIA

ION ABUNDANCE CRITERIA	METHOD T014	METHOD 524	METHOD 624	METHOD 8240	CLP SOW
50 % of mass 95	15-40%	15-40%	15-40%	15-40%	8.0-40.0%
75 % of mass 95	30-60%	30-80%	30-60%	30-60%	33.0-66.0%
95	100%	100%	100%	100%	100%
96 % of mass 95	5-9%	5-9%	5-9%	5-9%	5.0-9.0%
173 % of mass 174	<2%	<2%	<2%	<2%	<2.0%
174 % of mass 95	>50%	>50%	>50%	>50%	50.0-120.0%
175 % of mass 174	5-9%	5-9%	5-9%	5-9%	4.0-9.0%
176 % of mass 174	95-101%	95-101%	95-101%	95-101%	93.0-101.0%
177 % of mass 176	5-9%	5-9%	5-9%	5-9%	5.0-9.0%

TABLE 4. COMPARISON OF DFTPP RELATIVE ION ABUNDANCE CRITERIA

ION ABUNDANCE CRITERIA	METHOD T013	METHOD 525	METHOD 625	METHOD 8270	CLP SOW
51 % of mass 198	30-60%	10-80%	30-60%	30-60%	30.0-80.0%
68 % of mass 69	<2%	<2%	<2%	<2%	<2.0%
70 % of mass 69	<2%	<2%	<2%	<2%	Present
127 % of mass 198	40-60%	10-80%	40-60%	40-60%	25.0-75.0%
197 % of mass 198	<1%	<2%	<1%	<1%	<1.0%
198	100%	100%	100%	100%	100%
199 % of mass 198	5-9%	5-9%	5-9%	5-9%	5.0-9.0%
275 % of mass 198	10-30%	10-60%	10-30%	10-30%	10.0-30.0%
365 % of mass 198	>1%	>1%	>1%	>1%	>0.75%
441	<mass 443	<mass 443	<mass 443	<mass 443	<mass 443
442 % of mass 198	>40%	>50%	>40%	>40%	40.0-110.0%
443 % of mass 442	17-23%	15-24%	17-23%	17-23%	15.0-24.0%

TABLE 5. COMPARISON OF QC REQUIREMENTS FOR PESTICIDE/PCB ANALYSIS METHODS

PROCEDURE	508	608	8080	CLP
IC: Levels	3-5	3	5	3 (1 for multi-component)
Criteria (%RSD)	<20%	<20%	<20%	<10.0-15.0%
DDT/Endrin Breakdown	<20%	NS	<20%	<20.0%
Resolution	NS	NS	NS	90-100%
CC: Frequency	Beg. and end	Daily	Daily	12 hrs
Criteria (RPD)	±20%	±15%	±15%	±25.0%
RT	NS	NS	NS	±0.02 min of mean RT
BLK: Frequency	1/batch	1/batch	1/batch	1/batch
Criteria	<MDL	In Control	In Control	<CRQL
SPIKES: Frequency	10%	10%	5%	5% or 1/SDG
%Recovery	Avg %Rec. ±3S	Varies	Varies	Varies
REPLICATES: Frequency	Quarterly	NS	5%	5% or 1/SDG
Precision	<20% RSD	NS	Varies	RPD Varies
HOLDING TIME (days)	Extract: 7 C* Analyze: 14 E*	Extract: 7 C* Analyze: 40 E*	Extract: 7-14 C* Analyze: 40 E*	Extract: 5-10 R* Analyze: 35 E*
SURROGATES	1 @ 25 ug/L	NS	2 @ 1 ug/L	2 @ 0.2 ug/L
Criteria	70-130% Recovery	NS	Lab QC limits	60-150%; RT ± 0.02 min
ANALYTE ID	RT within 3XSD std. RT window	RT within 3XSD std. RT window	RT within 3XSD std. RT window	RT ± 0.02 min of std. RT on both columns; Conc. ±25.0%
Confirmation	2nd column or detector for positive ID	2nd column for unknown samples	2nd column for positive ID	2 columns required; GC/MS if >10ng/ul

NS: Not Specified; IC: Initial Calibration; CC: Continuing Calibration;
C*: Days from Collection; R*: Days from Receipt; E*: Days from Extraction
Note: For more detailed information, refer to the corresponding method document.

TABLE 6. COMPARISON OF VOLATILE SURROGATE RECOVERY LIMITS

COMPOUND	METHOD 524	METHOD 624	METHOD 8240 WATER	METHOD 8240 SOIL	CLP SOW WATER	CLP SOW SOIL
4-Bromofluorobenzene	80-120%	NS	86-115%	74-121%	86-115%	59-113%
1,2-Dichloroethane-d4	80-120	NS	76-114	70-121	76-114	70-121
Toluene-d8	80-120	NS	88-110	81-117	88-110	84-138

TABLE 7. COMPARISON OF SEMIVOLATILE SURROGATE RECOVERY LIMITS

COMPOUND	METHOD 525	METHOD 625	METHOD 8270 WATER	METHOD 8270 SOIL	CLP SOW WATER	CLP SOW SOIL
Nitrobenzene-d5	80-120%	NS	35-114%	23-120%	34-114%	23-120%
2-Fluorobiphenyl	80-120	NS	43-116	30-115	43-116	30-115
p-Terphenyl-d14	80-120	NS	33-141	18-137	33-141	18-137
Phenol-d6	80-120	NS	10-94	24-113	10-110	24-113
2-Fluorophenol	80-120	NS	21-100	25-121	21-110	25-121
2,4,6-Tribromophenol	80-120	NS	10-123	19-122	10-123	19-122
1,2-Dichlorobenzene-d4	80-120	NS	NS	NS	16-110	20-130
2,4,6-Tribromophenol	80-120	NS	NS	NS	33-110	20-130

TABLE 8. COMPARISON OF PESTICIDE SURROGATE RECOVERY LIMITS

COMPOUND	METHOD 508	METHOD 608	METHOD 8080	CLP SOW
4,4-Dichlorobiphenyl	70-130%	NS	NS	NS
Tetrachloro-m-xylene	NS	NS	Lab Limits	60-150%
Decachlorobiphenyl	NS	NS	NS	60-150%
Dibutylchlorendate	NS	NS	Lab Limits	NS

NS Not Specified

TABLE 9. COMPARISON OF QC REQUIREMENTS FOR EPA METALS ANALYSIS METHODS BY ICP

PROCEDURE	CLP SOW	METHOD 6010	METHOD 200.7
Initial Calibration	2: 1 standard and a calib. blank	Calibrate and check with 2 stds. and blank	Calibrate with 1 standard (min) and a blank
• Frequency	Daily or every 24 hours	Daily	Daily
• Criteria	±5% of true value	NS	NS
Calibration Verification	Mid-range standard	Mid-range standard	Mid-range standard
• Frequency	Beg., end and every 10 samples or every 2 hrs	Every 10 samples and at end	Every 10 samples
• Criteria	90-110% Recovery	90-110% Recovery	95-105% Recovery
Other Standards	2x CRDL or IDL	Highest mixed std.	Highest mixed std.
• Frequency	Beg. and end of each sample run or 2 per 8 hr shift	Before sample analyses	Before sample analyses
• Criteria	EPA QC limits	95-105% Recovery	95-105% Recovery
Calibration Blanks			
• Frequency	Beg., end, and 10% of samples or every 2 hours	Every 10 samples and at end	Every 10 samples
• Criteria	All ≤ CRDL	±3 SD of mean value	±2 SD of mean value
Preparation Blanks			
• Frequency	1/SDG/digestion batch	1/batch	1/batch
• Criteria	All ≤ CRDL	NS	NS
Laboratory Control Standard			
• Frequency	1/SDG or dig.batch/matrix	Each IC and weekly	Each IC and weekly
• Criteria	80-120% Recovery	90-110% Recovery	95-105% Recovery
Matrix Spike Samples			
• Frequency	5% or 1/SDG/matrix/level (predigestion)	5% or 1/batch	New sample matrix
• Criteria	75-125% Recovery	75-125% Recovery	90-110% Recovery
Duplicate Samples			
• Frequency	5% or 1/SDG/matrix/level	5% or 1/batch	NS
• Criteria	±20% RPD	±20% RPD for values >10x IDL	NS
Interference Check Sample			
• Frequency	Beg. and end of each run or 2 per 8 hr shift	Beg. and end of each run or 2 per 8 hr shift	Beg., end & periodic intervals
• Criteria	80-120% Recovery	80-120% Recovery	±1.5x SD of mean value
Serial Dilution			
• Frequency	1/SDG/matrix/level	New sample matrix	New sample matrix
• Criteria	5x Dil. within ±10%	4x Dil. within ±10%	Dilution within ±5%

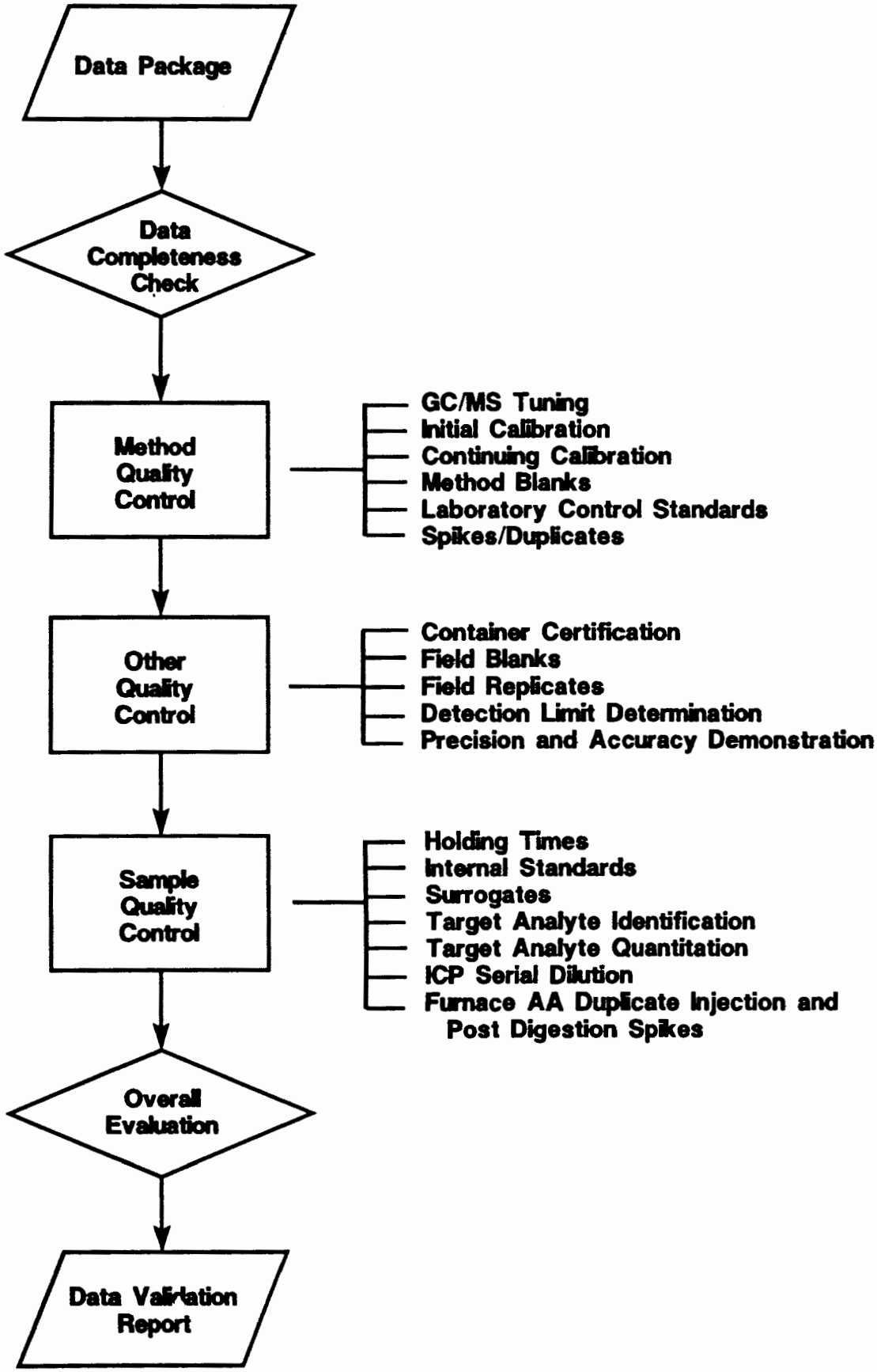
NS Not Specified

TABLE 10. COMPARISON OF QC REQUIREMENTS FOR EPA METALS ANALYSIS METHODS BY AA

PROCEDURE	CLP SOW	METHOD 7000	SECTION 200.0
Initial Calibration	4: blank and 3 standards	4: blank and 3 standards	4: blank and 3 standards
• Frequency	Daily or every 24 hours	Daily	Daily
• Criteria	±5% of true value	± 10% of true value	NS
Calibration Verification	Mid-range standard	Mid-range standard	At or near MDL
• Frequency	Beg., end, and every 10 samples or every 2 hrs	Every 10 samples	Every 20 samples
• Criteria	90-110% Recovery	80-120% Recovery	90-110% Recovery
Other Standards	2x CRDL or IDL	NS	NS
• Frequency	Beg. of each sample run	NS	NS
• Criteria	EPA QC Limits	NS	NS
Calibration Blanks			
• Frequency	Beg., end, and every 10 samples or every 2 hours	After each calibration	After each calibration
• Criteria	All ≤ CRDL	NS	NS
Preparation Blanks			
• Frequency	1/SDG or digestion batch	Each digestion batch	Each digestion batch
• Criteria	All ≤ CRDL	NS	NS
Laboratory Control Standard			
• Frequency	1/SDG/matrix	After each calibration	NS
• Criteria	80-120% Recovery	90-110% Recovery	NS
Matrix Spike Samples			
• Frequency	5% or 1/SDG/matrix/level (predigestion)	5% or 1/batch	NS
• Criteria	75-125% Recovery	85-115% Recovery	NS
Duplicate Samples			
• Frequency	5% or 1/SDG/matrix/level	5% or 1/batch	10% or 1/batch
• Criteria	±20% RPD	NS	±20% RPD
Furnace QC			
• Frequency	Duplicate injections on all; Post-digestion spikes on all samples, blanks and LCS	NS	NS
• Criteria	Duplicate injections: ±20% RSD or CV; Spikes: 85-115% Recovery	NS	NS

NS Not Specified

FIGURE 1. DATA VALIDATION PROCESS



METHOD DATA REVIEW CHECKLIST

PARAMETER _____ ANALYSIS METHOD _____

JOB/CASE _____ DATES ANALYZED _____

PROCEDURE	YES	NO	QUALIFIER	COMMENTS
TUNING				
• Required compound?				
• Correct frequency?				
• Criteria met?				
INITIAL CALIBRATION				
• All analytes present?				
• Required levels?				
• Correct frequency?				
• Criteria met?				
CONTINUING CALIBRATION				
• Correct concentration?				
• All analytes present?				
• Correct frequency?				
• Criteria met?				
METHOD BLANKS				
• Correct source?				
• Correct frequency?				
• Criteria met?				
SPIKES				
• All analytes present?				
• Required concentration?				
• Correct frequency?				
• Criteria met?				
DUPLICATES				
• Required type?				
• Correct frequency?				
• Criteria met?				
QC CHECK SAMPLE				
• Required frequency?				
• Criteria met?				

Figure 2. Data Validation Checklist for Method Quality Control Review

SAMPLE DATA REVIEW CHECKLIST

SAMPLE NO. _____

PARAMETER _____ DATE COLLECTED _____

METHOD _____ DATE(S) PREPARED _____

JOB/CASE _____ DATE(S) ANALYZED _____

PROCEDURE	YES	NO	QUALIFIER	COMMENTS
HOLDING TIME				
• Preparation holding times met?				
• Analysis holding times met?				
INTERNAL STANDARDS				
• Areas within limits?				
• RRTs within limits?				
SURROGATES				
• Required spikes included?				
• Recoveries within limits?				
• Reanalyses within limits?				
FOUND TARGET ANALYTES				
• RTs/RRTs within limits?				
• MS comparable to standard?				
• Calculations correct?				
• Concentrations within range?				
TENTATIVELY IDENTIFIED COMPOUNDS				
• Major non-target analyte peaks identified?				
• Identifications OK?				
• Calculations correct?				
REPORTED DATA				
• Agrees with raw data?				
• Appropriate QLs/DLs?				
OTHER CRITERIA				

ADDITIONAL COMMENTS

REVIEWED BY _____ DATE _____

Figure 3. Data Validation Checklist for Sample Quality Control Review

35 USE OF PERFORMANCE EVALUATION SAMPLES IN ASSESSING ENVIRONMENTAL DATA QUALITY

Diann Sims Dwight, Peggy Zawodny, U.S. Environmental Protection Agency, Region III, Central Regional Laboratory, 839 Bestgate Road, Annapolis, Maryland 21401.

Abstract: Performance evaluation (PE) samples have been historically employed to assess laboratory proficiency and to validate analytical methods. Periodic use as part of a laboratory quality assurance program provides indicators of analytical performance and analyst proficiency. The PE sample is also used as a component of certification and accreditation programs. Based on study results that are summarized in this paper, results of matrix specific PE samples submitted and analyzed with environmental samples can indicate systematic error that is not apparent in routine precision and accuracy measurements. Example cases will be presented to demonstrate the effectiveness of PE samples as an external quality assessment tool. The cases will show that PE sample results can be evaluated with respect to a specific sample batch and the associated data quality objectives. Case study results confirm that the PE sample data are effective when used to diagnose and verify the analytical performance and capability demonstrated with a given sample batch. This substantiates that the data quality achieved satisfies data quality requirements.

INTRODUCTION

Performance evaluation samples are defined as certified materials with established limits of uncertainty. The composition and concentration of constituents are unknown to the analyst. An environmental sample is collected from an environmental source and may be of any material or component. The sample serves to characterize or represent the environmental condition of interest.

Historically, PE samples have been employed to assess laboratory proficiency and to validate analytical methods. PE sample studies are used as a component of certification and accreditation programs. Generally, the sample identity is known to the participating laboratories but the sample formulation is unknown. The results of PE studies are used to estimate bias, and demonstrate lab performance and analyst proficiency.

However, to be able to assess environmental data quality, it is necessary to determine routine performance with respect to the ability of the method to recover the analyte of interest within a sample batch. An analytical sample batch is a group of samples processed together and considered to be uniform in the properties upon which the measurement system is based. The results of matrix specific PE samples submitted and analyzed with environmental samples indicate systematic error that is not apparent in routine precision and accuracy measurements.

The example cases demonstrate the effectiveness of the PE sample as an external quality assessment tool. PE sample results can be evaluated with respect to a specific sample batch and the associated data quality objectives. Case study results confirm that the PE sample data are effective when used to diagnose and verify the analytical performance and capability demonstrated with a given sample batch. This substantiates that the data quality achieved satisfies data quality requirements.

BACKGROUND

PE samples for this study were secured from the ICF Quality Assurance Technical Support (QATS) Lab in Las Vegas, Nevada which is under contract to EPA. The samples are provided to EPA requestors for inclusion in batches of Superfund environmental samples. The QATS lab maintains the inventory and ships samples to the designated laboratory adhering to Agency procedures for shipping and Chain-of-Custody. Sample composition is verified by using multi-laboratory studies and method performance data.

Prior to scheduling of P.E. sample shipments to designated laboratories, an EPA scientist reviews the site history, existing data summaries, and the data quality requirements. With this information, the PE sample is selected based on contaminants of concern and the known or suspected concentration range. The sample is also matrix matched to the extent possible. When data are generated in support of regulatory requirements (e.g. SDWA), it is imperative that the compounds and concentration ranges of the PE are targeted to the action levels.

Data from three laboratories performing analytical work in support of Regional environmental investigations were used in the study. PE samples were shipped directly to the laboratories from the QATS lab. The shipments and accompanying documentation included method specifications, sample preparation and analysis instructions reporting requirements, and the analysis due date. The laboratory also received instructions to analyze PEs with environmental samples from the specified CERCLA site.

The PE sample results were initially assessed with PEACTOOLS, a software program developed by the QATS lab. PEACTOOLS does not assign numerical scores. The results are reported relative to whether the concentrations fall within acceptance criteria. Acceptance criteria are based on the calculated mean and measured variance from multi-laboratory studies. The summary of results also indicates whether the laboratory failed to report all components of the sample (Misses) and denotes compounds reported by the lab that were not present in the sample (Contaminants). The acceptance limits are based on three standard deviations around the mean value generated from multi-laboratory studies.

Because the PE sample is selected based upon site specific data quality requirements the greater focus of the overall performance assessment is

placed on the contaminants of concern and their degradation products. If the initial assessment indicates significant error, a check of the PE sample selection, shipping, and PEACTOOLs data entry is made. If no errors are noted in any of the processes, the laboratory is asked to perform a corrective actions study on the data and systems that generated the data associated with the PE sample. If the corrective actions study does not yield findings which account for noted errors, other investigative tools may be used. These tools may include third party data review, GC/MS tape audits, and on-site audits.

DISCUSSION

Case Study One:

Laboratory A_1 received PE samples for analysis of Volatile Organics, Base Neutral Acids, and Inorganic fractions. The laboratory was operating under a Quality Assurance Project Plan reviewed and approved by several EPA regions.

The initial assessment of PE sample results showed that reported concentrations for Volatile Organics and Base Neutral Acids were acceptable. PE sample results for Inorganic Metals indicated that four analytes were present but not reported and that of the nine analytes detected, seven concentrations were outside of acceptance windows.

Corrective actions findings indicated that calibrations had been done improperly due to inaccurate calibrants and that some values had been transposed during reporting. Systematic errors were incurred with the use of inaccurate calibrants. Because other quality control criteria (e.g. Matrix Spikes, Duplicates, continuing calibration checks) were within acceptance range, the error was unknown throughout the process. Any data generated and calculated using an incorrect calibration are questionable. Re-analysis of all affected samples was required.

Case Study 2

Laboratory A_2 received an aqueous PE sample for analysis by CLP Low Concentration Inorganic Statement of Work (ILM01.0). The scored results showed that all reported concentrations were outside acceptance range. Six of nine reported analytes had results that were outside the lower acceptance limit (low bias).

The laboratory response was that the corrective action study revealed no problems and that all reported concentrations were based on verified calibrations. An initial examination of the data package indicated that all quality control criteria were met. However, further review of the data revealed that the PE sample was not included on the digestion log. The laboratory verified that the sample had not been digested.

Since all associated quality control data were acceptable, this indicates that sample results generated at the time of analysis are

credible. The error was probably confined to the inability to follow directions specified on the PE instruction sheet. The reliability of the environmental sample results was confirmed by data from split samples from an independent laboratory.

Case Study 3

Lab A_3 was selected to analyze samples for an environmental data collection activity that was expected to last for approximately one year. Three major sampling events were projected and PE samples were scheduled to coincide with the arrival of each sample delivery group. Data collection activities, including data validation, are expected to be concluded by December of 1992.

The laboratory reported a significant number of compounds inaccurately for the PE volatiles fraction and the metals on two occasions. The reported results for the pesticides were inaccurate with a low bias consistently for all PE samples. The laboratory conducted a corrective actions investigation and noted problems with the instrumentation and the source of the calibrants.

The laboratory has been required to correct the identified deficiencies and analyze PE samples to determine whether the sources of error were accurately defined. Pending successful re-analysis of the PE samples, an assessment of all affected data generated through the life of the project must be made. This assessment will aid the data users in determining whether data quality requirements were met and if data use was compromised.

SUMMARY

In each of the case studies presented, data review of the environmental sample results showed that associated routine quality control criteria were met. However, the PE sample results, serving as external performance checks, indicated systematic error including uncorrected bias measurements. Study data illustrates that PE sample data are effective in verifying analytical performance and capability associated with individual sample batches as well as data generated during multiple sampling event projects. PE samples are effective external performance evaluation tools and can be beneficial in assessing whether the data quality achieved during environmental data collection activities satisfies data quality requirements.

36

QUALITY ASSURANCE PRACTICES FOR DATA ENTRY AND ELECTRONIC DATA TRANSFER

L. M. Tomczak, Sr. Staff Scientist, J. C. Gore, Technologist I, and J. W. Nixon, Technologist III, Radiological Environmental Monitoring, WEMCO* and H. B. Spitz, PhD., J.J. Cardarelli, Lia Dai, Ning Liu, and Sue McGimpsey Graduate Students, University of Cincinnati, Cincinnati, OH 45221-0072. Westinghouse Environmental Management Company of Ohio* Fernald Environmental Management Project P.O. Box 398704, Cincinnati, Ohio 45239-8704.

ABSTRACT: The Radiological Environmental Monitoring (REM) group at the Fernald Environmental Management Project is involved in two practices that will result in the improved quality assurance of collected data (1) Quality Assurance Program for Manually Entered Data, and (2) Electronic Data Transfer. The first practice focuses on adopting strict quality assurance guidelines for manual database entry. The second practice focuses on electronic data transfer from the recording instrument in order to reduce the manpower normally required for manual data entry.

The application of these two practices can enhance any data collection program where instruments with electronic memories and a signal output are utilized. Organizations employing either or both of these practices, as applicable, can strengthen the quality and efficiency of their data collection program. The use of these practices can assist in complying with Quality Assurance requirements under ASME NQA-1, RCRA, CERCLA, and DOE Order activities.

QUALITY ASSURANCE PROGRAM FOR MANUALLY ENTERED DATA

OVERVIEW

Data are currently obtained from field installed Pylon AB-5 radon monitors, configured to print data to a paper tape. The data are entered manually into a PC database on a weekly basis. To ensure that data are correctly entered, an oversight process has been developed. Basically, a two-person team is assigned the task of ensuring correct data entry. One individual performs the initial data entry and confirms the entered data. The second individual is responsible for verifying that all of the data have been correctly entered. Automated computer checks are also conducted for data validity between recorded intervals due to light leaks etc. and the detection of outliers.

This portion of the paper will discuss the protocol that is followed to ensure correct data entry, the process of resolving incorrect entries, the validity of the data collected, and documentation of the data entry process. The results of this protocol lead to a data management system that is capable of successfully meeting the requirements of an external audit.

INTRODUCTION

Fifteen continuous radon monitors have been installed at the DOE Fernald Environmental Monitoring Project (FEMP) at both on-site and off-site locations to measure what, if any, contribution to the natural radon background is made by sources of radon located on the Fernald project. On-site outdoor locations for each of the samplers have been selected to provide representative measurements of radon that are either close to the sources of emission (K-65 silos that contain byproducts from the Manhattan Project) or near buildings and areas which are occupied by the majority of the workforce. Several monitors also measure radon at the FEMP fenceline. One background monitor is located approximately 13 miles from the project in the direction of the prevailing wind. An additional background monitor is also being considered.

Each monitor prints the results of hourly measurements and also stores the data in the instrument computer memory. Each result consists of four fields of data: sequence number, hour (24 hour clock), instrument response (counts/hour), and radon concentration (pCi/l). Data is retrieved from each instrument by data collection personnel on a weekly basis.

Data collection personnel initial each data paper tape and reset the instrument sequence number to initiate another run. An identification number, calibration factors, and other data constants are printed on the data tape whenever the instrument is reset. The instrument response is also conducted using a check source on a weekly/monthly basis per established protocol.

The radon collection instruments are housed in environmental enclosures to protect them from the direct adverse effects of the environment but are not heated or sealed in any manner. They operate 24-hours a day and are expected to function properly in all types of weather and generate 168 hourly readings each week.

The instruments sample radon in the ambient air based upon the diffusion principle and, thus, have no moving parts or pumps. Other than weekly inspection by the data collection personnel to retrieve data, reset the instrument, and insure that the instrument is still operating, no other operator attention is provided or required. Instrument re-calibration is scheduled on an annual basis contingent upon the satisfactory instrument source check results.

OBJECTIVE

A formal quality assurance program will improve the accuracy and reliability of data, by establishing formal procedures and review processes to reduce the occurrence of systematic interferences. The quality assurance process will make it possible to identify problems and implement corrective actions before errors are introduced into the data analysis process. Data accuracy and reliability is essential because these monitoring results are associated with radiological protection programs and governmental compliance requirements.

Any instance of a failure of data quality is not tolerable. Therefore, formally documented quality assurance activities and responsibilities will minimize the likelihood of an unknown interference which could sacrifice data accuracy or reliability and permit propagating an unknown bias into the data analysis.

The occurrence of random or intermittent electrical failures or other systematic instrument-related problems are infrequent but non-negligible. At times, data printed by the instrument is not completely legible or the paper tape may jam or run out. Data collection personnel may also fail to properly identify each data print-out or accurately reset the instrument. In addition, a few hours of radon measurement data collected immediately following instrument performance checks using the standard source is censored/rejected, since radon measurements cannot be performed immediately following use of the standard source due to the persistence of the photo-multiplier tube.

After collection, each data print-out must be independently previewed to insure that all the data is complete, legible, and accurately labeled for proper identification. The process of data preview is an important element of the quality assurance program and should be as comprehensive as possible. Following data preview, the validity of the data can be evaluated. Data is invalid if the results fail to represent actual radon concentration measurements.

Electronic noise or other detector interferences can produce results which can be differentiated from valid data by using statistical tests. These tests are based upon the known radiological characteristics and the physical behavior of radon. Comparisons are also made with other results using instruments in similar locations. Activities associated with data preview and tests to insure data validity are independent and provide two separate checks of data quality. However, feedback between these activities is needed to resolve outstanding data discrepancies and to identify systematic errors which may not have been addressed in the overall quality assurance plan.

METHODOLOGY (Specific Elements of Data Quality Assurance)

Procedures

Figure 1 illustrates the elements of the radon monitoring project for which a data quality assurance program was developed. Most of the activities and tasks illustrated in Figure 1 are documented via procedures. These procedures assign responsibilities and duties, and provide instructions for properly accomplishing each of these tasks. Major emphasis of the data quality assurance program is directed toward data validity activities since these tasks involve quantitative numerical analyses using computer programs and technically-based formal procedures.

Data collection personnel have procedures for performing instrument checks and retrieving data from each of the instruments. They observe instrument operation and determine that the data output tape appears normal. They also initial the data tape and reset the instrument. Should the instrument appear to be malfunctioning, they will notify management and initiate a service request from the instrumentation group. Periodically, the data collection personnel perform an instrument response check by removing the radon sampler and attach a check source. Following the performance check, the data collection personnel re-attach the radon sampler to the monitor and reset the instrument.

Data Preview

The process of data preview is performed by a member of the technical staff familiar with both the technical performance characteristics of the instruments and the technical requirements of the radon monitoring program. Data preview involves insuring that the data received from each of the fifteen radon monitors is legible, properly identified, and complete. No evaluation of the radon monitoring data is required at this point, other than to insure that each instrument has provided the expected amount of data and that it can be easily interpreted for data input. Whenever the data collection personnel perform an instrument performance check, data preview will include updating the response check control charts for each instrument and initiating remedial action whenever an instrument fails to perform within specifications.

Data printed by the monitoring instrument is photocopied to improve legibility and to provide a format that is more suitable for review and archival purposes. Data preview is essential since computer input is performed by an independent organization that may be unfamiliar with the application of the data or its meaning. Provisions are made to encourage communications between the data input group and the data previewer so that questions can be resolved by those most technically knowledgeable about the radon monitoring program. Likewise, data previewers have direct contact with data collection personnel should questions arise about instrument performance.

When the data has been fully previewed it is submitted for data input where it will be digitized and prepared for quantitative analysis. The individual performing the data preview will provide a dated signature on the data sheet to signify that the data has been previewed and provide a reference for future contact.

Data Input and Validation

The team of individuals that perform data input use a LOTUS 123 spreadsheet which has been designed in a manner consistent with the format of the data output produced by the radon monitoring instrument. A new LOTUS file having a unique name is created every week for each instrument and contains all appropriate data printed on the data tape from each instrument. The name of the person who entered the data is also entered onto the spreadsheet.

At least two people are required to perform data input since the data is entered in duplicate using two independent LOTUS spreadsheets. Data input errors are identified using a LOTUS command to compare the duplicate files. Original and discrepant data are compared to the original radon monitor data records and corrections are made to the LOTUS file. If the error cannot be resolved, the data in question is returned for additional data preview.

Correction of typographical errors represents the most frequently encountered source of error that can be addressed by the quality assurance program. Assuming that the data being entered into the LOTUS 123 file is legible and easily deciphered, the mechanical process of data entry represents a significant source of systematic error that can be eliminated using double data entry.

After the data input errors have been corrected, a listing of the radon measurement data for all the monitoring instruments is printed and the LOTUS files are stored on the computer hard drive. Individual disks are also prepared which contain all the radon measurement data for one week from all the monitoring instruments in the program. In this manner, duplicate computer records are maintained using more than one type of computer media so that the likelihood of any permanent loss of data is minimized. Paper listing of the radon monitoring data is also archived.

Data validation includes many other provisions for assuring the accuracy and validity of the radon monitoring data. Results for measurement periods immediately following performance tests are intentionally discarded since the process of exchanging the radon detector for the standard source allows light to enter the monitor and artificially increases the instrument background for up to three hours after the performance tests. Data censoring associated with the performance check may occur during data preview otherwise it will occur during the data validation process.

Occasionally, the instrument will produce one or more spurious results which, if not censored, would make a significant impact to the results of the radon monitoring program. Incidents of spurious or questionable data can be identified as a discontinuous increase or decrease in the data which is physically not possible based upon the response characteristics of the detector or the ambient meteorological conditions. Events of spurious results may appear for one hour or extend for several hours, even for several days. Most of these events are related to light leaks in the monitoring instrument or extremes of ambient temperature or humidity which may produce an intermittent failure in an electronic component.

Statistical tests have been developed to identify data which may be related to spurious data. The first test for a questionable result involves calculating whether any result differs from a neighboring result by 100 pCi/l. It is very unlikely that the radon concentration would change by this magnitude in one hour. This test is used to locate events in the data set which require further evaluation. No data will be censored as a result of

this simple test without further review and documentation of the cause of the event. The frequency of such events may lead to an investigation of the instrument calibration or other possible remedial actions.

Another statistical test is based upon the characteristic time for the build-up and decay of the short-lived radon decay products and is used to identify a series of increasing or decreasing results which may not be wholly related to the change in the radon concentration. This test is needed for a series of suspect data having a magnitude which does not exceed 100 pCi/l. The suspect data will be evaluated for validity by comparison with meteorological and other radon monitoring data. No changes or censoring will occur without proper documentation of the changes. This documentation will include at a minimum: names of individuals involved in the correction of data, date of the change, data corrected, and the reason for the correction of such data.

Data Reports

Data Reports and graphical analyses are important elements of the overall quality assurance program. Graphs are useful for identifying trends and determining whether the results are meeting expectations. Besides lists of data and results of statistical analysis, individual reports of discrepant data will be provided to specifically identify what, if any, data was censored.

SUMMARY

Incorporation of the aforementioned activities into a formal quality assurance program will improve the accuracy and reliability of data, by establishing formal procedures and review processes to reduce the occurrence of systematic interferences. The quality assurance process will make it possible to identify problems and implement corrective actions before errors are introduced into the data analysis process. Data accuracy and reliability is essential where any instance of a failure of data quality is not tolerable. Therefore, formally documented quality assurance activities and responsibilities will minimize the likelihood of an unknown interference which could sacrifice data accuracy or reliability and permit propagating an unknown bias into the data analysis.

ELECTRONIC DATA TRANSFER

OVERVIEW

The REM group has also developed a process to electronically transfer stored data. The data are transferred between each Pylon AB-5 field instrument and a Hewlett Packard portable hand computer, model HP95LX. Later, all the data is transferred to a PC database as an electronic file for analysis. The advantage of this system is twofold: (1) Manual data entry errors are eliminated and (2) considerable data entry time is eliminated.

This portion of the paper will discuss the interface and connector components that allow this transfer of data from the Pylon to the PC to take place.

INTRODUCTION

Collection of data, albeit an important function, comprises only half of the environmental monitoring activity. Sometimes it can be just as cumbersome to appropriately deal with the data that has been collected, as it can be to collect the data. The Radiological Environmental Monitoring group at the DOE FEMP facility has identified a solution, to at least take some cf the dread and monotony out of the voluminous environmental data reduction and reporting activity, without sacrificing quality.

OBJECTIVE

Much of the preceding section dealt the quality assurance activities associated with compiling data obtained from the data tape produced by the Pylon AB-5 unit and preparing an electronic data file for use in accurately reporting the data collected by the instrument. This section of the paper deals with the process that is used to electronically transfer the data from the instrument to an electronic data file that is used in generating reports.

There are essentially two steps in the electronic data transfer process. The first step is the transfer of an electronic data file from the Pylon AB-5 unit to a handheld computer in the field. The second step is the transfer of field data to an electronic data file back at the office on the hard drive of a PC.

This data is then transferred via disk along with the hard copy data tape of the Pylon AB-5 data to a data previewer, and then to an independent organization that produces the environmental reports. This activity should eliminate data errors and data entry form.

MATERIALS NEEDED

The following is a list of equipment that is needed to complete the electronic data transfer from the AB-5 Pylon to a personal IBM disk operating system computer.

- Pylon AB-5 Radon Monitor
- Pylon Model PPT-1 Printer
- Pylon Model CI-55 Computer Interface
- CPRD (radon detector) or a 300A Lucas cell
- DB15 Female A/B Switch Box
- DB15 3 foot M.M. Transfer Cable
- DB15 3 foot M.F. Transfer Cable
- DB25/9 M.M. Gender Changer
- DB15 M.M. Gender Changer

. HP95LX Computer
. HPF1001A Connectivity Pack

METHODOLOGY

The steps that are needed to transfer the electronic data file from the Pylon AB-5 unit to a personal IBM disk operating system computer and finally to a 3.5 inch computer disk is presented in figure 2. Each type of transfer will be discussed in detail in the appendix.

SUMMARY

Once the data is transferred to a disk, the data can be previewed by the individual assigned the task of quality assurance. A check of data will then need to be conducted to confirm that the data was correctly transferred. It will also be necessary to parse the data using this lotus function to further manipulate the data to work with each of the columns.

By utilizing the electronic transfer of data, considerable time can be saved in both the areas of manual data entry, and the checks that are required to ensure that the data is correct. Activities that had previously taken more than a day can be performed in much less than a day without sacrificing data quality.

ACKNOWLEDGEMENT - The authors wish to thank Mr. D. W. Muller and Ms. J. A. Peters for their assistance in the preparation of this paper.

REFERENCES

HP 95LX User's Guide, Hewlett-Packard Co., 1991, Corvallis, OR

APPENDIX A

Transferring Data From the Pylon Monitor to the HP95LX Computer

1) Hook up the HPF100A1 Connectivity Pack to the HP95LX and the CI-55 Computer Interface
   Connect the CI-55 to a DB-15 M.M. Transfer Cable.

2)Prepare the HP95LX for use

Turn on the HP95LX
   Press:**ON/OFF** key

   Press: **BLUE FILER** key
          Select PRN (DIR)
    Press: **CURSOR DOWN** key

   Press: **F3** key
          Y key (to delete)
          MENU key
          Note: Delete all PRN files to start off the day. This will ensure that sufficient memory will be available on the unit to collect the data.
          Press: Q key to quit

3) Press: **COMM** key
   Press: **MENU** key
          Press S key for **SETTINGS** selection
   Press: U key for **USE** selection
   Press:Cursor Arrow ---> key over to File (PYL.DCF)
   Press: **ENTER** key
          Check the following setup information:

```
      Port:
            Inter.   1
            Baud     3
            Stop     1
            Parity   none
            Char     8
     Dial:
            Type     Pulse
```

   Press: Q key for **QUIT** selection
   Hold **CTRL** key and press **F-5** key simultaneously
   Backspace to **DAT** and delete by using the **<---(BREAK)** key
       Type **PRN\filename.prn**
       Press: **ENTER** key

Note: 8 characters max. name
Press: **MENU** key
Press: **C** key for **CONNECT** selection
(at this point set up the pylon to send data)

4) Transferring data from the pylon unit to the HP95LX:

Switch Box
Place the **A/B** switch to the **B** position

Pylon AB-5 unit
Press the **RECALL** key
Press the **PROG STEP** key, this will show the most current run.
If it is necessary to collect a different run use the **PUMP** key to change the first digit and the **START/STOP** key to change the second digit.
After the **RUN** is selected press the **PROG/STEP** key three times.
Press and hold the **STATUS** key; the display will show the run, cycle and interval.
While continuing to hold the **STATUS** key press the **PROG/STEP** to start the data transfer.
Release the **PROG/STEP** and the **STATUS** key.
When the data transfer is complete the Pylon AB-5 display will show ready.

Switch Box
Reposition the **A/B switch** to the **A** position
Disconnect the CI-55 Computer Interface cable from the transfer cable on the Black Box.

HP95LX Computer
Press: **MENU** key to exit program
Press: **Q** key for **QUIT** selection

5) Checking data transfer
Press: **FILER** key
Select the **PRN (dir) ENTER** key
(check if file and data exists)
Press: **MENU** key
Press: **Q** key for **QUIT** selection
Turn off instrument
Press **ON/OFF** key
Note: Prepare for next station. At the next location it is not necessary to repeat step #2, but step #1, the hookup is still applicable.

<u>Data Transfer from the HP95LX to the PC</u>

1) Setting up the HP95LX for data transfer to the PC

Turn on the HP95LX
Press: **OFF/ON** key
Press: **LOTUS 123** key
Press: **MENU** key
Press: **F** key for **FILE** selection
 I key for **IMPORT** selection
 T key for **TEXT** selection
Arrow to ---> **_PRN** enter
Search for file of interest
Press: **ENTER** key

2) Saving the file
Press: **MENU** key
 F key for **FILE** selection
 S key for **SAVE** selection
Type in file name
Press: **ENTER** key
Press: **R** key for **REPLACE** selection
Press **ENTER** key
Repeat this step to transfer the files to the LOTUS (dir)

3) Setting up the PC for Transfer
Hook transfer cable to the HP95LX and the PC

4) Transferring the data

On the PC select **CPACK** from the menu screen

Select **FILER** on PC
Press **ALT 2** key

Turn on HP95LX
Press: **ON/OFF** key
Press: **FILER** key

Press: **F6** on the PC keyboard (remote)

Press: **F7** on the PC keyboard (split screen)

Highlight and tag **F9** file or files to transfer

Press: **F2** (copy) on PC keyboard

Screen will query where to copy files to,
type in c:\123

When complete exit on PC, press: **CTRL** and **F1** to
exit to main screen

On the HP95LX press: **CTRL**, **UP ARROW** , and **BREAK** simultaneously to return to normal operation

Unplug transfer line from HP95LX

Press: **MENU** key on HP95LX

Press: **Q** key for **QUIT** selection

Press: **ALT 0** to exit PC

5) Transfer Data From C Drive To B Drive 3.5 inch Disc

Select **LOTUS 123**
Press:
- **MENU** key *
- **F** key for **FILE** selection
- **R** key for **RETRIEVE** selection
- **F3** key

Select desired radon file location
Press: **ENTER** key
Press:
- **MENU** key
- **F** key for **FILE** selection
- **S** key for **SAVE** selection

Press: **Esc** three times
Type **B:\Location** **
Press: **ENTER** key
Return to step * and repeat thru step ** until all locations are transferred.

Checking Data Transfer

1) Press **MENU** key
   Press: **F** key for **FILE** selection
   Press: **R** key for **RETRIEVE** selection
2) Press **ESC** key two times
3) Type B:\
4) Press **ENTER** key
5) Scan Data
6) If you want to retrieve data, highlight, locations then press **ENTER** key.

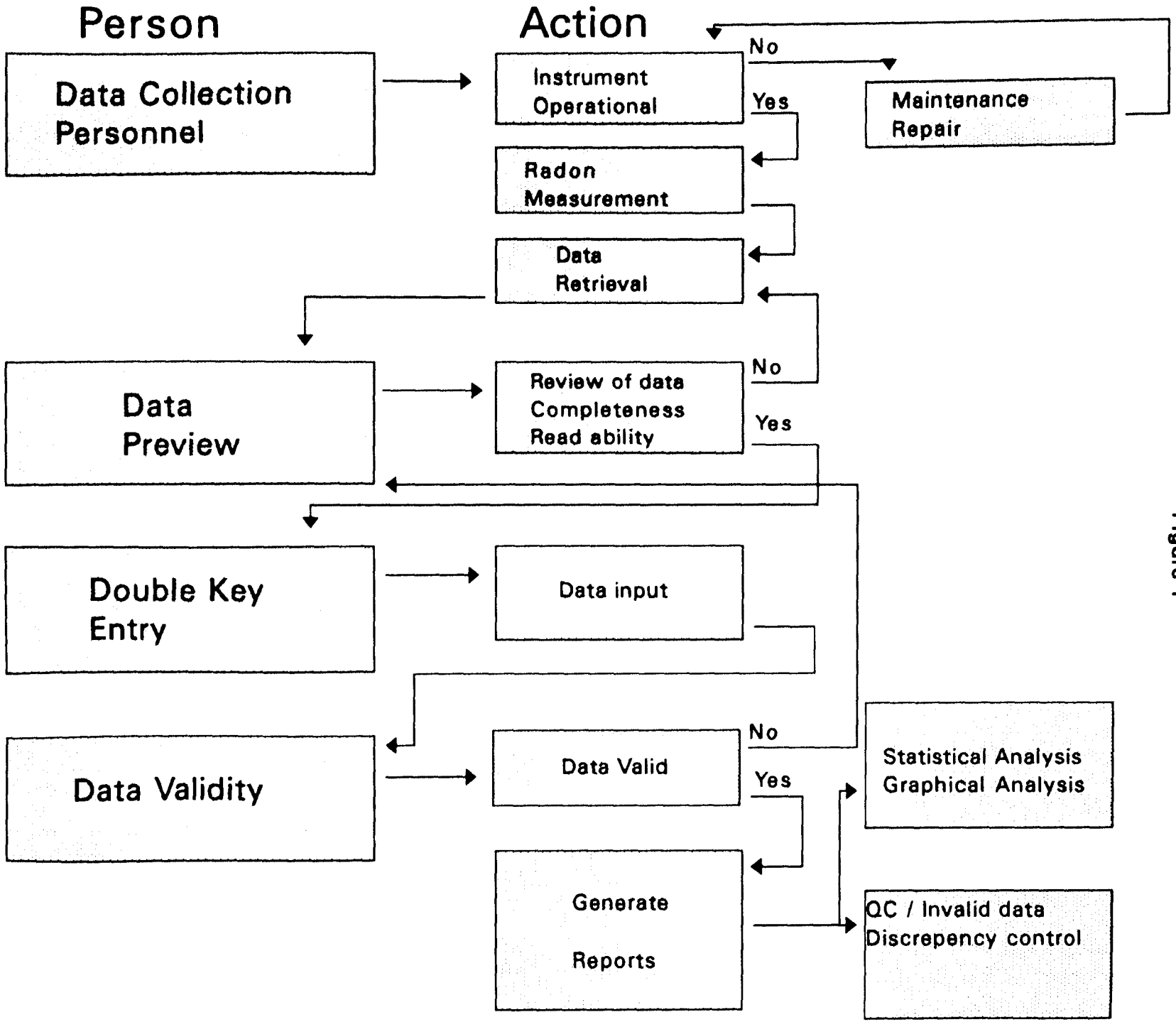
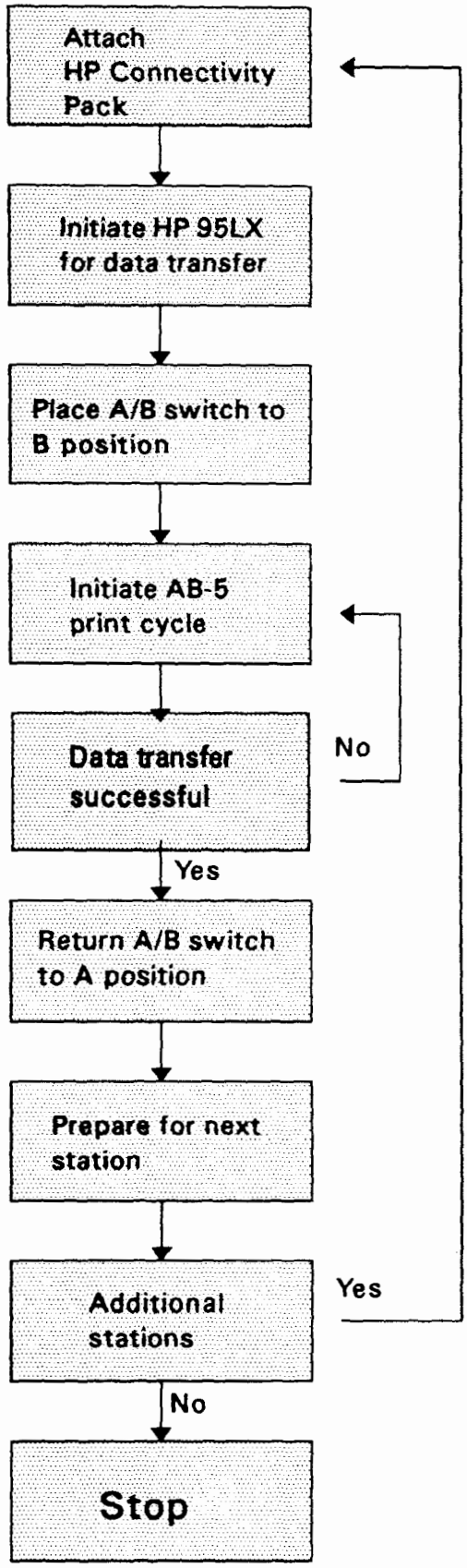

Person
Action
Data Collection Personnel
Instrument Operational
No
Yes
Maintenance Repair
Radon Measurement
Data Retrieval
Data Preview
Review of data Completeness Read ability
No
Yes
Double Key Entry
Data input
Data Validity
Data Valid
No
Yes
Statistical Analysis Graphical Analysis
Generate Reports
QC / Invalid data Discrepency control

Figure 1

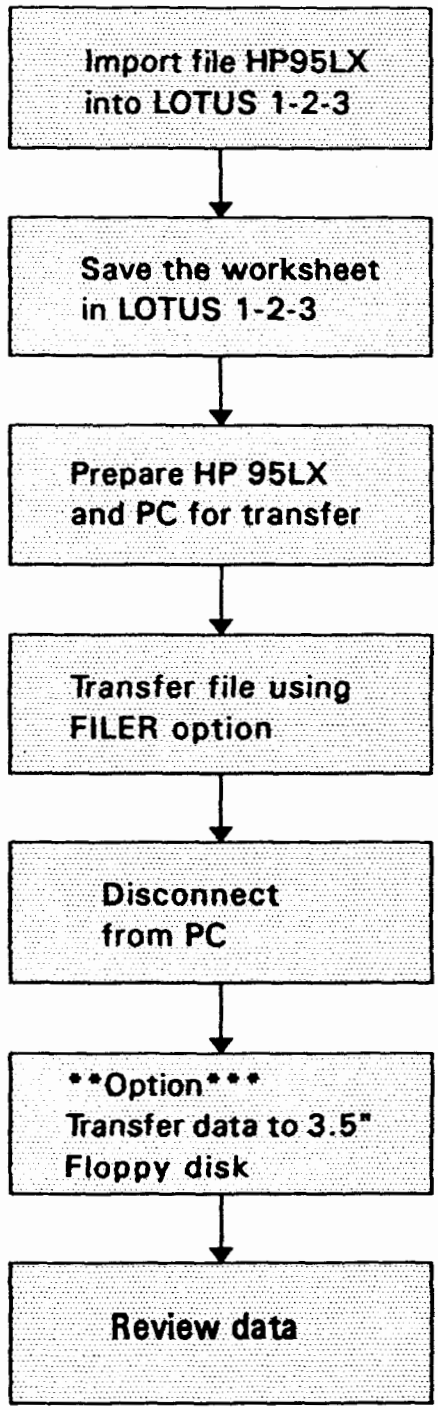
FIGURE 2

Data Transfer To HP 95 LX From AB-5 Unit



Transfer Data From HP95 LX To PC

FIGURE 2 Con'td



Copyright Statement

By acceptance of this paper, the publisher and or recipient acknowledges the U. S. Government's right to retain a non-exclusive royalty free license in and to any copyright covering this paper.

Notice

This abstract/paper was prepared as an account of work sponsored by an agency of the United States Government. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government, Westinghouse Electric Company, or any of its wholly owned subsidiaries, or any agency thereof.

37 THE IMPACT OF THE GC/MS RAW DATA AUDIT IN THE MONITORING THE USEPA CONTRACT LABORATORIES

Mary K. Wolf and Darlene J. Elkins, Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119 and Edward Kantor, USEPA Environmental Monitoring System Laboratory, Las Vegas, Nevada 89193.

ABSTRACT

The GC/MS raw data audit, performed by Lockheed Engineering & Science Company (LESC), is a quality assurance tool that is used by the USEPA to monitor the quality assurance and technical performance of the laboratories in the Contract Laboratory Program. EMSL-LV maintains a GC/MS raw data audit facility that has stand alone data systems for all of the commonly used data systems in the Contract Laboratory Program. The quality assurance evaluators, using the electronically stored data, generate a new set of data using different identification files. This evaluator generated data is then compared to the laboratory generated data to determine if there are any discrepancies between the two sets of data. The procedures used in the review of the laboratory GC/MS raw data will be discussed. A comparison of the changes and frequency of previously found defects will be compared to defect trends occurring over the last twelve months.

Notice:

Although the research described in this article has been supported by the United States Environmental Protection Agency through contract 68-C0-0049 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ORGANICS

39 Paper unavailable

40

DETERMINING TCLP VOLATILES IN WASTE OIL AT REGULATORY LEVELS

Paul Marsden, Science Applications International Corporation, 10260 Campus Point Dr., San Diego, California 92121; Bruce N. Colby, C. Lee Helms, Pacific Analytical, 6349 Paseo Del Lago, Carlsbad, California 92009

ABSTRACT

Method 1311, the Toxicity Characteristic Leaching Procedure, is used in part of the evaluation process for RCRA controlled wastes. This procedure can be aplied readily to most solid wastes and to aqueous wastes but it has proven difficult when working with oily wastes, such as waste motor oil, in part because the volatile TCLP analytes cannot be determined using traditional purge and trap preparation technology. In order to overcome the purge and trap problems, a study was undertaken to evaluate headspace analysis as an alternative. Because significant matrix effects were anticipated, isotope dilution GC/MS was identified as the most likely means to generate accurate analytical results. A simpler alternative to the isotope dilution GC/MS method was also investigated. It involves diluting waste oil 1:1 with heaxdecane followed by syringe injection of a 2-uL aliquot into a GC/MS. This approach requires a modern highly sensitive instrument in order to achieve the necessary detection limits for analytes such as vinyl chloride at 0.2ppm. Performance data for both the headspace and syringe injection methods are presented to demonstrate their effectiveness with waste motor oil samples. The relative technical and logistic merits of the two methods are also discussed.

INTRODUCTION

Quantitative determination of volatile organic analytes (VOAs) in waste oil presents a challenge to the analyst. The use of conventional techniques for analysis of volatiles (i.e., purge-and-trap [Method 5030]) in oil generally results in severe contamination of analytical instrumentation. Recoveries are poor; traps, transfer lines, and chromatography columns may become contaminated. System contamination leads to elevated baselines, hydrocarbon background in subsequent analyses, and unacceptable blanks. Problems with the purge-and-trap apparatus may be reduced by diluting a sample in methanol ("Waste Dilution", draft Method 3585). However, this approach is not appropriate for petroleum products that have poor solubility in methanol. Another disadvantage of waste dilution with purge-and-trap is that it increases method detection limits. Headspace and direct injection analysis are potential alternate approaches to the analysis of oils. However, headspace (Method 3810) is currently allowed only as

a screening procedure in SW-846. Guidance and performance data for the use of direct injection is not currently included in Method 8260.

In order to provide a suitable method in SW-846, the Methods Section of the Office of Solid Waste (OSW) tasked Science Applications International Corporation (SAIC) to provide performance data for the determination of volatiles in oil. SAIC engaged Pacific Analytical Laboratory in Carlsbad, CA, as an analytical subcontractor for this project. Data were collected for both headspace and direct injection analysis of volatiles in oil. The results of this study indicate that both headspace/isotope dilution and direct injection may have application for the analysis of volatiles in oil. This report provides performance data for both headspace/isotope dilution GC/MS and direct injection GC/MS (using isotope dilution and internal standard quantitation).

MATERIALS AND METHODS

Headspace apparatus: Headspace analysis was accomplished using a Hewlett Packard Headspace analyzer (Model 19395A), a Hewlett Packard Model 5890 Series II gas chromatograph and a VG Trio-1 mass spectrometer. Oil samples analyzed using headspace were heated overnight (80 °C) in 10-mL vials sealed with Teflon-faced septa. After heating, a volume of headspace was drawn automatically into the GC/MS system for analysis by Method 8266. Carrier flow was diverted through the headspace sample loop to introduce samples onto the GC column. Column head pressure was maintained using the backpressure control on the GC. Some adjustment of flows and pressures were required to achieve reliable operation.

Direct injection apparatus: Direct injection analysis was accomplished using a Hewlett Packard Model 5890 Series II gas chromatograph and a VG Trio-1 mass spectrometer. Oil samples were diluted 1:1 (v/v) in hexadecane and analyzed using Method 8260. A 2-µl injection volume was used. The injection port liner was modified by placing a 1-cm plug of pyrex wool approximately 50-60 mm down the length of the liner (towards the oven). An 0.53 mm id column was mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

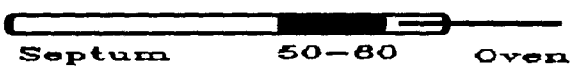


Figure 1 Modified Injector

Gas chromatography: Separation of samples introduced by either headspace or direct injection was accomplished using a 75 m x 0.53 mm DB-624 column. The carrier gas was helium and the flow rate was approximately 4 ml/min. The oven temperature was programmed from 40 to 260 °C at 8 °C/minute after an initial hold of 3 minutes. The GC effluent was introduced into the mass spectrometer through an 0.25 mm id uncoated restrictor column that was butt-sealed to the analytical column with "press-tight" connectors. It was necessary to "bake out" the oven at 260 °C for 75 minutes following direct injection analysis to ensure that hexadecane and high boiling interferences did not interfere with subsequent analyses. A much shorter bake out was required for headspace analysis.

Mass spectrometry: Mass spectra were collected using a VG Trio-1 tuned using p-bromofluorobenzene according to criteria specified in Methods 8260 and 8266. The instrument was calibrated using five solutions of standards to establish linearity. The stability of the response was established by daily comparison of the response factors for the mid-point calibration solution with the initial calibration curve. The MS source was maintained at 220 °C. Isotope dilution calculations were used for 14 method analytes; internal standard quantitation was used for the remainder. Some direct injection data was reduced using both internal standard technique described in Method 8260 and isotope dilution calculations the described in Method 8266.

Significant mass interferences were observed for two internal standards, a stable-labeled analog, and some target analytes. Internal standards 2-bromo-1-chloropropane and 1,4-dichlorobutane were not used for quantitation due to matrix interference. Interferences of target analytes included: iso-butanol (43), n-butanol (41), 4-methyl-2-pentanone (43, 58), ethyl acetate (43, 45) and pyridine (79, 52, 51 and 50). Major interferences were encountered for pyridine-d_5 (84, 56, and 52).

Reagents and Chemicals: Isotopically labeled standards and target analytes were obtained from Cambridge Isotope Laboratories and Aldrich Chemicals. All solutions were prepared from neat isotopically labeled standards prepared in hexadecane at Pacific Analytical.

A total of 29 chemicals were evaluated as target analytes for headspace and direct injection analysis (Table 1). Target analytes included 25 of the 27 compounds listed in Revision 0 of the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311). Methanol fragments are all too small (m/z < 33) which results in severe mass spectral interferences. 1,1,1-

TABLE 1. TARGET ANALYTES AND ISOTOPICALLY LABELED ANALOGS

Compound Name	CAS No.	Regulatory limit
Acetone	67-64-1	
Benzene	71-43-2	0.5
Benzene-d_6	1076-43-3	
n-Butanol	71-36-3	
iso-Butanol	78-83-1	
Carbon tetrachloride	56-23-5	0.5
Carbon tetrachloride-^{13}C	32488-50-9	
Carbon disulfide	75-15-0	
Chlorobenzene	108-90-7	100
Chlorobenzene-d_5	3114-55-4	
Chloroform	67-66-3	6.0
Chloroform-d_1	835-49-6	
1,4-Dichlorobenzene	106-46-7	7.5
1,4-Dichlorobenzene-d_4	3855-82-1	
1,2-Dichloroethane	107-06-2	0.5
1,1-Dichloroethene	75-35-4	0.7
1,1-Dichloroethene-d_2	22280-73-5	
Diethyl ether	60-29-7	
Ethyl acetate	141-78-6	
Ethylbenzene	100-41-1	
Ethylbenzene-d_{10}	25837-05-2	
Hexachloroethane	67-72-1	3.0
Hexachloroethane-^{13}C	93952-15-9	
Methylene chloride	75-09-2	
Methyl ethyl ketone	78-93-3	200
4-Methyl-2-pentanone (MIBK)	108-10-1	
Nitrobenzene	98-95-3	2.0
Nitrobenzene-d_5	4165-60-0	
Pyridine	110-86-1	5.0
Pyridine-d_5	7291-22-7	
Tetrachloroethene	127-18-4	0.7
Trichlorofluoromethane	75-69-4	
1,1,2-Trichlorotrifluoroethane	76-13-1	
Toluene	108-88-3	
Toluene-d_8	2037-26-5	
Trichloroethene	79-01-6	0.5
Trichloroethene-d_1		
Vinyl chloride	75-01-4	0.2
o-Xylene	95-47-6	
o-Xylene-d_{10}	56004-61-6	
m-Xylene	108-38-3	
p-Xylene	106-42-3	
p-Xylene-d_{10}	41051-88-1	

Trichloroethane was not included because of its propensity to dehydrochlorinate. Loss of hydrogen chloride from 1,1,1-trichloroethane produces 1,1-dichloroethylene, which results in spurious recoveries for both compounds.

Clean 30 weight motor oil (Citgo) was purchased from a local 7-11 store; residual volatiles were removed by heating a volume of 200 ml overnight at 80°C. The resulting oil had a small concentration of toluene (7 ppm). Benzene, ethylbenzene, xylenes, pyridine and other target analytes were not detected after heating (estimated detection limit 0.05 ppm). Used motor oil was collected during oil changes of passenger automobiles. The contaminated oil was stored in a garage for several months prior to the initiation of this project. The used oil had 20-300 ppm of BTEX compounds and isobutanol.

Principles of headspace analysis: The concentration of volatile constituents in solids and liquids can be measured by analyzing the vapor phase (headspace) above a sample. As headspace analysis involves a separation of the target analytes from a condensed phase, it is well suited for the analysis of highly complex samples like oil. Concentration of target analytes in headspace can be related to their concentration in a solid or liquid sample by this equation:

$$C_H = KC_S$$

where:

C_H = Analyte concentration in the headspace
K = Distribution Coefficient
C_S = Analyte concentration in the sample

The distribution coefficient between sample and headspace is extremely matrix-dependent.

Isotope dilution quantitation: As target analytes and their labeled analogs have the same distribution coefficients, isotope dilution seems well suited for headspace analysis. Isotope dilution is a GC/MS technique in which the ratio of the quantitation ions from environmentally incorporated target analytes (m_1/z) and spiked isotopically labeled analogs (m_2/z) are compared in order to calculate analyte concentrations. The relative response (RR) of each target analyte (m_1/z) and its analog (m_2/z) is established during calibration by analyzing different concentrations of target analytes. Headspace isotope dilution analysis allows correction for differences in distribution coefficients.

RESULTS FOR HEADSPACE ISOTOPE DILUTION

Method linearity: The linear range of the headspace method was established by analyzing mixtures of standards prepared at eight concentrations in hexadecane. Calibration standards of target analytes were prepared at 0.2, 0.5, 2.0, 5.0, 25, 50, 100, and 200 µg/ml, labeled analogs were present at 5.0 µg/ml in each calibration standard. Isotope dilution response factors were determined for 14 of the 15 targets for which isotopically-labeled analogs were added. Mass spectral interferences precluded the use of pyridine-d_5 for this application. Internal standard response factors were calculated for pyridine and the remaining 14 target analytes for which suitable isotopically-labeled analogs were not available. Table 2 provides the linear range, the average response factors over the linear range, and the percent relative standard deviation for the calibration curve of each compound.

System Stability: Stability of the measurement system was monitored by using a daily continuing calibration solution of 5 ppm. The continuing calibration solution was prepared with all 29 target analytes and 14 isotopically labeled analogs in hexadecane. Average percent recoveries for 14 of the target analytes with isotopically-labeled analogs were calculated using isotope dilution. Recoveries of pyridine, the 14 analytes without analogs and the 14 isotopically labeled analogs were calculated using the internal standard technique. The average recovery of most compounds were 80-120%. Average recoveries outside of the 80-120% window were obtained for 1,1-dichloroethene-d_2, pyridine-d_5, pyridine, 1,4-dichlorobenzene-d_4, nitrobenzene-d_5, nitrobenzene, carbon disulfide, tetrachloroethene, trichlorofluoromethane, iso-butanol, and n-butanol. RSDs of greater than 20 % were obtained for 1,4-dichlorobenzene-d_4, nitrobenzene-d_5, and nitrobenzene. As a result of the recovery correction inherent in isotope dilution, RSDs for each of the 14 target analytes determined using isotope dilution were smaller than the RSDs than the isotopically-labeled analogs quantitated using the internal standard technique.

Headspace isotope dilution performance: Performance of the headspace isotope dilution technique was established by analyzing two sets of seven replicate samples prepared by spiking "new" and "used" oil. All TCLP target volatiles except methanol were spiked at regulatory action levels, non-TCLP alcohols and ketones were spiked at 200 ppm, chlorinated and aromatic compounds were spiked at 5 ppm, and isotopically-labeled analogs were spiked at 5 ppm. Compounds spiked at 200 ppm generally saturated the mass spectrometer. This resulted in apparently poor recoveries for the butanols and relatively

TABLE 2 - Linear Range, Headspace/Isotope Dilution

Compound Name	low	high	%RSD	RRF
*Acetone	5.0	100	12.9	4.620
Benzene	0.2	100	11.6	1.025
*n-Butanol	0.5	200	18.1	2.916
*iso-Butanol	0.5	100	13.3	4.767
Carbon tetrachloride	0.2	100	10.5	1.009
*Carbon disulfide	0.2	100	11.2	7.604
Chlorobenzene	0.2	200	9.5	0.826
Chloroform	2.0	200	9.3	1.072
1,4-Dichlorobenzene	0.2	200	5.5	1.694
*1,2-Dichloroethane	0.2	200	16.2	3.001
1,1-Dichloroethene	0.5	50	5.7	1.981
*Diethyl ether	0.2	200	17.9	1.810
*Ethyl acetate	2.0	200	15.3	1.708
Ethylbenzene	0.2	200	7.1	0.356
Hexachloroethane	2.0	200	9.9	0.870
*Methylene chloride	2.0	200	12.4	2.917
*Methyl ethyl ketone	0.2	25	5.9	1.398
*MIBK	0.5	200	18.0	1.182
Nitrobenzene	0.5	200	9.0	0.700
*Pyridine	5.0	200	15.1	1.759
*Tetrachloroethene	0.2	200	5.4	0.426
*Trichlorofluoromethane	0.2	200	10.2	4.006
*1,1,2-Trichlorotrifluoroethane	0.2	200	16.2	2.497
Toluene	0.2	200	5.1	0.889
Trichloroethene	0.2	100	11.0	1.387
*Vinyl chloride	0.2	25	18.3	3.226
o-Xylene	0.2	200	10.1	0.457
m/p-Xylene	0.2	200	9.4	0.472

* Internal standard quantitation

poor analytical precision for the alcohols and ketones. Recoveries of greater than 150% which were obtained for 11 of the 14 labeled analogs used in this study (i.e., 1,1-dichloroethene, chloroform, carbon tetrachloride, benzene, toluene, chlorobenzene, ethylbenzene, p-xylene, o-xylene, hexachloroethane, and nitrobenzene).

Method accuracy and precision is improved when all of the target analytes are spiked at 2 ppm rather than at the regulatory limit. Even so, toluene (142%), pyridine (51%), nitrobenzene (41%), methylene chloride (130%), methyl ethyl ketone (137%), 1,2-dichloroethane (138%), MIBK (127%), diethyl ether (147%), trichlorofluoromethane (163%), 1,1,2-trichlorotrifluoroethane (153%), iso-butanol (266%), n-butanol (233%), and ethyl acetate (146%) were outside the 80-120% acceptance windows. Toluene in the oil prior to spiking and an interference for iso-butanol may have contributed to the performance problems with those compounds. Data for the seven replicates of new oil spiked at 2 ppm are provided in Table 3.

RESULTS FOR DIRECT INJECTION

System Contamination: Instrument contamination will be a problem with direct injection analysis of oil. Most of the heavy molecular weight materials (e.g. asphaltenes) remain in the quartz wool plug, but semi-volatiles and hexadecane are volatilized onto the chromatography column. For this reason, a bake out period is included in the oven temperature program. Hexadecane and the oil hydrocarbons elute after the target analytes. Conducting this study had a negative impact on instrument performance; column resolution and instrument sensitivity were lost. Examination of the system revealed that some oily residue remained in the column and oil contamination was evident on the source of the mass spectrometer.

It was recognized that the quartz wool plug would have a limited capacity to hold up non-volatile contaminants. Because laboratories are accustomed to a 12-hour shift for analytical instruments, replacement of the injector liner and the septa every 12 hours was selected as a reasonable maintenance requirement. Ten replicate injections of used oil spiked at 5 ppm were made over a 12 hour period in order to demonstrate that analyte response factors could be stable in a production environment. Response factors for labeled benzene, toluene, ethylbenzene and pyridine obtained on injections 1, 5 and 10 are provided in Table 4. The response factors for the BTEX compounds are quite stable but the response factor for labeled pyridine drifted downward through the shift.

TABLE 3 - Headspace Analysis of New Oil at 2 ppm

Compound	Recovery (%)	%RSD	Blank (ppm)	MQL
Acetone**	105	12.7	0.4	0.8
Benzene	103	8.2	0.1	0.5
Benzene-d_6	159	4.0	7.2	
n-Butanol**	233	12.2	0.7	1.7
iso-Butanol*,**	266	11.6	0.8	1.8
Carbon tetrachloride	107	7.6	0.0	0.5
CCl_4-^{13}C	141	4.3	6.0	
Carbon disulfide**	89	8.0	0.0	0.4
Chlorobenzene	117	7.2	0.0	0.5
Chlorobenzene-d_5	124	5.3	5.4	
Chloroform	88	7.9	0.0	0.4
Chloroform-d_1	151	3.0	6.9	
1,4-Dichlorobenzene	90	8.1	0.0	0.4
1,4-Dichlorobenzene-d_4	81	6.2	3.3	
1,2-Dichloroethane**	138	7.5	0.0	0.6
1,1-Dichloroethene	85	8.6	0.0	0.4
1,1-Dichloroethene-d_2	173	8.6	7.4	
Diethyl ether**	147	10.6	0.0	0.9
Ethyl acetate**	146	8.5	0.0	0.7
Ethylbenzene	98	8.5	0.1	0.5
Ethylbenzene-d_{10}	166	6.7	7.1	
Hexachloroethane	104	8.0	0.0	0.5
Hexachloroethane-^{13}C	121	9.2	5.0	
Methylene chloride**	130	7.6	0.2	0.6
Methyl ethyl ketone**	137	8.3	0.1	0.7
4-Methyl-2-pentanone**	127	8.9	0.0	0.7
Nitrobenzene	41	11.0	0.0	0.3
Nitrobenzene-d_5	123	12.7	3.6	
Pyridine**	51	18.6	0.7	0.6
Pyridine-d_5	106	6.7	3.9	
Tetrachloroethene**	90	9.3	0.0	0.5
Trichlorofluoromethane**	163	8.0	0.0	0.8
1,1,2-Cl_3F_3ethane**	153	6.3	0.0	0.6
Toluene	117	6.5	0.6	0.6
Toluene-d_8	150	6.1	6.6	
Trichloroethene	113	7.6	0.0	0.5
Trichloroethene-d_1	99	5.3	4.3	
Vinyl chloride**	46	15.3	0.0	0.4
o-Xylene	108	8.3	0.2	0.5
o-Xylene-d_{10}	144	6.5	6.0	
m-/p-Xylene	110	7.3	0.5	1.0
p-Xylene-d_{10}	157	6.4	6.5	

Based on 7 measurements
*Alternate mass employed
** IS quantitation

Table 4 - Stability of Response, Direct Injection

	Benzene-d6	Et Benzene-d10	Toluene-d8	Pyridine-d5
Inj 1	1.9483	1.1936	1.1458	1.0715
Inj 5	2.2302	1.3101	1.2989	0.8057
Inj 10	2.0212	1.2997	1.2920	0.5969

Method linearity: The linear range of the direct injection method was established by analyzing mixtures of standards prepared at eight concentrations in hexadecane. Calibration standards of non-labeled target analytes were prepared at 0.2, 0.5, 2.0, 5.0, 25, 50, 100, and 200 µg/ml, labeled analogs were present at 5.0 µg/ml in each calibration standard. Isotope dilution response factors were determined for 14 of the 15 targets for which isotopically-labeled analogs were added. Mass spectral interferences precluded the use of pyridine-d_5 for this application. Internal standard response factors were calculated for pyridine and the remaining 14 target analytes for which suitable isotopically-labeled analogs were not available. Table 5 provides the linear range for each compound, the average response factors over the linear range, and the relative standard deviation for the calibration curve of each compound.

System Stability: Stability of the measurement system was monitored by using a daily continuing calibration solution prepared at 5 ppm. The continuing calibration solution was prepared with all 29 target analytes and 14 isotopically labeled analogs in hexaecane. Average percent recoveries for 14 of the target analytes with isotopically-labeled analogs were calculated using isotope dilution. Recoveries of pyridine, the 14 analytes without analogs and the 14 isotopically labeled analogs were calculated using the internal standard technique. The calibration for direct injection appears more stable than with headspace. Average recoveries were within an 80-120% acceptance window except for ^{13}C-carbon tetrachloride and pyridine. RSDs of greater than 20 % were obtained only for ^{13}C-carbon tetrachloride, nitrobenzene and pyridine. As with headspace, RSDs were smaller for each of the 14 target analytes determined using isotope dilution than the corresponding isotopically-labeled analog quantitated using the internal standard technique.

Performance of Direct Injection: Performance of the direct injection isotope dilution technique was established by analyzing two sets of seven replicate samples prepared using

TABLE 5 - Linear Range, Direct Injection with Isotope Dilution

Compound Name	low	high	rsd	RRF
*Acetone	5.0	200	11.0	2.488
Benzene	0.2	200	17.9	1.054
*n-Butanol	0.5	200	17.2	3.224
*iso-Butanol	0.5	200	15.4	4.507
Carbon tetrachloride	0.2	200	14.9	1.025
*Carbon disulfide	0.2	200	14.5	2.031
Chlorobenzene	0.2	200	9.9	0.914
Chloroform	0.2	200	9.6	1.116
1,4-Dichlorobenzene	0.2	200	6.4	1.462
*1,2-Dichloroethane	0.2	200	15.3	4.822
1,1-Dichloroethene	0.2	100	13.1	1.612
*Diethyl ether	0.2	200	4.1	1.891
*Ethyl acetate	0.5	200	15.5	1.566
Ethylbenzene	0.2	200	11.6	0.337
Hexachloroethane	0.2	200	17.4	0.895
*Methylene chloride	2.0	200	8.9	3.510
*Methyl ethyl ketone	0.2	200	5.3	2.480
*MIBK	0.2	200	6.9	4.057
Nitrobenzene	0.2	200	4.1	0.399
*Pyridine	0.2	200	9.9	8.940
*Tetrachloroethene	0.2	200	6.1	2.906
*Trichlorofluoromethane	0.2	200	4.4	4.103
*1,1,2-Trichlorotrifluoroethane	0.2	200	11.5	1.938
Toluene	0.2	200	9.3	1.071
Trichloroethene	0.2	100	12.3	1.661
*Vinyl chloride	0.2	200	18.0	3.229
o-Xylene	0.2	200	10.3	0.488
m/p-Xylene	0.2	200	16.6	0.450

* Internal standard quantitation standards prepared in hexadecane

"new" and "used" spiked oil. All TCLP target analytes were spiked at regulatory action levels, non-TCLP alcohols and ketones were spiked at 200 ppm, chlorinated and aromatic compounds were spiked at 5 ppm, and isotopically-labeled analogs were spiked at 5 ppm.

These data demonstrate that direct injection can be used for the analysis of volatiles in motor oil. Data for n-butanol and iso-butanol appeared to show the greatest improvement using direct injection rather than headspace analysis. Recoveries of all analytes were comparable with those obtained using headspace analysis. However, these analyses caused noticeable contamination of the mass spectrometer source which means that direct injection will require more frequent instrument maintenance. Difficulties with interferences required the use of four alternate quantitation masses during the analysis of used oil.

As was the case for headspace, performance of direct injection analysis was evaluated over a narrower concentration range than the three order of magnitude range (0.2 - 200 ppm) required to satisfy the TCLP regulation. New oil was spiked with 5 ppm of target analytes except where the regulatory limit was less than 5 ppm. In those cases target analytes were spiked at the regulatory limit (e.g., 0.5 ppm for benzene). Each of the 14 isotopically-labeled analogs were also spiked at 5 ppm. The recovery and RSDs of the target analytes and isotopically-labeled analogs calculated using isotope dilution and internal standard routines are presented in Table 6. Spike levels are also given in the table.

Isotope dilution results demonstrate that method accuracy using direct injection is comparable to headspace isotope dilution analysis. However, method precision is significantly worse using direct injection compared with headspace. Most reported RSDs for the spiked new oil are greater than 20%. RSDs for the analysis of used oil are generally 50-80%. This lack of precision is probably due to the build up of oil contamination in the instrument system during the conduct of this method performance study. Table 7 presents data for new oil spiked at low concentrations after recalculation using the internal standard technique for the 14 analytes with useful isotopically-labeled analogs.

TABLE 6 - Direct Injection Analysis of New Oil at 5 ppm

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike
Acetone**	91	14.8	1.9	5.0
Benzene	121	15.9	0.1	0.5
Benzene-d_6	71	7.3	3.2	5.0
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	73	40.9	0.0	0.5
CCl_4-^{13}C	106	9.6	4.7	5.0
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	110	26.9	0.0	5.0
Chlorobenzene-d_5	74	8.0	3.2	5.0
Chloroform	113	28.7	0.0	6.0
Chloroform-d_1	66	7.3	3.1	5.0
1,4-Dichlorobenzene	98	23.9	0.0	7.5
1,4-Dichlorobenzene-d_4	74	4.0	3.1	5.0
1,2-Dichloroethane**	101	23.1	0.0	0.5
1,1-Dichloroethene*	97	45.3	0.0	0.7
Diethyl ether**	76	24.3	0.0	5.0
Ethyl acetate**	113	27.4	0.0	5.0
Ethylbenzene	105	26.6	0.2	5.0
Ethylbenzene-d_{10}	79	9.3	3.1	5.0
Hexachloroethane	107	33.2	0.0	3.0
Hexachloroethane-^{13}C	67	5.9	3.4	5.0
Methylene chloride*,**	98	45.3	0.0	5.0
Methyl ethyl ketone**	79	24.6	0.4	5.0
MIBK**	93	31.4	0.0	5.0
Nitrobenzene	100	26.3	0.0	2.0
Nitrobenzene-d_5	88	8.5	3.8	5.0
Pyridine**	31	35.9	0.0	5.0
Pyridine-d_5	71	7.8	2.6	5.0
Tetrachloroethene**	82	27.1	0.0	0.7
Trichlorofluoromethane**	76	27.6	0.0	5.0
1,1,2-Cl_3F_3ethane**	69	29.2	0.0	5.0
Toluene	98	14.4	0.6	5.0
Toluene-d_8	75	11.6	3.2	5.0
Trichloroethene	72	30.4	0.0	0.5
Trichloroethene-d_1	44	8.8	1.9	5.0
Vinyl chloride**	63	35.2	0.0	0.2
o-Xylene	101	25.4	0.4	5.0
o-Xylene-d_{10}	81	9.5	3.2	5.0
m/p-Xylene	107	25.9	0.6	10.0
p-Xylene-d_{10}	77	8.1	3.1	5.0

*Alternate mass employed
** IS quantitation

TABLE 7 - Direct Injection Analysis using Method 8260
New Oil spiked at Low Concentrations

Compound Name	IS RSD	IS Recovery (%)	ID Recovery
Benzene	21.3	86	121
Carbon tetrachloride	44.7	86	73
Chlorobenzene	29.7	81	110
Chloroform	29.3	84	113
1,4-Dichlorobenzene	24.9	72	98
1,1-Dichloroethene	16.6	153	133
Ethylbenzene	30.1	83	105
Hexachloroethane	30.3	71	107
Nitrobenzene	30.3	89	100
Toluene	21.9	73	98
Trichloroethene	28.0	66	72
o-Xylene	29.5	83	101
m/p-Xylene	29.5	84	107

SUMMARY

Headspace/isotope dilution/GC/MS and direct injection/GC/MS can be used for the analysis of 28 of the 29 target analytes for this study. Table 8 presents 95 percent confidence intervals for measuring each of the TCLP target analytes using headspace and direct injection analysis. Reliable analysis of pyridine at regulatory limits may be difficult to achieve without use of replicate analyses for individual samples. Each technique can provide useable analytical data; the particular advantages and disadvantages to each procedure are listed below.

HEADSPACE

- Performed with older MS (adv)
- Uses isotope dilution (dis)
- Requires new methods (dis)
- Uses additional hardware (dis)
- Overnight equilibration (dis)
- Uses larger sample size (adv)
- More complex procedure (dis)
- Less cross-contamination (adv)
- Safety hazard (F.P.<90) (dis)
- Fewer matrix probs (adv)
- Poor partition coeff (dis)
- Possible use for oily soil (adv)

DIRECT INJECT

- Requires sensitive MS (dis)
- Uses IS calculations (adv)
- Uses existing method (adv)
- No new hardware required (adv)
- Quick turnaround (adv)
- 0.5-1 g sample (dis)
- Simpler procedure (adv)
- Instrument contamination (dis)
- Little explosion hazard (adv)
- More matrix difficulties (dis)
- Good recovery (adv)
- Not suitable for soil (dis)

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Dan Bolt of Cambridge Isotopes Laboratory for providing several labeled analogs of TCLP target analytes. The authors also gratefully acknowledge the guidance and management provided by Mr. John Austin and Mr. Barry Lesnik of the Office of Solid Waste, U.S. EPA.

TABLE 8 - 95% Confidence Intervals for TCLP Volatiles in New Oil

Analyte/regulatory limit	Headspace/ID	Direct injection/ID	Direct injection/IS
Benzene, 0.5 ppm	93-129 %	82-160%	11-161 %
Carbon tetrachloride, 0.5 ppm	112-190 %	0-173 %	0-204 %
Chlorobenzene 100 ppm	73-111 %	44-176 %	8-154 %
Chloroform 6 ppm	68-106 %	43-184 %	12-156 %
1,4-Dichlorobenzene, 7.5 ppm	70-112 %	39-156 %	41-133 %
1,2-Dichloroethane, 0.4 ppm	143-193 %	-	45-158 %
1,1-Dichloroethene, 0.7 ppm	68-126 %	58-208 %	113-193 %
Hexachloroethane, 3 ppm	81-117 %	26-188 %	0-146 %
Methyl ethyl ketone 200 ppm	100-158 %	-	75-116 %
Nitrobenzene 0.8 ppm	6-102 %	35-164 %	16-162 %
Pyridine, 5.0 ppm	3-107 %	-	0-119 %
Tetrachloroethene, 0.7 ppm	107-145 %	-	16-149 %
Trichloroethene, 0.5 ppm	95-129 %	0-147 %	0-141 %
Vinyl chloride, 0.2 ppm	94-238 %	-	0-149 %

ID - isotope dilution
IS - internal standard

41

AN ALTERNATIVE METHOD FOR THE ANALYSIS OF VOLATILE ORGANICS IN SOILS

Paul E. Kester
Tekmar Company
PO Box 429576
Cincinnati, OH 45242-9576

Currently, the methods used for analysis of volatile organic compounds (VOCs) in soils matrices involve heated purge and trap. In order to prevent contamination of the purge and trap concentrator, and to ensure that analyte concentrations fall in the linear range of the GC detector, samples are typically screened by static headspace/GC/FID. With proper selection of analytical parameters, static headspace can also be used effectively as an alternate quantitative technique for the determination of VOC concentrations in soil samples.

A non-polluting, matrix modifying solution is added to the soil sample in a headspace vial, along with surrogates and internal standards. Samples are heated to 85° and mixed while in the heated zone. With these parameters optimized, most VOC's listed in Method 8260 can be determined with acceptable precision for a wide range of soil types.

Precision, accuracy, linearity, and carryover of this method are compared to existing methods. Sample collection, preservation, and storage are also discussed.

42 VACUUM DISTILLATION: AN ALTERNATIVE TO THE ANALYSIS OF VOLATILE ANALYTES BY CONVENTIONAL PURGE AND TRAP.

ORGANIC

David R. Youngman, Staff Scientist, Lockheed Engineering and Sciences Company, Las Vegas, Nevada 89119 and Michael H. Hiatt, Branch Chief, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119.

ABSTRACT

Vacuum distillation (VD) provides a low temperature alternative to the analysis of conventional purge and trap analytes. This technique offers the potential for analysis of large sample sizes as well as different matrices and analytes for which there are currently no analytical methods available.

The VD apparatus shown consists of a chilled condenser portion where water interference is removed at temperature of -15 C°. The analytes of interest are trapped on a stainless steel loop at liquid nitrogen temperatures and then desorbed and transferred to a gas chromatography/mass spectrometer using a six port valve and heated transfer line.

The authors will present the results of experiments conducted during development of this technique. Items to be discussed include development of the apparatus, precision, accuracy, and recovery data. The results will be discussed as they apply to current CERCLA VOA analytes, selected RCRA 8270 analytes and organic amines. Matrices considered are water, soil and simulated fish (cod liver oil).

43

OPEN TUBULAR SOLID PHASE EXTRACTION

Peter Del Mar, EM-9, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

ABSTRACT

A solid phase extraction technique is described in which the inside walls of relatively large bore polymer tubing comprise the sorbent surface rather than a packed bed. A practical ten channel extractor is described. The open tubular approach is compared to liquid/liquid extraction and to conventional solid phase extraction cartridges. Parameters affecting recovery are evaluated including tubing composition, inside diameter and flow rate. Data illustrating recovery, precision and detection limits for organo-chlorine pesticides and PCBs are presented. Accuracy is discussed in conjunction with results achieved on several EPA water studies. Preliminary data on the extraction of more polar compounds using "hybrid" column materials is presented.

INTRODUCTION

Liquid/liquid extraction of environmental water samples for selected organic chemicals has been the standard for many years. This approach requires an overnight extraction and consumes large amounts of regulated solvent, typically methylene chloride. Following extraction, a solvent reduction step, (K-D evaporation), is required along with a solvent exchange if an electron capture detector is being used. Because the extraction is non-specific, one or more additional cleanup steps are often required as well.

These time and solvent consuming steps have supplied much of the impetus for the continuing development of solid phase extraction. While modern SPE cartridges have successfully addressed these issues, they also have some limitations. Among these are a propensity to clog, (if the samples contain suspended solids), water retention and the presence of various interfering substances related either to manufacture and packaging or the chemical degradation of the bonded silica sorbents themselves (1).

In an attempt to overcome these limitations without giving up the advantages of solid phase extraction, the open tubular approach has been developed. Initially the work centered on the use of polyethylene tubing with an internal diameter of 1 to 2 mm, and was evaluated for the extraction of certain

non-polar target compounds such as organo-chlorine pesticides and PCBs. A prototype ten channel extractor has been built and used in the continued development of this technology for the extraction of actual field samples and in EPA Water Pollution and Water Supply studies. In spite of it's less efficient geometry as compared to packed bed systems, the open tubular system has a number of extremely practical advantages. The "columns" will not clog, do not retain water and are reusable indefinitely. We have also demonstrated that the system can be configured to greatly reduce the risk of operator exposure in the case of hazardous samples.

This paper will discuss the following parameters affecting extraction efficiency: column diameter, flow rate, and column composition. It should be noted that extraction efficiency is actually the product of two factors; how much of a given analyte is adsorbed onto the tubing walls, and then, how much of this trapped material is actually eluted by the solvent. This "elution efficiency" is also discussed. Though the column length is also an important variable, it is not discussed because of the limitations imposed by the commercially made tubing available at the inception of this project. Even the cleanest commercial tubing obtained contained additives, such as phthalate plasticizers which could not be completely removed even after prolonged solvent washing. The concentrations of these interferents in the extracts naturally increases in direct proportion to the length of the column; therefore it was decided to postpone that part of the study until "clean" tubing could be obtained. This work is now underway.

EXPERIMENTAL

All extracts were analyzed on an HP 5880 GC equipped with an ECD and a 7673A autosampler. The injection volume was 1 ul. The carrier gas was Helium with a linear velocity of 23 cm per second at 200 deg. C and the make up gas was Nitrogen at a flow rate of 40 ml per minute. Capillary columns were 30 meter, .32mm I.D., 0.25 um film; both "Supelco SPB-5" and "Restek Rtx-35" columns were used. The GC runs were programmed in two steps, from 100 deg. C to a final temperature of 240 deg. C.

Stock solutions of organo-chlorine pesticides were made from neat standards supplied by Chem Service. They were divided into three groups:

Group A	Group B	Group C
Aldrin	a-BHC	Chlordane
4,4'-DDD	b-BHC	Toxaphene
4,4'-DDE	d-BHC	
4,4'-DDT	Endosulfan I	
Dieldrin	Endosulfan II	
Endrin	Endosulfan sulfate	
Heptachlor	Endrin aldehyde	
Hep. Epoxide		
Lindane (g-BHC)		
Methoxychlor		

The parent stocks were made up in Iso-octane, and then taken through parallel dilutions; one ending in Methanol for spiking solutions and the other ending in Hexane for calibration standards. The concentrations of spiking solutions were as follows: single component pesticides - 0.5 to 2.0 ug/ml, Chlordane - 1.6 ug/ml, and Toxaphene - 16 ug/ml.

The PCB studied was Arochlor 1242. A spiking solution in Acetone and a calibration standard in Hexane were derived from a standard containing 500 ug/ml in Iso-octane. The concentration of the spiking solution was 2.5 ug/ml.

One hundred ml samples were spiked with 100 ul of spiking solution and the sample extracts were reduced to a final volume of 1.0 ml prior to analysis. The calibration standards were made up at concentrations 1/10 those of the spiking standards.

An internal standard solution was made up in Iso-octane containing:

2,6-Dibromobiphenyl	5.0 ug/ml
2,4,6-Tribromobiphenyl	3.5 ug/ml
2,2',4,5',6-Pentabromobiphenyl	4.2 ug/ml

Forty ul of internal standard mix was added to each ml of extract or calibration standard.

Recoveries were calculated as follows: the peak areas were first normalized using the nearest eluting internal standard and then compared directly to a calibration standard made up as explained above. It can be seen that the final extracts would have the same concentrations as the calibration standards assuming a recovery of 100%.

The sample matrix for recovery studies was tap water that had been filtered through an 10 inch bed of 20-35 mesh activated charcoal and the sample size was 100 ml unless otherwise noted. All solvents used were "Baker Resi-Analyzed" grade.

The ten channel extractor, Figure 1, was built using off-the-shelf components including separatory funnels used as sample holders, Hamilton HPLC valves and a Masterflex ten channel peristaltic pump with reversable flow and pumping rates of 0.36 to 36 ml per minute. Connections between components were made with Teflon tubing.

The flow paths during separation and elution are shown schematically in Figure 2. The plumbing is arranged to pass the eluting solvent through the "columns" without coming into contact with the tubing in the pump heads since it could be damaged by the solvent. In operation, up to ten water samples are placed in the extractor, spiked as required, and then pumped through the columns. Following separation, the columns are eluted with 10.0 ml of solvent, typically Hexane. The sample extracts are blown down to a final volume of 1.0 ml under dry Nitrogen, and internal standards are added prior to analysis.

The effect of column I.D. on extraction efficiency was studied by pumping identically spiked aliquots through 2.5 meter polyethylene tubes with internal diameters of 1.4 mm, 1.6 mm, and 2.0 mm respectively. The flow rate was 1.0 ml per minute.

Flow rate was investigated by doing a series of extractions using 1.5 meter lengths of 1.1 mm I.D. polyethylene tubing while varying the pumping rate. The flow rates were measured by weighing the output of each column over a fixed time interval. Recovery of target compounds was then plotted versus volumetric flow rate.

The efficiency of removal of the adsorbed analytes from the tubing wall, (elution efficiency), was determined by analyzing the extracts produced by subjecting a column to successive elutions with 10 ml volumes of hexane.

Tubing with more polar composition was obtained from the Phillips Petroleum Plastics Technical Center. The 1.0 mm I.D. tubing made from a blend of high density polyethylene and polyethylene terephthalate, (PET). The compositions ranged from pure polyethylene to blends containing 3%, 5%, and 10% PET respectively. The recoveries of Lindane and 2,4-Dinitrotoluene were then determined for various compositions.

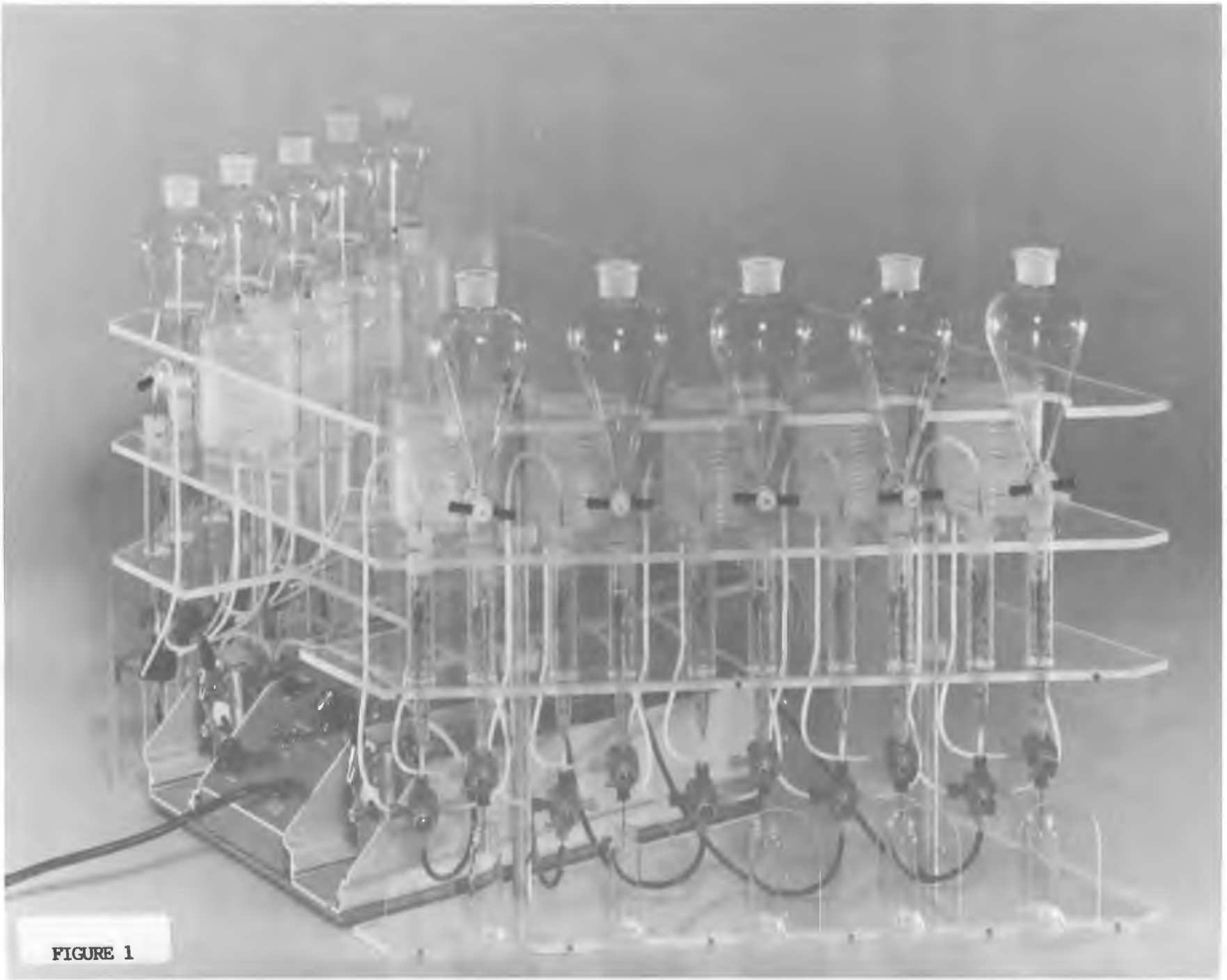


FIGURE 1

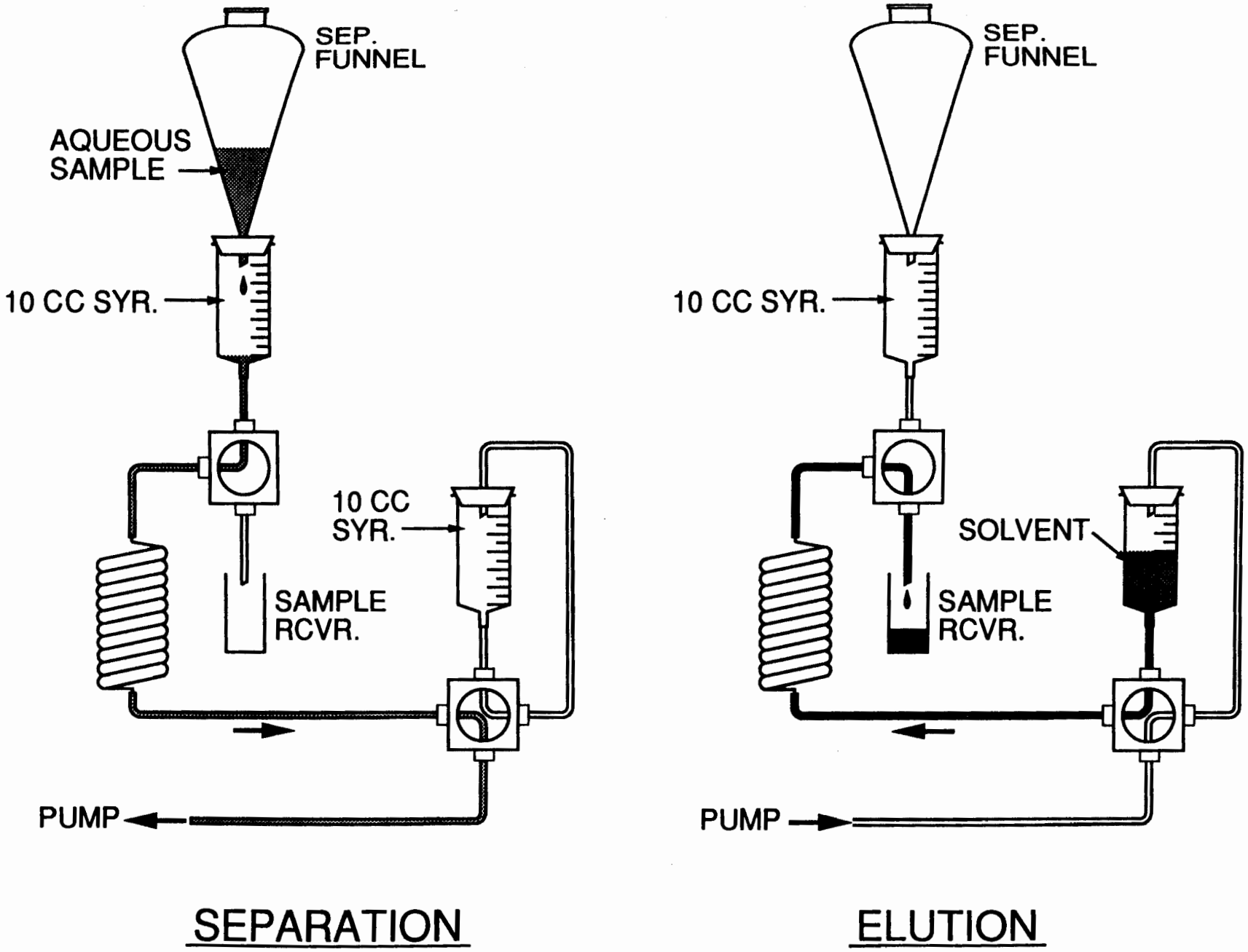


FIGURE 2. Flow Schematic.

RESULTS AND DISCUSSION

Column diameter: The average recovery of each of the ten group A pesticides was determined for each run and then normalized to the recovery obtained from the 2.0 mm I.D. column. The results are presented in Table I.

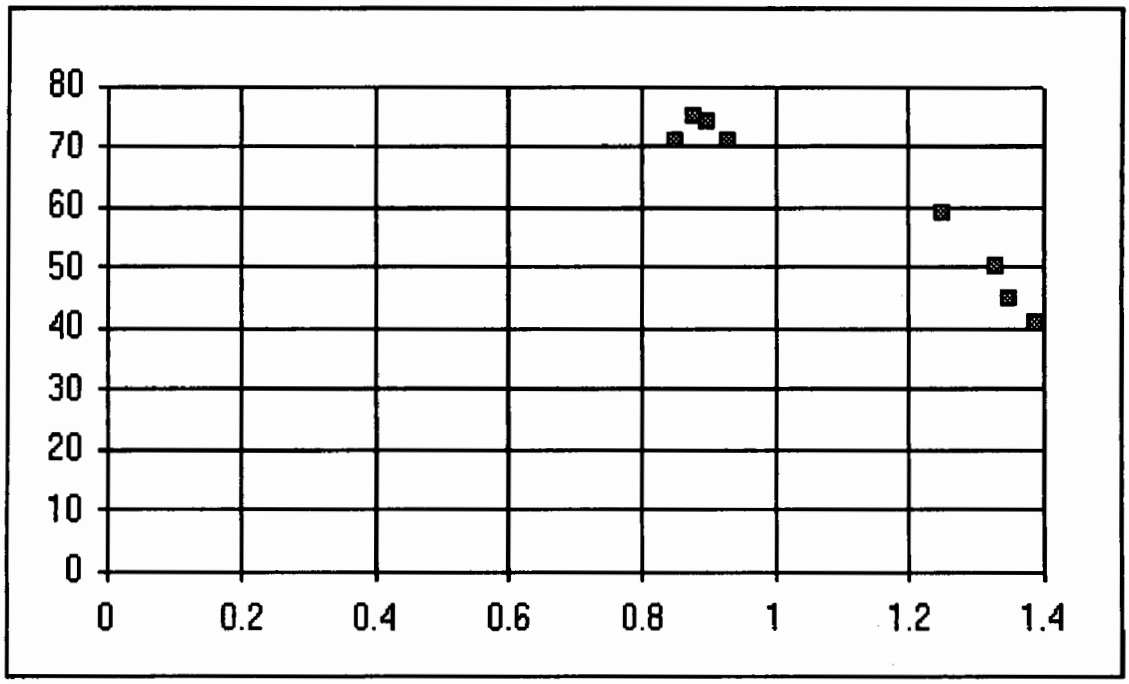
Table I. Recovery vs. Internal Diameter

2.0 mm i.d.	1.6 mm i.d.	1.4 mm i.d.
1.00	1.05	1.11

The average recovery for the 1.4 mm column was 11% higher than that of the 2.0 mm column. This is not a very large gain, but it should be remembered that at any given volumetric flow rate, when the diameter decreases 30%, the linear velocity doubles. Thus the shorter "residence time" of the water in the column offsets, to some extent, the advantages of smaller diameter. Although the smaller diameter results in somewhat higher recoveries, there are two offsetting factors which become increasingly important as the diameter decreases. The first is that the optimum flow rate, at which good reproducibility can be achieved, gets lower and thus extraction times get longer. The other is that the surface area available for adsorption is also decreased which reduces the extraction capacity of the column.

Flow rate: Figure 3 shows the recovery of Dieldrin for a 1.5 meter column with an i.d. of 1.1 mm at various flow rates.

For packed bed systems, the flow rate can be varied over a relatively wide range without adversely affecting reproducibility, but this is clearly not true with the open tubular configuration. This potential problem was easily overcome, however, since the ten channel pump used in the extractor has a variable speed feature which makes it easy to achieve and reproduce any desired flow rate. For a 1.6 mm i.d. tube, the optimum flow rate was found to be approximately .9 ml per minute.



Flow Rate ml/min

Figure 3. Percent Recovery of Dieldrin related to flow rate.

Elution efficiency: This was determined by analyzing successive 10 ml elutions from a given column. For organochlorine pesticides and PCBs, it was found that a single 10 ml Hexane elution removed 98% to 99% of the material trapped during separation. This figure applies to columns made of high density polyethylene; other polymers, notably low density polyethylene, were not as efficient.It was found that the flow rate during elution must also be controlled.

Recovery of target compounds: Table II gives recoveries and detection limits for pesticides and PCBs. The extractions were done with a 3 meter length of 1.6 mm i.d. commercial tubing. The detection limits are based on the recoveries achieved with the 3 meter length, extraction of 100 ml samples, a 1.0 ml final volume, a 1 ul injection volume, and a signal to noise ratio of approximately 10:1 for minimum detectable peaks..

Samples were spiked at the following levels: single component pesticides - 0.5 to 2.0 ug/L, Chlordane - 1.6 ug/L, Toxaphene - 16 ug/L, and Arochlor 1242 - 2.5 ug/L.

The recoveries vary over a fairly wide range and it has been found that the water solubility of a compound does not always correlate with it's recovery. It has also been found that the polarity of the tubing material is not the only factor affecting recoveries. An experiment was done in which the inner walls of the polyethylene tubing were coated with a thin layer of Iso-octane prior to performing an extraction. It was thought that the three dimensional hydrocarbon solvent layer might result in a longer "residence time" for the analytes than the two dimensional hydrocarbon wall of the tubing thus increasing recoveries. Instead, the recoveries of most of the compounds studied dropped significantly, showing that polarity alone is too general a property to accurately predict recoveries.

Precision: Table III illustrates the precision possible with this methodology. Ten replicates were spiked with Arochlor 1242 at a level of 2.5 ug per liter. The internal standard was 2,4,6-Tribromobiphenyl. The extracts were then compared to a standard prepared from the same stock. The recoveries calculated for normalized peak areas are presented. It is probable that one of the reasons for this precision is the absence of the aggressive Kuderna-Danish solvent reduction required with liquid/liquid extraction methods.

Accuracy: Perhaps the best indication of the accuracy possible with this method is the record achieved in EPA Water Supply and Water Pollution studies. The overall results of six EPA studies are summarized in Table IV. Included in these studies were the ten "Group A" pesticides previously mentioned, Chlordane and Toxaphene.

Table II. **Recovery and Detection Limits for Selected Analytes**

Analyte	% Recovery	LOD ug/L
Aldrin	55	0.03
a-BHC	53	0.02
b-BHC	23	0.10
d-BHC	26	0.12
Chlordane	74	0.25
4,4'-DDD	67	0.04
4,4'-DDE	52	0.04
4,4'-DDT	66	0.03
Dieldrin	79	0.04
Endosulfan I	60	0.05
Endosulfan II	61	0.08
Endosulfan sulfate	50	0.09
Endrin	90	0.03
Heptachlor	76	0.03
Heptachlor epoxide	63	0.04
Lindane	51	0.03
Methoxychlor	85	0.08
Toxaphene	84	2.5
Arochlor 1242	65	0.30

Table III. Recovery of Arochlor 1242

Replicate	% Recovery Peak 1	% Recovery Peak 2
1	63	64
2	63	64
3	64	65
4	64	65
5	64	65
6	64	65
7	64	64
8	65	66
9	64	66
10	65	66

Table IV. Results of EPA Water Studies.

Study Number	# of Results Reported	Percentage "Acceptable"	Average Error
WP 022	14	100%	7%
WP 024	14	100%	4%
WP 025	12	100%	8%
WS 026	4	100%	4%
WS 027	5	100%	8%
WS 029	6	100%	4%

It must be noted that these results were averages based on three replicates for each determination. To illustrate the accuracy of this method more fully, the data for the single component pesticides in studies WP 024, WS 026, and WS 029 were considered individually. The 22 reported values were derived from 66 individual data points. The average recovery for the 66 point set was 100% with a standard deviation of 5.8%.

Column composition: To be of practical value, and to preserve the desirable properties of this methodology, any prospective new column material must meet the following requirements:

1. Must be insoluble in the aqueous matrix.
2. Must be essentially impervious to the eluting solvent.
3. Must have an affinity for the target compounds under consideration.
4. Must be chemically stable in the pH range of the extraction.
5. Must have physical properties such that it can be formed into tubing.

Polyethylene has these properties when used for certain non-polar target compounds. The problem with the polyethlyene tubing used initially was that commercial tubing always contained additives, which become interferents in the extracts. Tubing has recently been obtained made from pure polyethylene resin which gives extracts virtually free of interfering substances. The largest limitation remaining is that polyethylene does not appear to extract some of the more polar target compounds such as nitroaromatics and phenols efficiently. To get a more polar column material, tubing was obtained made from blends of polyethylene and polyethylene

terephthalate, (PET). The 1.0 mm i.d. tubing ranged in composition from pure polyethylene to blends containing 3%, 5% and 10% PET. Figure 4 shows the recovery of 2,4-Dinitrotoluene plotted against the increasing percentage of PET.

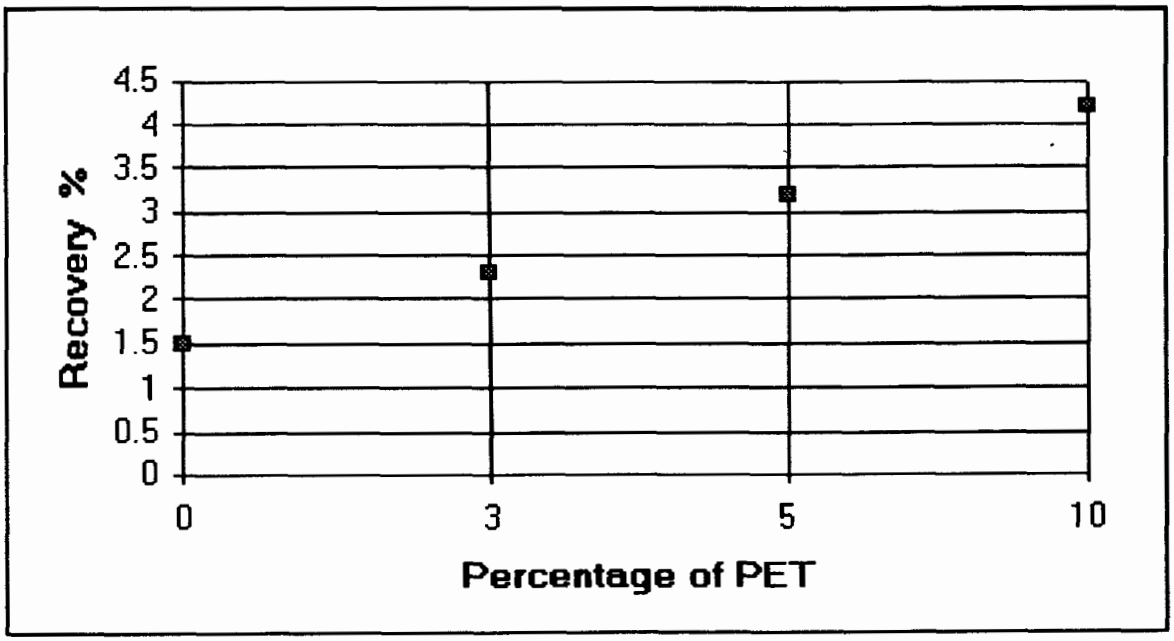


Figure 4. Recovery of 2,4-Dinitrotoluene

This extraction was done on a 3 meter column and although the recoveries are low, there is a clear correlation between recovery and the increasing percentage of the PET polymer. In a separate experiment, the 5% PET composition was found to increase the recovery of Lindane by 33% as compared with a pure polyethylene tube of the same deimensions. Future work will focus on defining the possibilities and limits of improved materials.

SUMMARY

A solid phase extraction technique for organic pollutants in water which employs open tubular "columns" has been described. A ten channel prototype extractor has been built and validated for organochlorine pesticides and PCBs. This method has the low solvent consumption characteristic of solid phase systems

and is much faster than the liquid/liquid extractions now in wide use. With the multi-channel device, ten samples can be extracted, blown down and on the GC in less than 3 hours. The extraction is quite specific and after some 200 field samples, none has ever required any further cleanup. Several practical advantages of the system have been pointed out; the open columns will not clog, do not retain water and can be reused indefinitely. The method is valuable from the waste minimization point of view since no throw away trash is generated. This is particularly desirable when the sample matrices are radioactive, which is often the case for environmental work done in the DOE complex.. It should also be underlined that this method does not add anything to the sample during extraction. Liquid/liquid extraction contaminates a sample with methylene chloride and some commercial SPE cartridges contain phthalate esters which are water soluble to some extent. Thus, a hazardous waste may be created by the extraction process even if the original sample was clean. Since it is a pumped system, it could also reduce operator exposure to hazardous samples. A sample could be pumped from a container or waste stream without actually being handled by a technician. The possibility of the use of new materials has been discussed. The method works well for non polar compounds but more work will be required to determine if it can be extended to more difficult target compounds such as those specified in EPA's Toxicity Characteristic Leaching Procedure, a list containing compounds with appreciable water solubility.

Acknowledgement: The help of Mr. Joe Harder of the Phillips Petroleum Plastics Technical Center in the fabrication of specialty tubing used in this work is gratefully acknowledged.

Literature Cited

(1) Junk,G.A.;Avery,M.J.;Richard,J.J. Anal.Chem. 1988, 60, 1347

44

ACCELERATED LIQUID/LIQUID EXTRACTION WITH REDUCED SOLVENT VOLUME

Mark Bruce, Director of Research and Development, and Marvin W. Stephens, Technical Director, Wadsworth/ALERT Laboratories, Division Of Enseco, Inc., 4101 Shuffel Dr. N.W., North Canton, Ohio 44720.

James Carl, Product Development Manager, Bruce Killough, Product Development Technician, Tony Zine, Senior Development Consultant, Science Products Division, Corning Incorporated, Corning, New York 14831.

David Burkitt, President, Burkitt Consultants, Inc., 2 Captain's Way, Exeter, New Hampshire 03833.

ABSTRACT

Two years ago Corning introduced the One-Step™ apparatus which combined extraction and concentration glassware into one unit. Labor requirements were reduced and most of the solvent was recaptured during the concentration step. The new One-Step apparatus maintains these advantages and reduces both extraction time and solvent volume.

Maintaining a solvent boiling/condensation rate of 15 mL/min allows the analytes to be extracted from a 1 L water sample in less than 6 hours.

The solvent pool at the bottom of a conventional continuous liquid-liquid extraction chamber holds about 200 mL. The analytes must be transferred from the solvent pool to the boiling flask. The new One-Step™ apparatus eliminates this step shortening the extraction time while reducing the amount of solvent needed.

Solvent vapor is lost through many joints in the glassware. Careful re-design has reduced the solvent vapor loss to 40 mL. Not only does this reduce the total solvent requirement, but more importantly reduces analyst and environmental exposure to solvent vapor.

The liquid/liquid extraction time has been shortened from 18 hours to less than 6 hours. Total solvent volume has been reduced from 500 mL to 100 mL.

INTRODUCTION

Solvent reduction has become one of the battle cries of the Environmental Protection Agency for the early 1990's. Since the Montreal Protocol was signed there has been an effort to reduce or eliminate the use of many organic solvents in laboratory sample extractions. At the same time, pressure has increased to shorten sample turn-around time to speed the environmental cleanup process. Corning Incorporated has developed a new One-Step™ extraction/concentration apparatus which addresses both problems.

The largest volume of laboratory waste is from the organic solvents required by current organic extraction methodologies. Both SW-846 methods 3510 (separatory funnel) and 3520 (continuous liquid-liquid) are used for aqueous samples and require large amounts (400-500 mL) of organic solvents such as methylene chloride. The solvent pool at the bottom of a conventional liquid-liquid chamber holds about 200 mL. Transferring analytes from the solvent pool to the boiling flask requires about 2 hours under typical conditions.

The boiling flask starts with 300 mL of solvent. Evaporative solvent losses through the ground glass joints and the condenser may total 100 mL during the extraction. In addition, continuous liquid-liquid extraction times are typically 18 hours plus setup and cleaning time.

The accelerated One-Step™ extraction/concentration apparatus reduces solvent volume to 100 mL and extraction time to 6 hours. This new extractor was evaluated in several areas to test its viability for routine organic extractions. **Analyte**, can the target compounds covered by the Contract Lab Program be quantitatively extracted? **Matrix**, can all usual water matrixes be extracted without mechanical problems from emulsions or particulate plugging? **Accuracy & precision**, are method bias and reproducibility equal to or better than conventional liquid-liquid extraction? **Ruggedness**, is the method and glassware durable enough to tolerate misuse and still produce acceptable results? Is the extract "dry" enough that drying with sodium sulfate is no longer needed?

In short, the goal was to develop an apparatus which would extract as well as conventional liquid-liquid extraction for all common environmental water matrixes yet be safer and more cost effective.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Hardware
- Accelerated One-Step liquid/liquid prototype (see Figure 1.)
- Neslab refrigerated circulator, CFT-25
- VWR heated circulator, 1130

Reagents and Standards
- Methylene chloride
- Hexane
- Sulfuric acid

Table 1. Representative Analytes

BNA	Pest/PCB
Surrogate Spike	
Nitrobenzene-d5	Tetrachloro-m-xylene
2-Fluorobiphenyl	Decachlorobiphenyl
Terphenyl-d14	
Phenol-d5	
2-Fluorophenol	
2,4,6-Tribromophenol	
Matrix Spike	
Phenol	gamma-BHC (Lindane)
2-Chlorophenol	Heptachlor
1,4-Dichlorobenzene	Aldrin
N-Nitroso-di-n-propylamine	Dieldrin
1,2,4-Trichlorobenzene	Endrin
4-Chloro-3-methylphenol	4,4'-DDT
Acenaphthene	
4-Nitrophenol	
2,4-Dinitrotoluene	
Pentachlorophenol	
Pyrene	

RESULTS & DISCUSSION

Glassware

The accelerated One-Step™ apparatus differs from conventional continuous liquid-liquid extraction (and the current One-Step™ extractor) in several key areas. 1) The solvent pool at the bottom of the conventional extraction chamber has been eliminated. The solvent is returned from the bottom of the extraction chamber to the distillation flask (or K-D) via gravity feed rather than syphon action. A hydrophobic membrane is placed across the bottom of the extraction chamber. Organic solvent is dripped through the sample in the conventional manner. However the solvent passes through the membrane at the bottom and runs back to the distillation flask. No pool of solvent is required at the bottom of the extraction vessel for syphon purposes. Thus less solvent is required. The extraction time is also shorter since it is not be necessary to transfer analytes from the solvent pool to the distillation flask via the solvent pool dilution process of a conventional liquid-liquid extractor. Figure 1 shows the flow of solvent. 2) The hydrophobic membrane effectively excludes water from the solvent thus eliminating the need for a sodium sulfate drying step. 3) The solvent volume in the boiling flask has also been reduced from 300 mL to 100 mL. 4) Careful design of the apparatus has decreased the places solvent can be lost. Thus, evaporative solvent losses can be halved. Employee and environmental exposure to solvent vapor is reduced. Also, initial solvent volume can be reduced, which saves on solvent cost.

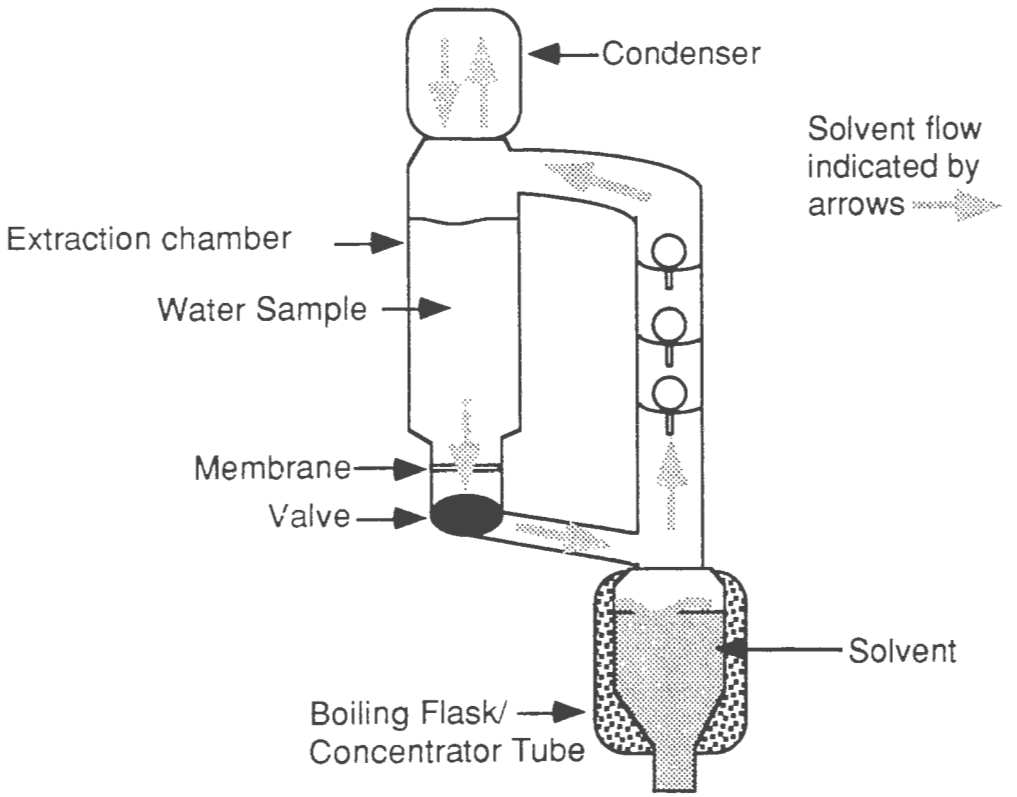


Figure 1. Accelerated One-Step™ Extractor / Concentrator

Method

All extraction parameters are the same as described in SW-846 Method 3520 except for glassware assembly and use, solvent volume and extraction time. The disposable hydrophobic membrane is sealed in place above the valve. The valve is closed and 100 mL of methylene chloride is added to the extraction chamber. The water sample is poured into the extraction chamber. Surrogate and matrix spiking are performed normally, as well as pH adjustment. Once the boiling flask is hot, open the valve allowing the solvent to run through the membrane into the flask. Solvent cycles through the extraction system. The solvent should boil off at a rate of 15 mL/min. When the extraction is complete in 5.5 hours close the valve to concentrate the extract to the desired volume.

Attainment of Goals

Analyte, the compounds listed in Table 1 were selected to represent the range of analytes normally extracted from water matrixes. All surrogate and matrix spike compound percent recoveries were well within CLP limits. **Accuracy & precision**, the average percent recovery for the accelerated One-Step™ system was nearly the same as the average recovery with conventional liquid-liquid extractors. Reproducibility was within CLP specifications.

Extraction time, the required length of the extraction was determined with a time study that measured analyte recovery at 3 hour intervals. Figures 2 and 3 show the results for the matrix spike and surrogate compounds. Most analyte recovery is achieved in the first 3 hours. Small amounts of a few analytes were recovered between 3 and 6 hours.

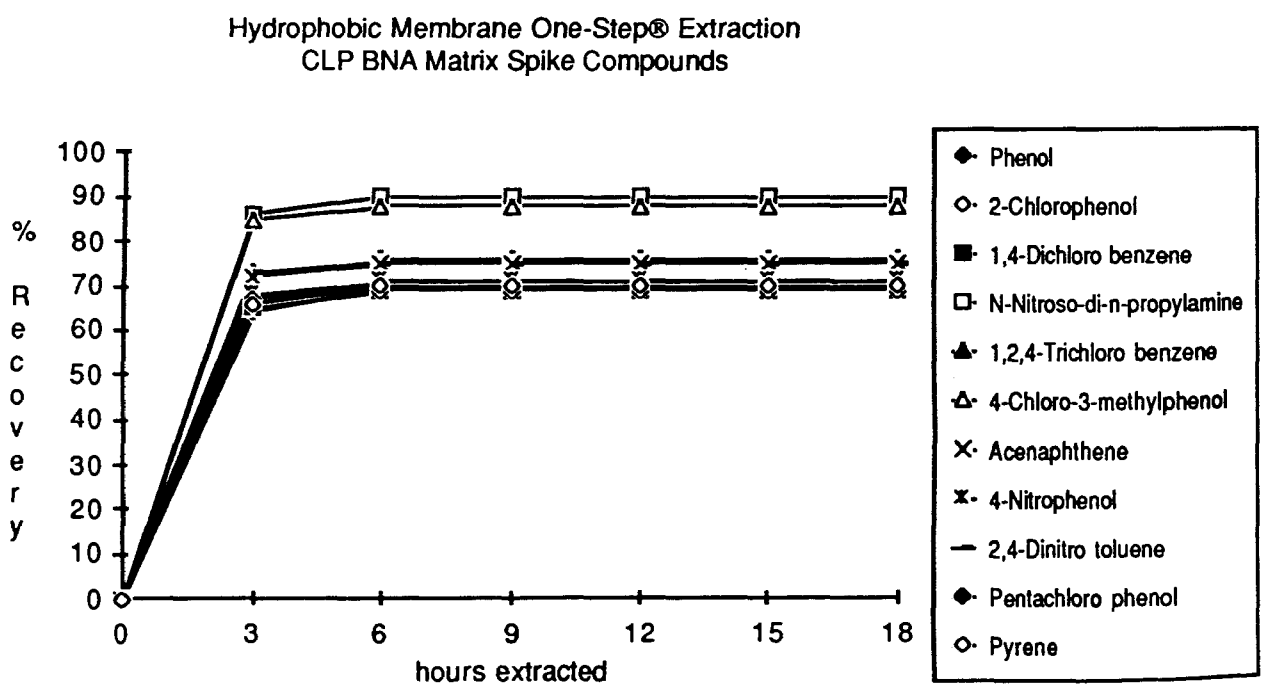


Figure 2. Extraction Time Study for BNA Matrix Spike Compounds

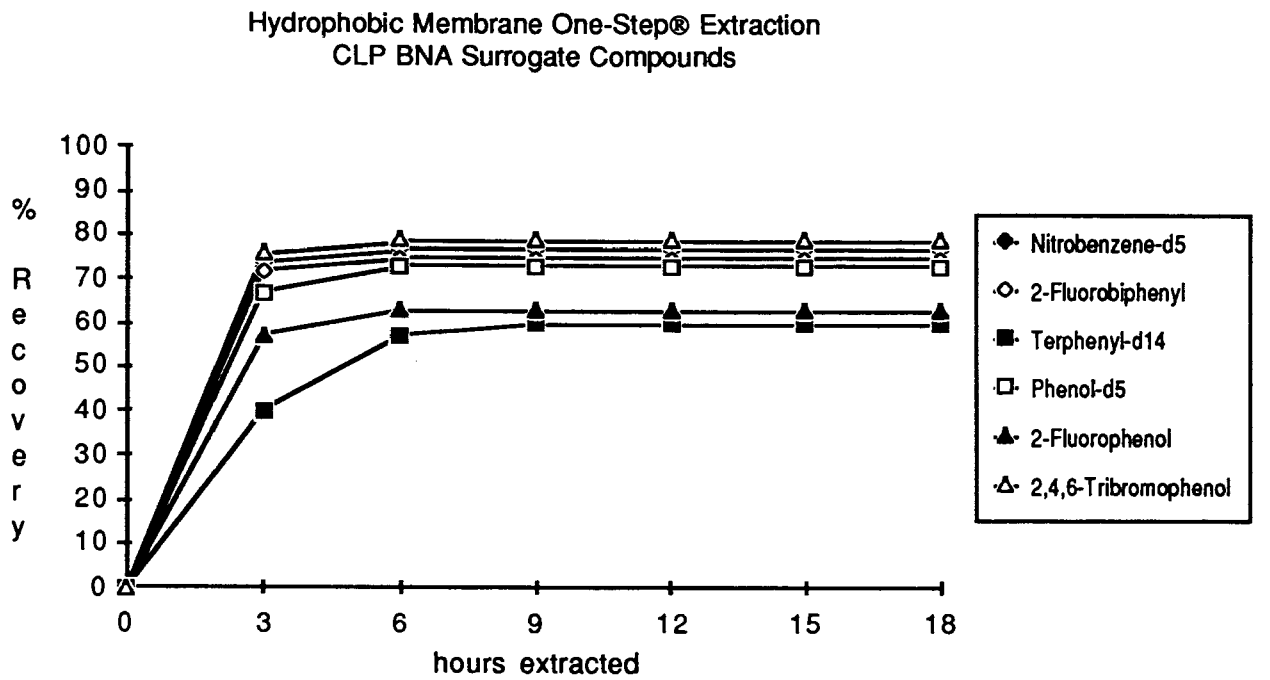


Figure 3. Extraction Time Study for BNA Surrogate Compounds

Matrix, the accelerated One-Step™ apparatus was challenged with various water matrixes to ensure that the system would cycle properly with all typical samples. No plugging or flow restriction problems were noted with samples that were 5% by weight insoluble solids. Both organic "muck" and inorganic clays were tested. Soluble organic and inorganic materials did not present a problem either. An organic loaded pond water and the acetic acid/sodium acetate buffer from the toxicity characteristic leaching procedure were tested. Small emulsions formed on top of the membrane but did not restrict flow.

Ruggedness, the glassware is as easy to assemble as a conventional liquid-liquid extractor. The system has been designed for durability and is more compact than the original One-Step™ apparatus. The membrane "dries" the solvent passing through it very well. Drying tests performed at Corning indicate that a column packed with sodium sulfate, the drying tube adaptor (available for the original One-Step™ system) and the hydrophobic membrane all reduce the water content to 0.005% or less. This is the same water content as brand new methylene chloride.

SUMMARY

The accelerated One-Step™ extractor/concentrator apparatus quantitatively extracts base/neutral/acid analytes (BNAs) and pesticides from 1 L water samples with 100 mL of solvent in less than 6 hours. The membrane is resistant to plugging by particulate loaded or emulsion forming samples. The system is easy to assemble and use. Impact on the environment is minimized because the initial solvent volume and solvent losses are less than conventional liquid-liquid extractors. Analyst exposure to solvent vapors is also reduced. This new One-Step™ system uses $^1/_5$ the solvent and $^1/_3$ the time of a conventional liquid-liquid extractor.

ACKNOWLEDGEMENTS

ERCO, Nancy Rothman, Peter Kane

Wadsworth/ALERT, Don Kirstead, Brian Haueter, Chuck Jacobs, Dave Counts, Tom Hula, Craig Hacket, Kim Davis

"The more I study nature, the more I stand amazed at the work of the Creator."
Louis Pasteur

45 A RELIABLE AND COST-EFFECTIVE METHOD FOR THE DETERMINATION OF EXPLOSIVES COMPOUNDS IN ENVIRONMENTAL WATER SAMPLES

Michael G. Winslow, Manager, Organic Analytical Division, Bradley A. Weichert, Manager, GC/HPLC Department, Robert Baker, HPLC Group Leader, and Preston F. Dumas, Manager, Sample Preparation Department, Analytical Services, Environmental Science & Engineering, Inc., P.O. Box 1703, Gainesville, Florida 32602.

ABSTRACT

Although extraction of environmental water samples with solid-phase extraction (SPE) cartridges has gained increasing acceptance in recent years, specific applications of this sample preparation technology are conspicuously absent from standard EPA methods, despite the cost-effective and health and safety advantages that these cartridges potentially offer. For the past five years, we have used SPE cartridges for the extraction of nitroaromatic and nitramine compounds from ground and surface water samples collected on and near various military installations. Last year at this conference, we presented a comparison of our SPE technique with the salting-out solvent extraction technique proposed in Draft Method 8330 for the determination of nitroaromatic and nitramine compounds in water samples using high performance liquid chromatography (HPLC).[2,6] The intent of that presentation was to demonstrate numerous advantages offered by solid-phase extraction and to suggest that it be seriously considered for adoption in SW846 Method 8330. This paper presents the results of the analysis of over 450 water samples collected at military installations using SPE cartridges and HPLC with UV detection. The following areas are discussed: (1) a detailed review of the method; (2) results of the method detection limit (MDL) study; and (3) the target analyte and QC data obtained from the analyses of environmental water samples. Results to date demonstrate that the proposed method using SPE cartridges with HPLC/UV analysis for the determination of explosives compounds in environmental water samples proves both rugged and cost-effective in extensive real-world tests.

INTRODUCTION

Nitroaromatic and nitramine compounds are the most widely used class of chemicals in munitions components. They are produced in large quantities and, along with some of their production impurities and degradation products, are subject to environmental regulation. Throughout the 1990's and beyond, there will be a need for an analytical method that can acheive low limits of detection in water (< 1 µg/L) for as broad a scope of munitions compounds as possible, especially in light of the projected survey and remediation needs on and near numerous Department of Defense (DOD) and some Department of Energy (DOE) installlations.

Last year at this conference we presented the validation findings for a method that employs SPE with HPLC/UV analysis for the determination of 14 nitroaromatic and nitramine compounds in water. It was demonstrated that the method can achieve excellent precision and accuracy for all target compounds, and at the same time minimize labor and materials costs, solvent use, and waste disposal.

Over the past year, the method has been routinely applied to hundreds of surface and groundwater samples. Some of the data are presented and discussed below.

METHOD DESCRIPTION

Sorbent Cleaning

Prior to sample extraction, approximately 100 g of 80-100 mesh Porapak R (N-Vinyl 2-pyrrolidone divinylbenzene copolymer, normally used as a GC column packing and obtained from Waters) is cleaned by serially extracting with acetone, methanol and acetonitrile in a Soxhlet continuous extractor. The sorbent is placed in an extraction thimble and extracted for at least 2 hours with each solvent at a rate of about 12 cycles/hr. After final extraction with acetonitrile, the sorbent is air-dried in a hood and stored in a dessicator.

Column Packing and Conditioning

An empty 6-mL Baker SPE filtration column with a 20-µM frit at the base is packed with 0.5 g of cleaned Porapak R. Another 20-µM frit is placed at the top of the sorbent bed to assist packing and prevent channeling and disruption of the bed surface. The column is placed in Visiprep SPE Vacuum Manifold (Supelco) and conditioned by eluting 15 mL of ACN followed by 30 mL of ASTM Type II/HPLC water at a flow rate of 10 mL/min. Both eluents are discarded. It is important that the sorbent bed is not allowed to go dry before application of the water sample.

Sample Extraction/Extract Preparation

A 500-mL water sample is passed through the SPE column at 10 ml/min. The sorbent bed is then eluted with 3 mL of ACN at $\leq$ 3 mL/min. into a graduated centrifuge tube. The ACN eluent is concentrated to 2 mL under a gentle stream of nitrogen. The eluent is diluted to a final volume of 6 mL with ASTM Type II/HPLC water prior to HPLC analysis.

HPLC Analysis

The ACN/H_2O sample extracts are analyzed with an HPLC equipped with a variable wavelength ultraviolet absorbance (UV) detector set at 250 nanometers. ESE utilizes a Shimadzu model LC-6A HPLC equipped with a Kratos 757 UV detector, a Shimadzu SPD-6A autosampler, and a Nelson 2700 Turbochrom sytem for data collection and quantitation. The target analytes are separated on a 250 mm x 4.6 mm ID Phenomenex ODS reverse-phase column with a 5-µM particle size. Analyses are performed isocratically using a 55% methanol/45% H_2O (V/V) mobile phase at an 0.8 mL/min. flow rate. The injection volume is 500 uL. A chromatogram of a calibration standard is shown in Figure 1. Confirmation analyses are performed on a 250 mm x 4.6 mm ID Zorbax cyano column (5-µM mesh) with a 50% Methanol/50% H_2O (V/V) mobile phase at a flow rate of 1.0 mL/min.

Standards

Analytical standards are obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aldrich Chemical Co., and the Naval Surface Weapons Center (NSWC). Calibration standards are prepared in 30% acetonitrile (ACN)/70% H_2O to approximate final sample extract composition, 33% ACN/70% H_2O. The calibration standards are prepared at five to eight concentration levels in the range of 1 - 200 µg/L. Sample extracts with target analyte responses above the highest standard are diluted within the calibration range. Spiking

solutions are prepared in acetonitrile.

Optimization of SPE Variables

The successful application of an SPE technique requires optimization of numerous process variables, including sorbent type, sorbent mass, sample volume, sample flow rate, elution solvent, elution solvent volume, and elution solvent rate. The variables will generally be determined by the analyte set, analyte detection limit requirements, solvent extraction efficiency, and the suitability of the elution solvent to the analytical system. Two of the critical variables, sample volume (500 mL) and sample flow rate (10 mL/min.), were tested to ensure that analyte breakthrough during sample extraction was not compromising the reliability of the method.

Two surface water samples which had been collected from a military instrallation were selected for the first experiment. It had previously been determined that they contained high concentrations of several munitions compounds. A composite sample was made by combining one liter of each of these samples. Separate 500 mL and 1000 mL aliquots of this composite sample were extracted by SPE and analyzed by HPLC/UV with the conditions described in the above section. A direct injection analysis from the remainder of the composited sample was also performed.

Table 1 summarizes the results of the above analyses. There was no significant difference between the results obtained from direct injection analysis of the high level composite sample and the results obtained by employing the SPE technique to extract a 500-mL sample at a10 mL/min. flow rate. However, application of the SPE technique to the 1000 mL sample resulted in a greater than 20 percent loss of four of the eight target analytes found in the sample.

Figure 2 plots the results of a second experiment to determine the optimum sample flow rate through the extraction system when a 500 mL sample volume is employed. Five representative target analytes were spiked at 40 - 50 µg/L into 500 mL aliquots of ASTM Type II/HPLC water. Duplicate samples were extracted at five different flow rates ranging from 2 to 50 mL/min. Sample extracts were analyzed as described in the above section. The average percent recoveries indicate that at flow rates above 10 mL/min. target analyte breakthrough becomes evident.

METHOD DETECTION LIMIT (MDL) DETERMINATIONS

Lower limits of detection for the target compounds were estimated by determining the method detection limits (MDLs) as specified by the U.S. Environmental Protection Agency (U.S. EPA). [3] Seven 500-mL aliquots of HPLC grade water were equivalently spiked with an acetonitrile solution containing the 14 target analytes. The target concentration level was about 5 times the estimated MDL as determined by the analyst from instrumental responses and previous experience. The seven spiked samples and an unspiked aliquot were analyzed by the method described in the preceding section.

The MDL for each target compound is calculated by multiplying the standard deviation of the seven replicate concentration measurements by the appropriate one-sided t-value corresponding to n - 1 (6) degrees of freedom. The corresponding t-value for seven measurements is 3.143. Table 3 presents the results of the MDL determinations, including the

mean percent recoveries for each of the target compounds. The mean percent recoveries of tetryl (47.7%) and 1,3,5-TNB (68.2%) are low (<80%) compared to those of the other target analytes. Both compounds are unstable in water at room temperature. This is very noticeable at low concentrations. At concentrations greater than 1 µg/L, percent recovereies for both analytes are generally greater than 80%.

RESULTS AND DISCUSSION OF ENVIRONMENTAL SAMPLE ANALYSIS

481 surface and groundwater samples, collected at several military installlations during the late summer and fall of 1991, were analyzed for 14 nitroaromatic and nitramine compounds using the SPE with HPLC/UV detection procedure described above. The analytical protocol that was followed is described in detail in USATHAMA standard method UW32.[1]

One to eight of the 14 target compounds were confirmed in 82 of the 481 samples analyzed. Figure 3 shows a chromatogram of a surface water sample containing eight of the target analytes. The total target compound concentrations in the 82 samples ranged from 0.075 to 11,620 µg/L. Table 2 lists the distribution and concentration ranges of the target compounds in the 82 samples with positive identifications.

Table 4 summarizes the surrogate recovery data for all samples analyzed, including laboratory reagent blanks. With respect to method accuracy and precision as measured by the mean percent recoveries and associated standard deviations of the surrogate compound, there is a noticeable discrepancy between samples containing 2,4,6-TNT and those not containing 2,4,6-TNT. This phenomenon can be explained by referring to the chromatograms in Figures 1 and 3. The surrogate compound, 3,4-DNT, is not fully resolved chromatographically from 2,4,6-TNT, which elutes immediately after it. Quantification of the surrogate recovery is consequently less reliable than if baseline resolution were achieved. This is especially noticeable when the 2,4,6-TNT concentration is significantly higher than the 5 µg/L surrogate concentration.

The findings to date confirm that the method is very reliable when applied to various water matrices contaminated over a wide concentration range with the target nitroaromatic and nitramine compounds. Currently our laboratory is investigating the following: (1) extending the method to include two nitroaliphatic compounds, PETN and nitroglycerine; (2) including a wash step in the SPE process to help eliminate potential interfering contaminants; and (3) including mass spectrometer (MS) and photo diode array (PDA) detector options.

SUMMARY

An analytical method employing SPE with HPLC/UV analysis for the determination of 14 nitroaromatic and nitramine compounds in environmental water samples is reviewed in detail. MDL determinations are also presented. Data obtained from several laboratory experiments and the analysis of over 450 surface and groundwater samples collected at several military installations are presented and discussed. Current method development work is mentioned.

ACKNOWLEDGEMENTS

We thank P. Dumas, D. Dabney, and S. McMillen for their laboratory assistance.

REFERENCES

1. Environmental Science & Engineering, Inc., "Method for the analysis of Explosives in Water by High Performance Liquid Chromatography Precertification/Certification Report and Method Writeup", May 1991, Contract No. DAAA15-90-D015, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.

2. Environmental Science & Engineering, Inc., "Determination of Low-Level Explosive Residues in Water by HPLC: Solid-Phase Extraction vs. Salting-Out Solvent Extraction", Proceedings of the Seventh Annual Waste Testing and Quality Assurance Symposium, U.S. Environmental Protection Agency, July 1991.

3. Federal Register., "Definition and procedure for the determination of the method detection limit," Code of Federal Regulations, Part 136, appendix B, Oct 26 (1984).

4. C.L. Grant, A.D. Hewitt, and T.F. Jenkins, "Experimental Comparison of EPA and USATHAMA Detection and Quantitation Capability Estimators", American Laboratory, 15-33, February, 1991.

5. P.H. Miyares and T.F. Jenkins, "Salting-Out Solvent Extraction Method for Determining Low Levels of Nitroaromatics and Nitramines in Water", Special Report 90-3-, U.S. Army Corps of Engineers, Cold Region Research & Engineering Laboratory, 1990.

6. SW846 Draft Method 8330, "Nitroaromatics and Nitramines by High Pressure Liquid Chromatography (HPLC)", Revison 1, December 1990, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D. C.

Table 1: Recovery Comparison: SPE vs. Direct Injection

Target Analytes	----------CONCENTRATION (µg/L)---------- Direct Inj.	SPE/500 mL	SPE/1000 mL
HMX	1390	1400	754
RDX	3120	2800	2020
1,3-Dinitrobenzene	<DL	6.21	3.95
1,3,5-Trinitrobenzene	273	268	214
2,4,6-Trinitrotoluene	2000	2150	1950
2,4-Dinitrotoluene	274	290	273
2-Am-4,6-Dinitrotoluene	44.3	44.0	39.8
4-Nitrotoluene	<DL	2.28	1.94

Table 2: Target Compound Distribution and Concentration Range

Target Compounds	No. of Positive I.D.s	Conc. Range (µg/L)
1,3-Dinitrobenzene	10	0.7 - 8.8
2,4-Dinitrotoluene	28	0.08 -1750
2,6-Dinitrotoluene	26	0.08 - 584
HMX	20	1.28 -110
Nitrobenzene	13	0.90 - 82
RDX	41	1.33 - 645
Tetryl	1	4.9
1,3,5-Trinitrobenzene	11	0.59 -1320
2,4,6-Trinitrotoluene	31	0.72 -1950
2-Nitrotoluene	20	0.44 - 8330
3-Nitrotoluene	0	0
4-Nitrotoluene	0	0
4-Amino-2,6-Dinitrotoluene	0	0
2-Amino-4,6-Dinitrotoluene	0	0

Table 3: Method Detection Limit (MDL) Determinations

Compound	Target (µg/L)	Mean Found (µg.L)	Std. Dev.	CRL (µg.L)	Mean %Rec.
HMX	0.221	0.180	0.008	0.024	81.5
RDX	0.183	0.180	0.010	0.031	98.4
1,3,5-TNB	0.096	0.065	0.004	0.014	68.2
1,3-DNB	0.072	0.069	0.004	0.013	96.4
Tetryl	0.123	0.059	0.014	0.043	47.7
NB	0.090	0.087	0.007	0.022	96.5
2,4,6-TNT	0.101	0.085	0.008	0.025	83.9
4-Am-2,6-DNT	0.125	0.123	0.012	0.038	98.5
2-Am-4,6-DNT	0.102	0.095	0.009	0.027	93.5
2,6-DNT	0.101	0.095	0.007	0.023	94.9
2,4-DNT	0.062	0.059	0.002	0.007	96.5
2-NT	0.168	0.172	0.006	0.019	102
4-NT	0.217	0.190	0.008	0.025	87.4
3-NT	0.175	0.167	0.003	0.009	95.6

Note: n = 7, t-value = 3.143

Table 4: Surrogate Recovery Results

Sample Type	Number*	Mean %Rec.	Std. Dev.	Range (%Rec.)
Field	475	101	13	57 - 158
Field/Confirmations	76	98.4	19	57 - 158
Field/Confirmations (w/o 2,4,6-TNT)	46	101	9.5	81 -106
Field/Confirmations (with 2,4,6-TNT)	28	94,6	26	57 - 158
Reagent Blanks	35	100	8.4	81 -115

* outliers ommitted

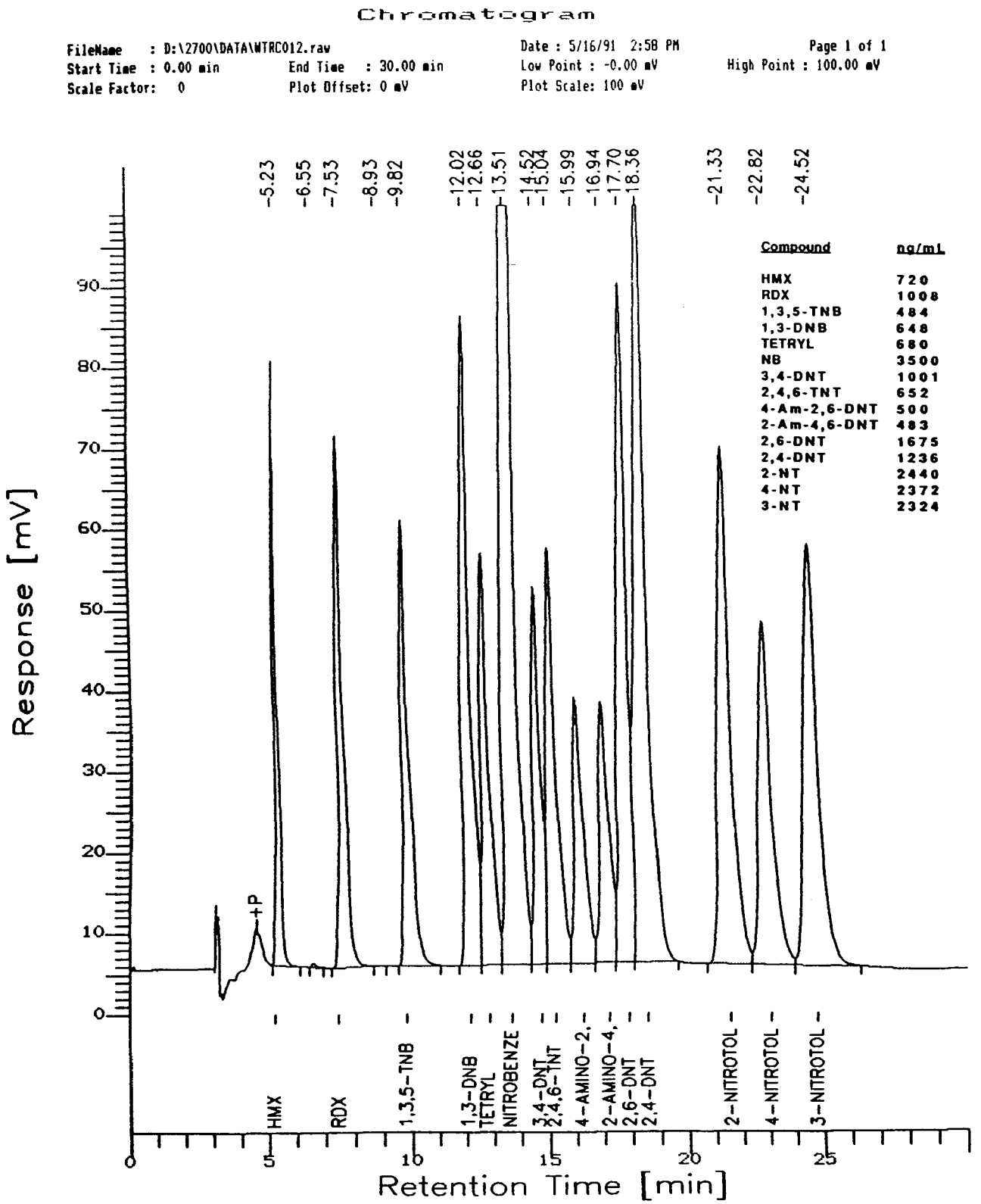


Figure 1: Chromatogram of a Calibration Standard

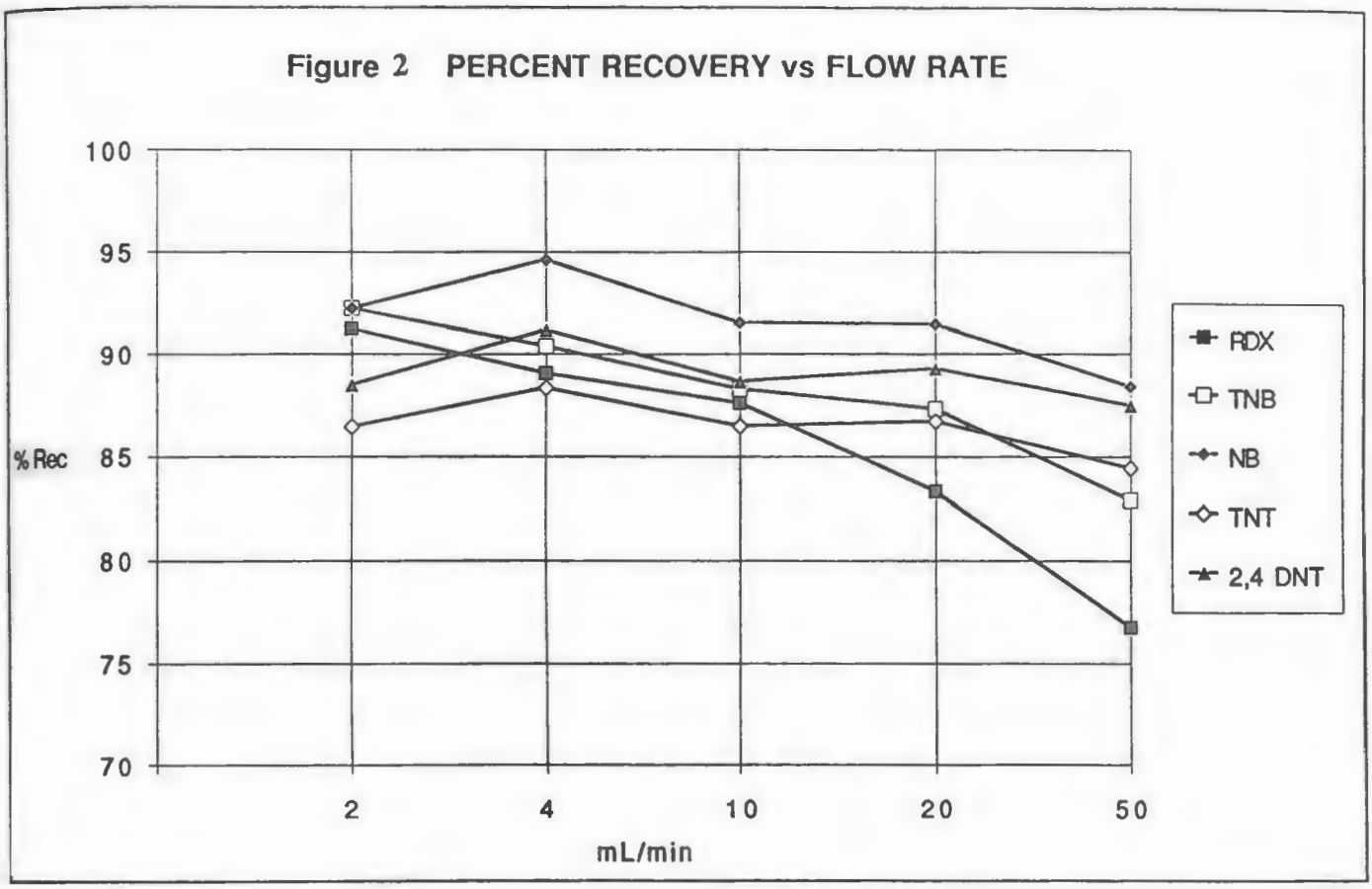


Figure 2 PERCENT RECOVERY vs FLOW RATE
100
95
90
85
80
75
70
% Rec
2
4
10
20
50
mL/min
RDX
TNB
NB
TNT
2,4 DNT

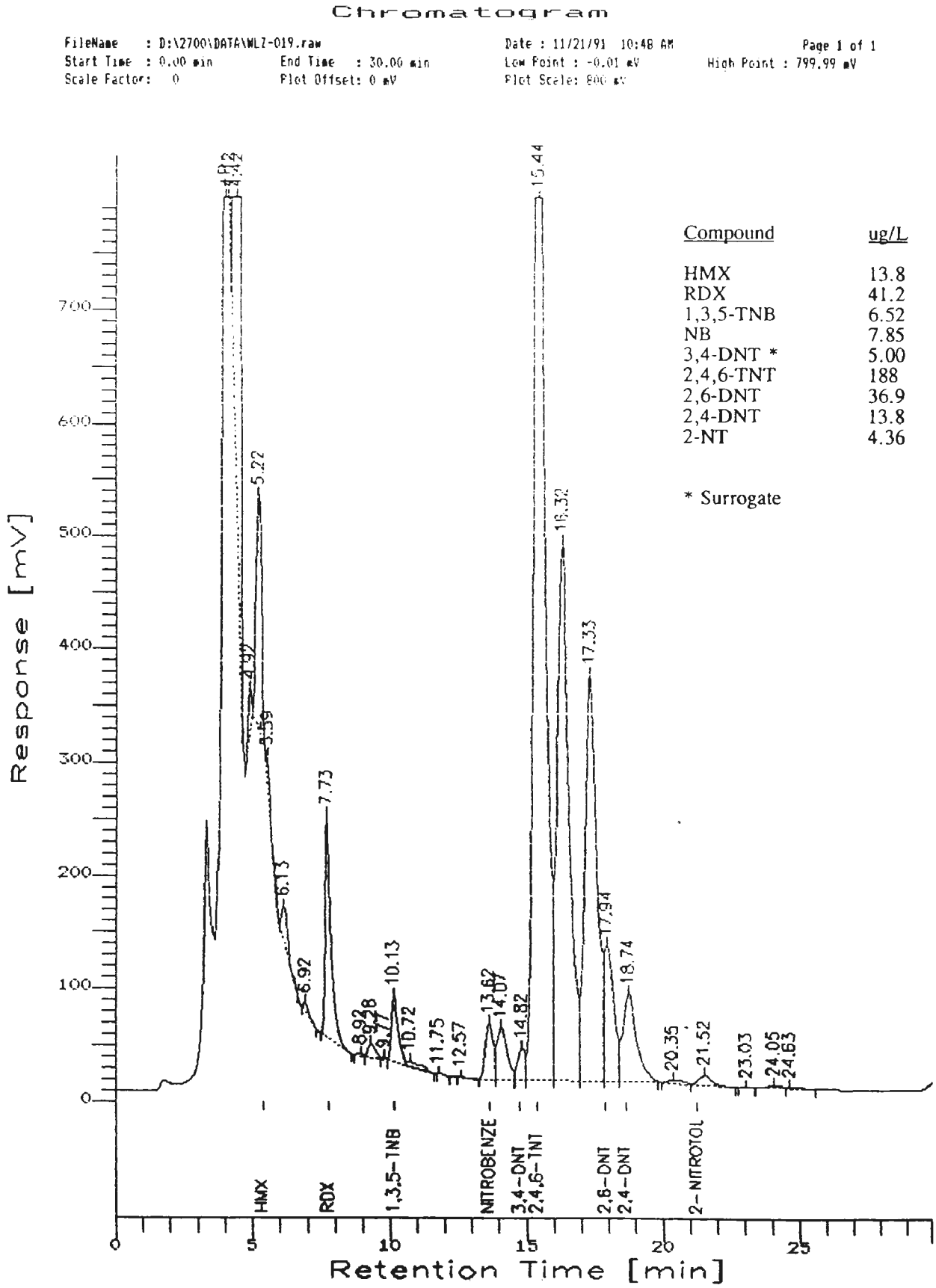


Figure 3: Chromatogram of a Surface Water Sample

6

A SOLID PHASE EXTRACTION DISK METHOD FOR THE EXTRACTION OF EXPLOSIVES FROM WATER

Gabriel Le Brun, Pat Rethwill and Jim Matteson, Pace INC., 1710 Douglas Drive N., Minneapolis, MN 55422 Phone: (612) 525-3352, FAX: (612) 525-3377

The analysis of water for explosives has traditionally been done by "dilute and shoot" methods, such as EPA's Method 8330, or by methods which give some degree of concentration, such as solid phase extraction (SPE) tubes or liquid/liquid extraction (LLE) techniques. Using 47mm SPE discs containing polystyrene divinyl benzene an alternative method was developed for explosives analysis. Features of the method are 500-ml water samples, elution with approximately 10-ml solvent, concentration to 2-ml, followed by HPLC determination of the 13 analytes. Good results were obtained for the analytes, with extraction times as short as 5-min./500-ml. This presentation will detail the extraction method development and the results obtained.

47

ANALYSIS OF ENVIRONMENTAL SAMPLES FOR METHYLMERCURY USING GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

Duane K. Root and Walter W. Li, Technology Development Laboratory, IT Corporation, Knoxville, Tennessee 37923

Gregory E. Johnson, EA Engineering, Science, and Technology, Sparks, Maryland 21152

Abstract

Work was conducted to define procedures for the analysis of soil, sediment and water samples for monomethyl mercury (MMHg) by gas chromatography and electron capture detection (GC/ECD). First attempts were conducted using published extraction and cleanup procedures employing a thiosulfate/$CuCl_2$ treatment and back extraction.[1,2] This procedure did not provide satisfactory results on our sediment matrix spike samples and an alternate procedure was modified and applied. The alternate procedure was adapted from a published fish analysis method, which employed a sample pre-extraction to remove organic interferences.[3] Extraction of MMHg was then performed with benzene after being released from the matrix as the chloride (MMHgCl) by addition of HCl. This procedure was used with success on the most difficult humic/organic sediment samples. The method provided reproducible results with quantification limits to 5 ppb Hg. Relative percent differences of matrix spike pair analyses were within ±22%, and analyte recoveries for the more organic sediments were in the range of 47-118%. A trend of higher analyte recoveries were obtained for the more humic/organic sediments; while a sandy/silicate soil consistently gave much lower recoveries. Analysis of surface water samples at these concentrations (3 ppb) did not present many problems because of the significantly lower amount of extractable interferences compared to soil or sediment samples.

Introduction

Specialized analytical procedures have proven to be particularly useful for characterization of potential risk to ecological receptors at hazardous waste sites. The ability to characterize potential bioavailability of site contaminants is further enhanced through the use of analytical procedures that can provide more information than is typically available using standard TCL/TAL analyses. Procedures such as acid volatile sulfide with simultaneously

extracted metals (AVS/SEM) and direct quantification of organometallics such as organolead, tributyltin and methyl mercury have significantly benefitted the risk assessment community.

Several studies have noted significant correlations between monomethyl mercury (MMHg), total mercury and total organic carbon.[4-6] Accurate knowledge of MMHg concentrations are necessary to develop these relationships which assist in prediction of methyl mercury exposure concentrations. In a recent project application, direct quantification of MMHg was used in conjunction with other analyses such as total mercury, total organic carbon, pH, Eh and temperature to characterize mercury contamination in sediment samples from a southern Gulf Coast hardwood riverbottom swamp. The data were used in conjunction with surface water analyses, biota tissue analyses, and ecological risk modeling and risk calculation to assess potential impacts to ecological receptors.

To quantify speciated forms of mercury in a sample, most often the organic mercury component is extracted after acid halide addition with an organic solvent. Organic mercury can then be determined by analyzing the extract separately, or it can be obtained as a difference from total mercury analyses of a sample before and after extraction. MMHg specificity can be achieved by GC/ECD analysis of the organic extract, but in practice the analysis, particularly for sediment samples, is hampered by matrix interferences and constant GC column conditioning steps. The objective of our work was to develop a reliable GC/ECD protocol for analysis of environmental samples, i.e., soils, sediments and waters to determine concentrations of MMHg in the low ppb range.

GC/ECD methods of analysis specific for MMHg have been developed and used for analysis of biological samples,[1-3,7,8] but at the time of our work, procedures for environmental samples had not been as successfully developed. One widely used procedure for biological samples isolates the MMHg from interferences in the organic extract of a sample by employing a sodium thiosulfate ($Na_2S_2O_3$) solution extraction followed by $CuCl_2$ or $CuBr_2$ addition and an organic back extraction prior to GC analysis.[1,2,8] This procedure was tested on organic extracts of sediment samples, but gave unsatisfactory results for the sample matrices we were analyzing due to low analyte recoveries. An alternative procedure for biological samples is to extract the sample three times with acetone and then once with benzene to remove interferences. The sample is then acidified with HCl and re-extracted with benzene to extract

MMHg as the chloride (MMHgCl).[3] The extract is then analyzed directly by GC/ECD. This procedure was adapted and used for the analysis of MMHg in soil and sediment samples. Surface water samples did not present difficulty for analysis at 1-3 ppb concentrations by direct analysis of the organic extract of an acidified sample.

Experimental

Sediment and Water Analytical Procedures - The sediment extraction procedure was adapted from a fish analysis method from AOAC.[3] The sediments and soils were extracted by weighing a 4g aliquot into a 40 milliliter glass vial and adding 30 mls of acetone. The vial was shaken by hand for 30 seconds and centrifuged at 1700-1800 rpm for 10 mins. The acetone was decanted off and discarded and a second and third pre-extraction with acetone was also decanted off and discarded. Next, 30 mls of benzene was added to the vial and shaken and centrifuged. The solvent was again discarded and then 4 mls of 1:1 HCl was added and mixed with the sediment. Then, 5 mls of benzene was added to the vial. The vial was shaken by hand for 2 minutes and centrifuged as before with the benzene layer being pipetted off and collected into a separate vial. The extraction was carried out twice more with all the successive extracts combined into one vial and the final volume was measured. The volume needs to be determined because there will be some residual benzene from the pre-extraction step. In some cases there were emulsions present. These were broken up by using a glass stirring rod, adding more 1:1 HCl, or centrifuging the vial again at higher rpm. The benzene extract was then dried over anhydrous sodium sulfate and analyzed directly.

Water samples were extracted by placing a 10 ml aliquot of the sample into a 40 ml glass vial, adding 1 ml of 1:1 HCl and mixing the solution. Then 3 mls of benzene were added and the vial shaken for 2 minutes. After allowing the layers to separate, the benzene layer was drawn off and another 3 ml portion of benzene was added to the water. The vial was again shaken and the benzene layer was removed and combined with the first benzene extract for a total volume of 6 mls. The extract was then dried over anhydrous sodium sulfate and analyzed directly.

Matrix spike samples were prepared by spiking a solution of MMHgCl in benzene onto the matrix at a concentration of 2-3 times the anticipated sample concentration.

The analysis was performed on an Hewlett Packard 5890 gas chromatograph equipped with an electron capture detector. Data was collected on a Perkin Elmer/Nelson Turbochrome

software system. A Restek Rt_x-5 GC column (30M x 0.53 mm ID, 1.0 uM film thickness) was used to perform the chromatography. The following GC temperatures were used; injector temperature, 210°C; detector temperature, 270°C; GC oven, 110°C for 5 minutes then increased to 115°C at 10°C/min. and held for 2 minutes. The helium carrier flow was 7 mls/min. The GC column was initially pretreated with several 25 ul injections of 1000 ppm mercuric chloride in benzene. Then at the beginning of each shift, two 10 ul aliquots a few minutes apart were injected. Once the baseline became stable, standards and samples could be run.

Concentrations were determined using a five point external standard initial calibration of monomethyl mercuric chloride (MMHgCl) and daily continuing calibrations (within $\pm$25%) bracketing the analyses. Chromatographic conditions were monitored by running a standard every few samples and noting peak shape and retention time as well as response.

Thiosulfate/CuCl2 Cleanup - This cleanup was used on standard solutions and a few matrix spike samples to assess performance, but was not used in the analysis of samples. Cleanups were performed as described below and in previous work.[1,2] One milliliter of benzene extract was placed in a glass vial and shaken with 1 ml of .01M or 0.1M $Na_2S_2O_3$ for 30 seconds. After allowing the layers to separate, the benzene layer was removed and 0.5 ml of 0.5M $CuCl_2$ solution was added to the thiosulfate solution extract. A fresh 0.5 ml aliquot of benzene was then added to the vial and the mixture was shaken for 30 seconds. The layers were allowed to settle and the benzene layer was analyzed directly.

Results

Chromatography - Much of the preceding work, which used GC analysis for MMHg determination, utilized packed GC columns (5% DEGS).[3,7] These columns need to be conditioned and continually refreshed by injecting a solution of mercuric chloride in benzene. We explored the use of megabore columns seeking a column which might provide good resolution with good durability and require little conditioning. Our efforts centered on using the Restek Rt_x-5 column. The Rt_x-5 GC column provided reasonable resolution of MMHg with retention times generally less than five minutes; however, the system suffered the same need for conditioning with 1000 ppm $HgCl_2$ in benzene as others have described.[3,7] The resolution and retention time of methyl mercuric chloride was dependent on the condition of the system. The GC peak broadened with increased tailing and the retention time increased as the system condition degraded. Figures 1a and 1b show the chromatographic response of a 31.3 ng/ml MMHgCl

standard on a fresh conditioned GC system, and after degradation from sample analysis, respectively. When the system degraded the column required reconditioning to refresh performance. The rate of system degradation was most dependent on the amount of co-extractant material that was in the extracts being injected. Little degradation was noted with analysis of standards or water sample extracts; however, analysis of sediment extracts without cleanup steps degraded the system rapidly. In some cases, reconditioning was required after analysis of a single extract. Sample cleanup procedures were essential to maintain chromatographic performance. Using the sample cleanup described, 20-30 samples could be analyzed between conditionings.

In addition to column conditioning, we also had difficulty maintaining good chromatographic peak shape if we were not careful about maintaining a clean and inert injection port. The chromatography suffered considerable tailing and what appeared to be peak splitting unless the injection port and liners were silanized prior to use and the liners were exchanged regularly.

The performance of the GC analytical system was characterized using our lowest calibration standard at 5 ng/ml MMHgCl. Analysis of the standard was performed five times and the mean and RSD of the responses were calculated. The instrument detection limit was calculated to be 0.65 ng/ml (3x Stand. Dev.) and the quantification limit was 1.1 ng/ml (5x Stand. Dev.).

Water Samples - The surface water samples presented little difficulty for MMHg analysis in the low ppb concentration range. The solids content of samples were well below 1%, and little chemical interference was encountered in the analysis. The estimated quantification limit for the water samples was 3 ppb as MMHgCl. Matrix spike and spike duplicate QC analyses were performed by spiking sample aliquots prior to extraction. Table 1 details analyte recovery and relative percent difference (RPD) results. Precision of the analyses expressed as RPD was within 1.9 to 21%, and analyte recoveries ranged from 67% to 102%.

Thiosulfate/CuCl2 Cleanup of Sediment Samples - Initial work on sediments was conducted using the $Na_2S_2O_3/CuCl_2$ extraction/back extraction cleanup procedure. The cleanup steps were first performed on standard solutions of monomethyl mercuric chloride (MMHgCl) in benzene.

Recoveries of MMHgCl from this work ranged from 44% to 90%. It was noted that some analyte recoveries were improved by a second extraction of the thiosulfate/$CuCl_2$ solution with an additional portion of benzene.

The cleanup steps were then performed on two different sediment matrix spike extracts, and the results are detailed in Table 2. The MMHgCl analyte recoveries for both samples were low, 13% to 46%, and the lower recoveries for sediment #1 is consistent with what was judged to be a higher level of interferences present in that sample. A subsequent analysis of the extract from that sample, which had been treated with the thiosulfate/$CuCl_2$ cleanup, revealed that a significant amount of MMHg was not being extracted into the thiosulfate solution in the first step of the cleanup. To look at the effect of matrix interferences on cleanup recovery, the extract from sediment #1 was subsequently diluted 1:1 to reduce the concentration of interferences, and then an aliquot was extracted with thiosulfate solution. An analysis of the benzene layer showed that at least 74% of the MMHgCl still had not been extracted into the thiosulfate solution. Further dilution of sample extracts to reduce the concentration of interferences was not investigated because analyte detection limits would have been compromised. No further work was done with this cleanup procedure.

Pre-extraction Cleanup of Sediment Samples - Sample cleanup steps are desired to remove chemical interferences, but it is equally important to remove organic co-extractants from the extracts being analyzed to provide stability to the chromatographic system. The pre-extraction cleanup procedure, which was applied in the analysis of sediment and soil samples, offered improved performance over the $Na_2S_2O_3$/$CuCl_2$ cleanup for samples with humic/organic character. Sample concentrations were reported down to an estimated maximum possible concentration of 5-10 ppb as MMHgCl. Figures 2a and 2b show the chromatographic responses for an unspiked and MMHgCl spiked sediment sample, respectively; both analyzed without using cleanup steps. Figure 2c shows the same MMHgCl spiked sample analyzed using the pre-extraction cleanup. The chromatogram displays a strong early response, which may be due to acetone residual in the extract; however, in the area of MMHgCl elution, the chromatogram is free of significant interferences. Table 3 details results of analyte recovery and relative percent difference (RPD) from matrix spike and spike duplicate QC samples of sediment and soil matrix types. Precision of the analyses expressed as RPDs were within 2.0% to 22%. Analyte recoveries ranged from 47% to 118% for organic matrices and were significantly lower for one light color sandy matrix

soil. A duplicate set of MS/MSD samples were prepared and analyzed for this matrix with similar recovery results as the first set. MMHgCl recoveries for this sample ranged from 11% to 22%.

It is apparent that the more humic/organic samples have more sites for MMHg to bind with the matrix, which allows the pre-extraction steps to remove organic material and leave MMHg behind. The addition of HCl is an important step to free MMHg from the matrix to allow the subsequent benzene extraction. It would be expected that sandy samples have fewer sites for MMHg to bind with the matrix so that the addition of HCl is probably not as important for the extraction of MMHgCl. Lower recoveries of MMHgCl for the sandy soil most likely occurred because of losses in the pre-extraction steps prior to HCl addition.

Summary

- The procedures provided consistent results which met performance objectives for the analysis of surface waters and most soil and sediment types.

- MMHgCl spike recoveries on soils and sediments were higher for the more humic/organic samples.

- Low MMHgCL spike recoveries were obtained for a sandy/silica type soil/sediment. This most likely reflects the smaller MMHg binding capacity of this matrix type, which allowed loss of MMHgCl through the pre-extraction steps of the sample cleanup.

- Quantification limits for MMHgCl were in the low ppb range for both water (3 ppb), and soil/sediment samples (5-10 ppb).

- Megabore GC column requires conditioning with $HgCl_2$; injection port components need to be silanized; and injection port liners need to be exchanged regularly, to obtain acceptable chromatography.

- GC performance and stability was maintained for a longer period of time when the amount of analyte co-extractants injected into the GC was minimized, emphasizing the necessity for sample cleanup steps.

- A comprehensive extract cleanup procedure is needed which can handle extracts from samples of all matrix types.

References

1. Filippelli, Marco, "Determination of Trace Amounts of Organic and Inorganic Mercury in Biological Materials by Graphite Furnace Atomic Absorption Spectrometery and Organic Mercury Speciation by Gas Chromatography," *Anal. Chem.*, 59, 116-118 (1987)

2. Baldi, Franco and Marco Filippelli, "New Method for Detecting Methylmercury by Its Enzymatic Conversion to Methane," *Environ. Sci. Technol.*, 25, 302-305 (1991).

3. Official Methods of Analysis, Association of Official Analytical Chemists (AOAC), 25.146-25.152, "Mercury (Methyl) in Fish and Shellfish Gas Chromatographic Method," Washington, DC (1984).

4. Bartlett, P. D. and P. J. Craig, "Total Mercury and Methyl Mercury Levels in British Estuarine Sediments-II," *Wat. Res.*, 15:37-47 (1981).

5. Rudd, J. W. M., M. A. Turner, A. Furutani, A. L. Swick and B. E. Swick, "The English-Wabigoun River System: II, *Can. J. Fish. Aquat. Sci.*, 40:2206-2217 (1983).

6. Winfrey, M. R. and J. W. M. Rudd, "Environmental Factors Affecting the Formation of Methylmercury in Low pH Lakes," *Environ. Toxicol. Chem.*, 9:853-869 (1990).

7. Horvat, M., A. R. Byrne and K. May, "A Modified Method For The Determination Of Methylmercury By Gas Chromatography," *Talanta*, 37, 2, 207-212 (1990).

8. Cappon, C. J. and J. Crispin Smith, "Chromatographic Determination of Inorganic Mercury and Organomercurials in Biological Materials," *Anal. Chem.*, 49, 365 (1977).

Table 1

Quality Control Summary For Water Samples

Results of Matrix Spike And Spike Duplicate Analyses

(MMHgCl)

	Spike Level	% Recovery		RPD
Number	(ppb)	MS	MSD	(%)
1	18.8	83.	84.	1.9
2	18.8	82.	102.	21.
3	18.8	89.	80.	10.
4	7.98	93.	99.	5.7
5	15.0	67.	73.	9.5
6	6.00	80.	75.	6.5

Table 2

Results of Matrix Spike Analyses Using Thiosulfate/$CuCl_2$ Cleanup

(MMHgCl)

Matrix	Spike Level (ppb)	% Recovery
Sediment #1	91.	13.
1:1 Ext. Dil.	91.	<26
Sediment #2	94.	45.
	94.	46.

Table 3

Quality Control Summary For Soil/Sediment Samples

Results of Matrix Spike And Spike Duplicate Analyses

(MMHgCl)

		Spike Level	% Recovery		RPD
No.	Matrix	(ppb)	MS	MSD	(%)
1	sediment	94.5	75.	74.	2.0
2	sediment	94.5	114.	118.	3.9
3	sediment	94.5	78.	79.	2.4
4	soil	20.1	95.	83.	11.
5	soil	19.6	47.	51.	9.0
6	soil	37.	85.	82.	2.6
7	soil	74.2	76.	73.	4.0
8	soil	25.	68.	64.	2.7
9	soil	35.	114.	83.	22.
10	soil	38.	87.	76.	6.6
11	soil	37.	63.	49.	19.
12	soil	25.	105.	88.	7.2
13	soil	37.5	59.	73.	20.
14	sandy soil	19.7	11.	13.	18.
		20.	21.	22.	6.1

FIGURE 1

Chromatograms of MMHgCl Standard

(31.3 ng/ml)

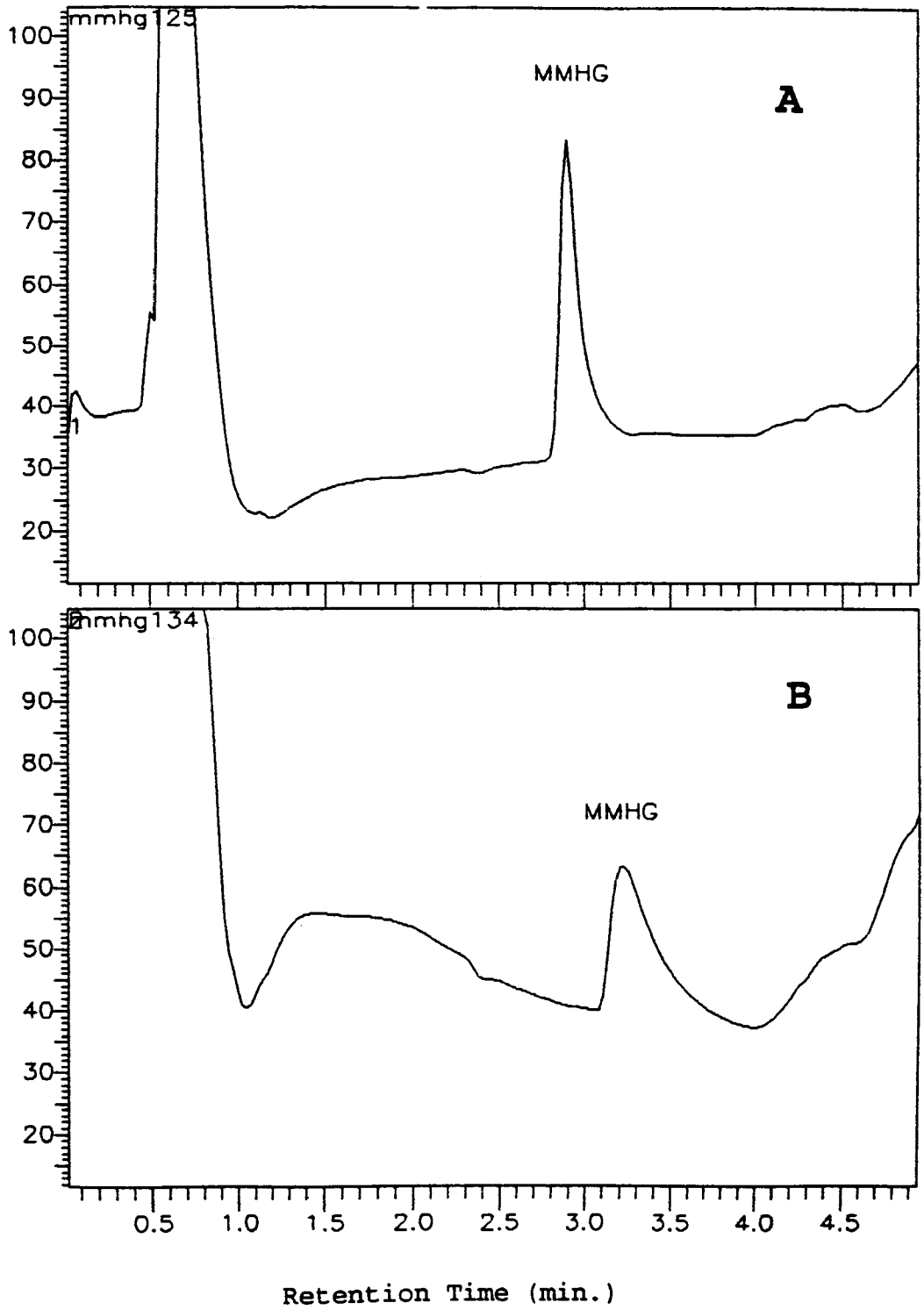
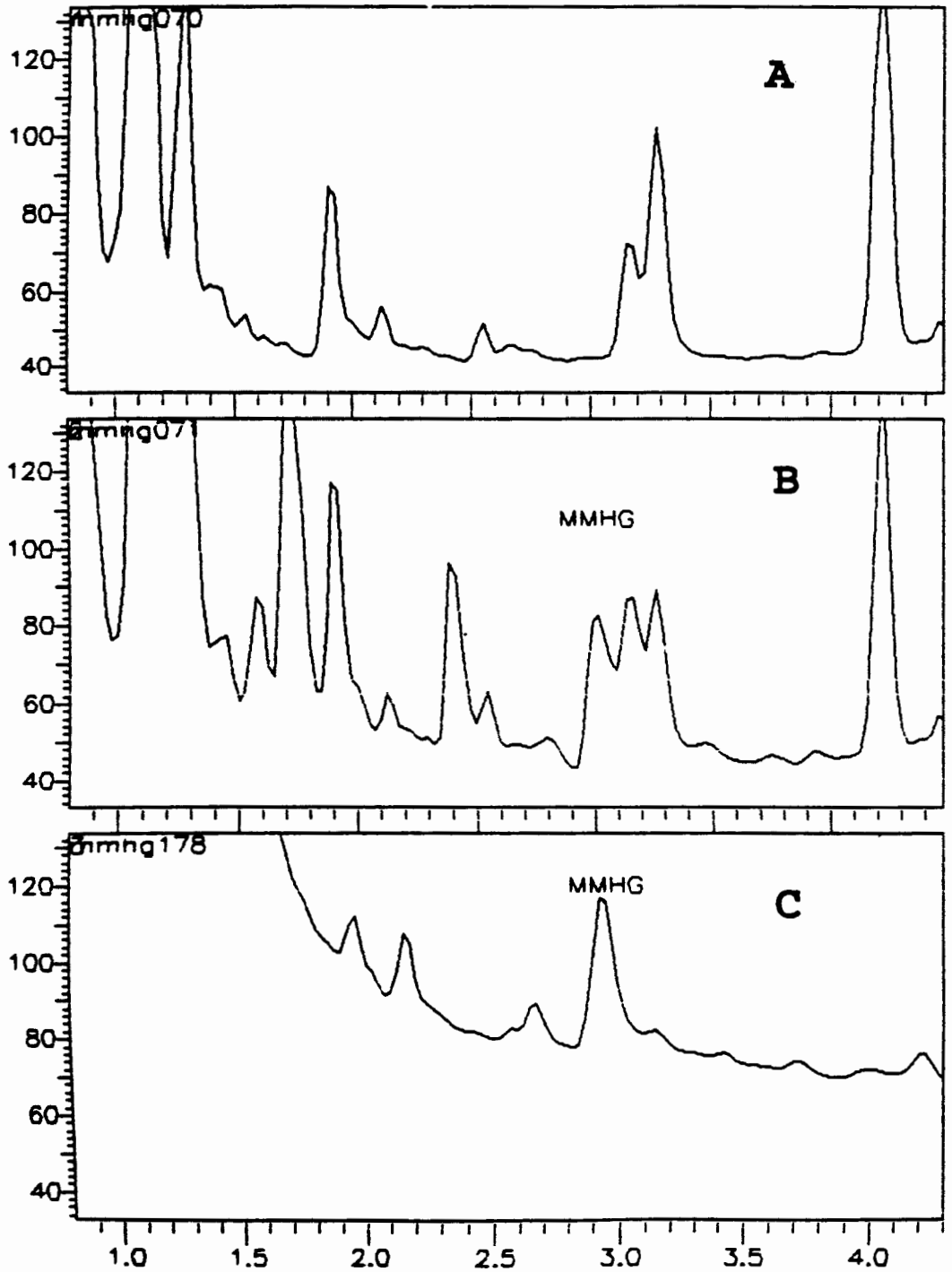


FIGURE 2

Chromatograms of Unspiked and MMHgCl Spiked

Sediment Sample



Retention Time (min.)

48

A PRACTICAL MEANS OF MEASUREMENT OF PURGEABLE ORGANIC HALIDES AT LOW CONCENTRATIONS BY OXIDATIVE PYROLYSIS/COULOMETRIC TITRATION

John Simon Jr., Chemist, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, Colorado 80225, J. Lowry, U.S. Environmental Protection Agency, NEIC, Denver, Colorado 80225, and C. Ramsey, U.S. Environmental Protection Agency, NEIC, Denver, Colorado 80225

ABSTRACT

Purgeable organic halides (POX) are low molecular weight, volatile organic compounds containing halogen atoms (Cl, Br, I) which may be "purged" from water by sparging at mildly elevated temperatures (e.g. 55 C). Examples include trihalomethanes such as chloroform, and common solvents such as methylene chloride and perchloroethylene. These POX compounds are measured to obtain non-compound specific, screening information about samples such as waste water and drinking water. POX data are useful for independently checking results obtained from more time consuming, more expensive GC/MS analyses. These POX species are routinely measured in process wastewaters by the pulp and paper industry. POX are typically measured by purging/combustion/coulometric titration methods. An appropriately collected sample is introduced into a sparging device, which is heated to 55 C. The sparged volatile compounds are then swept into a pyrolysis tube using a stream of oxygen. Hydrogen halides (HCl, etc.) are thereby produced, collected in a solution of aqueous silver acetate and are subsequently measured using a coulometric titration. Present implementations of the above POX technique, such as EPA Method 9021, have been found by the authors and others to be unacceptable for low concentration samples. When the total POX concentration is less than about 1000 ug/l, poor recoveries (i.e. less than 90 percent) are found for representative analytes such as chloroform, trichloroethene, chlorobenzene, etc. This limitation makes EPA 9021 unacceptable for routine analyses conducted at EPA-NEIC on low concentration samples such as drinking waters. Research at EPA-NEIC has identified the key factor responsible for low recovery to be an insufficient flow of the oxygen used for the combustion process. The purging/combustion/coulometric titration processes was systematically explored until this responsible component

was identified. Through these experiments it was determined that increasing the flow rate of oxygen in both the sparging device and the pyrolysis tube improved recoveries dramatically. In order to achieve recoveries satisfactory for drinking water analysis an oxygen flow rate of at least 800 ml/minute was required when using a 10 ml sample. This flow rate was found to be incompatible with an off-the-shelf instrument from one manufacturer but was compatible with another instrument from another manufacturer. A simple modification to the first type of instrument resulted in acceptable recovery for POX compounds. With increased oxygen flow, and depending on the POX compound(s) present, recoveries of 99 $\pm$ 9.6 (One S.D.) percent can be obtained with samples containing 11-20 ug/l purgeable organic chlorine. Because of the intrinsic low cost of POX measurements, and with this enhanced ability to provide reproducible results at low concentrations, we conclude that POX measurements at drinking water levels are practical using this approach. The technique allows for the screening of a large number of POX samples easily. Appropriate modifications to Method 9021 will be discussed.

INTRODUCTION

Purgeable Organic Halides (POX) are volatile organic compounds containing halogen atoms (Cl, Br, I) that can be purged at slightly elevated temperatures (i.e. 55° C). POX species include solvents such as trichloroethene, tetrachloroethene and other halogenated organics. Many of these compounds are toxic and some are thought to be carcinogenic; thus they are important from a regulatory stand point. POX compounds are also a good indication of anthroprogenic contamination in media such as ground water.

A common approach to POX analysis involves a oxidative pyrolysis/coulometric titration technique.(1-2) This method has been widely used in environmental analysis since the early 1980's due to the promulgation of regulations under the Resource Conservation and Recovery Act (RCRA). (Hazardous waste landfills are required under RCRA to monitor ground water for Total Organic Halides (TOX).) Diagram 1.1 shows the sequence of events involved in POX analysis using the oxidative pyrolysis/coulometric titration technique.

The above mentioned method of POX analysis can be broken down into three major components: 1) Purging, 2)

combustion/dehydration, and 3) titration. The first component of this sequence, purging, will be discussed next with the other components following.

POX analysis using the above method begins with the introduction of a 5-10 ml sample into a heated sparging chamber. The sparging chamber is heated to 23° C - 70° C to facilitate "purging". The sample is then sparged with oxygen and the volatile halogenated compounds are purged from the sample. These volatilized compounds are then swept into a pyrolysis tube via a stream of oxygen.

The second step, combustion/dehydration, includes separate combustion and a dehydration processes. The combustion process occurs in a pyrolysis tube heated by an electric furnace to approximately 900° C. After sparging the volatilized POX compounds enter the heated pyrolysis tube and combustion takes place in an oxygen enriched environment. During the combustion process halide ions disassociate from their parent compounds. These halide ions then react with hydrogen or each other forming hydrogen halide (HX) or X_2. The HX is then swept via an oxygen stream into a dehydrating tube which removes the water vapor present from both the combustion and purging steps. The water vapor is removed because water adversely effects the titration process. The mixture of gases containing HX enters the titration cell, again via an oxygen stream.

The third component of POX analysis described herein is a coulometric titration. This titration can be summarized by the following steps: Step 1) HX are introduced into an electrolyte solution containing electrolytically generated silver ions. Step 2) The silver ions and HX react to form AgX. Step 3) The amount of AgX generated is measured coulometrically and related to the POX concentration using Faraday's law.

The above mentioned technique provides the analyst with quick, inexpensive, non-compound specific screening information. This screening information can then be used to determine if more costly and time consuming GC/MS work must be done.

Present methods utilizing the oxidative pyrolysis/coulometric titration technique for POX analysis, such as EPA method 9021, have been found by the authors and

others to be produce low recoveries for low concentration (< 100 ug/l purgeable Cl) analysis.(3) Since these recoveries are less than 90 %, this method is unsuitable for accurate low level work. The present research has been conducted to investigate why recoveries were low when using commercial instrumentation for POX analysis. Also, of interest, was if the commercial instrumentation could be easily modified, if necessary, to obtain the desired recoveries at low POX concentrations.

It was determined that a deficiency of oxygen in the sparging and pyrolysis chambers was responsible for the low rSecoveries. A simple modification made to a commercial instrument allowing for an enhanced oxygen flow rate was made and recoveries greater than 90 % at purgeable Cl concentrations less than 1,000 ug/l were obtained.

A series of experiments utilizing the increased flow rate were then performed on a group of test compounds (trichloroethene, tetrachloroethene, chloroform, chlorobenzene) in distilled water. Results from these experiments will show that reproducible recoveries greater than 90% can be obtained at POX concentrations between 11 and 500 ug/l purgeable Cl.

EXPERIMENTAL

Materials and instrumentation: Deionized and distilled water was used as the solvent for all solutions. Reagent grade silver nitrate, laboratory grade acetic acid and high purity oxygen was obtained from commercial sources. Stock solutions of trichloroethene, tetrachloroethene, chlorobenzene and chloroform were prepared from US-EPA standards. Stock solutions were made from trichloroethene obtained from commercial sources. All stock solutions were prepared by diluting the appropriate volume of standard or neat compound with methanol. A portion of the stock solution was then spiked directly into a syringe containing 10 ml of deionized water. The spiked solution was then transferred to the sparger and sparged immediately thereafter.

A Mitsubishi total organic halogen analyzer model TOX-10 was used throughout. The instrument parameters for all analyses are in table 1.1 The TOX-10 was modified by attaching a commercial flow meter to the oxygen inlet. (See diagram 1.1 for attachment)

RESULTS AND DISCUSSION

Effect of oxygen flow upon POX recovery: A series of experiments were conducted which measured the recovery of trichloroethene (544 ug/l purgeable Cl) as a function of oxygen flow. Graph 1.1 depicts the results of this experiment. It is clear that recovery is greatly affected by the oxygen flowrate and that this should be adjusted to at least 800 ml/minute for quantitative (> 90 %) recovery. It was also found that argon is not needed for any part of the purging/pyrolysis/coulometric titration sequence.

The instrument manufacturer (Mitsubishi model TOX-10) recommends using an oxygen flowrate of 200 ml/min. The higher flowrates used herein were achieved by incorporating a ball-type flowmeter into the oxygen stream.

Recoveries of POX species from distiled water using enhanced O2 flow: Experiments were performed on a group of test compounds (trichloroethene, tetrachloroethene, chlorobenzene, chloroform.) in distilled water. Table 2.1 illustrates that the recoveries of these test compounds are favorable as the purgeable Cl concentration decreases from 500 ug/l to 11 ug/l. Also, the relative standard deviations in table 2.1 indicate that precisions at both the high and low POX concentration levels are favorable even at low POX concentrations.

CONCLUSIONS

It was described herein that increasing the oxygen flow rate in both the pyrolysis and sparging chambers increases recoveries to better than 90 % at low POX concentrations (10-20 ug/l purgeable Cl). The precisions are also favorable at the 10- 20 ug/l purgeable Cl levels. To achieve the flow rates needed for the improved recoveries a simple modification of a commercial instrument (addition of a flowmeter) is necessary and easily accomplished.

This study made use of number of test compounds in deionized water. While recoveries were favorable under these conditions, these conditions are not necessarily representative of samples where a substantial matrix is

present, such as contaminated industrial wastewater. Further study would be needed to determine if this modified method is applicable to adverse matrices.

DIAGRAM 1.1

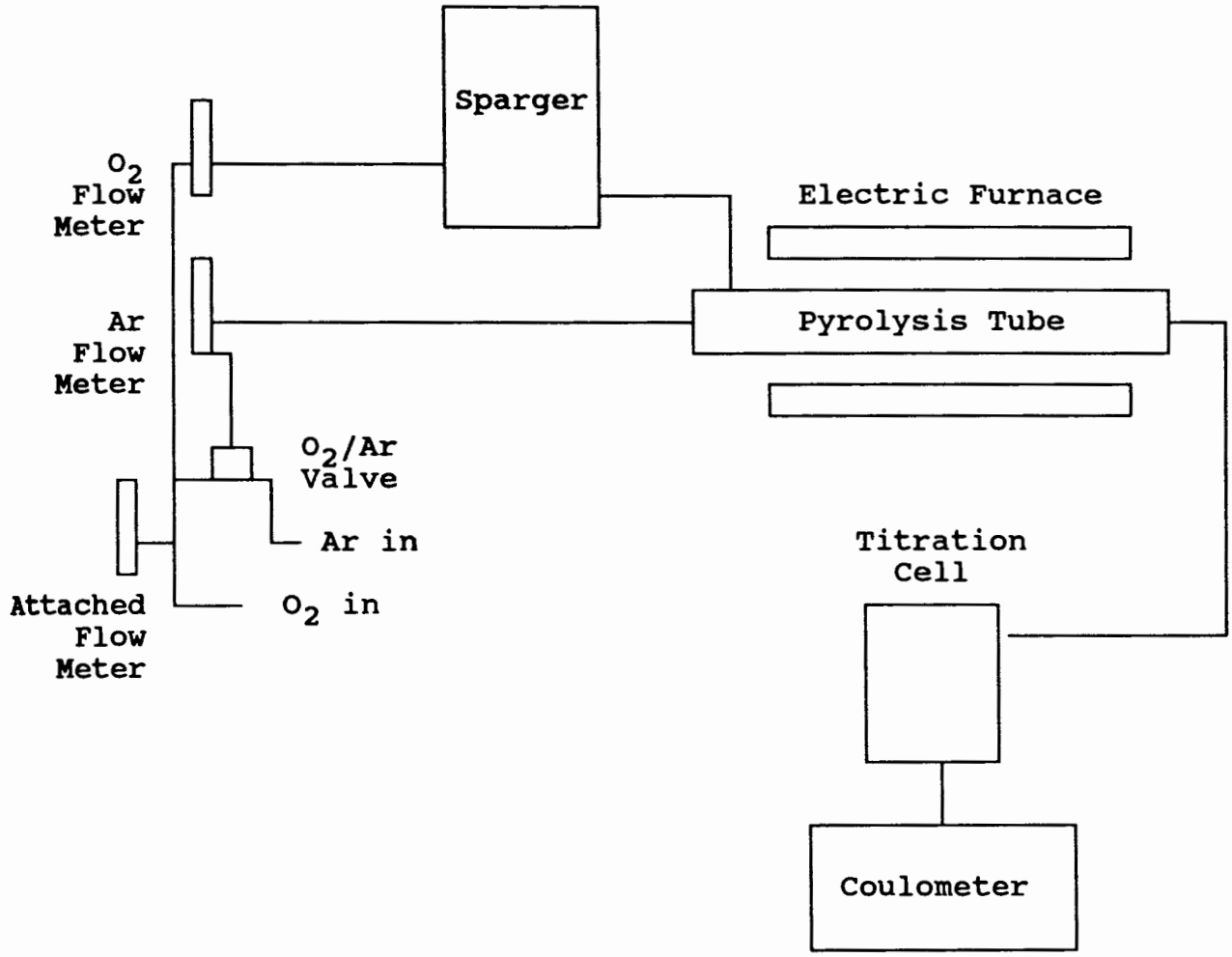

Sparger
O_2 Flow Meter
Electric Furnace
Ar Flow Meter
Pyrolysis Tube
O_2/Ar Valve
Ar in
Titration Cell
Attached Flow Meter
O_2 in
Coulometer

TABLE 1.1

PARAMETER	SETTING
$delay_1$	10min.
$delay_2$	0,0min.
$temp_1$	850°C
$temp_2$	900°C
$temp_3$	55°C
$gain_1$	1.5-2.5 Q/mV
$gain_2$	4.5-5.5 Q/mV
$gain_3$	9.5-10.5 Q/mV
end point	290-300 mV
sensitivity	1 mV
gas selection switch	O_2 mode
O_2 flow rate	> 800 ml/min.
Ar flow rate	0.0 ml/min.

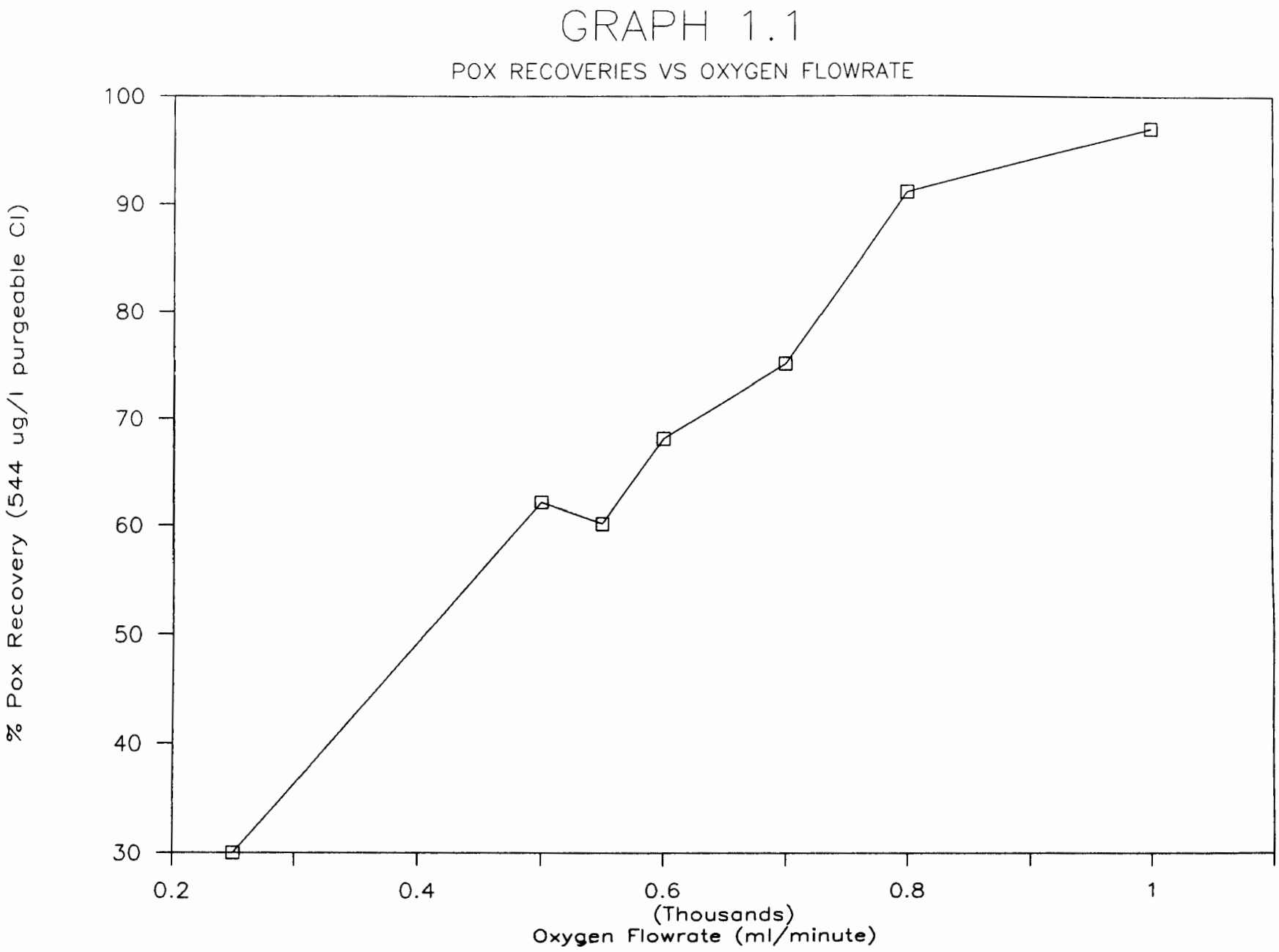

GRAPH 1.1
POX RECOVERIES VS OXYGEN FLOWRATE
% Pox Recovery (544 ug/l purgeable Cl)
100
90
80
70
60
50
40
30
0.2
0.4
0.6
0.8
1
(Thousands)
Oxygen Flowrate (ml/minute)

TABLE 2.1

POX PRECISION AND BIAS

Compound	Dose (ug/l as Cl^-)	Average Percent Recovery	%RSD	Number of Replicates
Tetrachloroethene	373	94	3.38	7
Chloroform	446	96	2.70	7
Trichloroethene	544	93	1.60	7
Chlorobenzene	789	93	2.10	7
Tetrachloroethene	19	96	10.48	7
Chloroform	11	99	9.73	7
Trichloroethene	11	104	13.32	7
Chlorobenzene	16	96	9.54	7

LITERATURE CITED

(1) Harper, F. Ground Water Monitoring Rev. 1984, Winter, 46-48.

(2) Takahashi, Y.; Joyce R.J. "Chemistry in Water Reuse": Ann Arbor Science: Ann Arbor MI. 1981; Vol. 2, Chapter 7.

(3) Riggin, R.; Lucas, S.; Lathouse, J.; Jungclaus G.; Wensky, A. "Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater", EPA-60014-84-008, January 1984, Contract Number 68-03-2984

49

ION TRAP MASS SPECTROMETRY FOR PESTICIDE ANALYSIS AND OTHER APPLICATIONS

Mike Zimmerman, ICF/QATS Laboratory, Las Vegas, Nevada, 89120

ABSTRACT

Determination of the CLP target pesticides in relatively clean samples has been performed in our laboratory using an ITS40 ion trap mass spectrometer in an effort to demonstrate and evaluate the performance of the instrument in several configurations, including electron impact (EI) and chemical ionization (CI). Splitless and on-column injection techniques were also compared. Results to date indicate that with EI ionization the instrument can detect and qualitatively identify most of the CLP target pesticides at levels equivalent to or below the CLP contract required quantitation limits (CRQLs) for electron capture (ECD) analysis. These EI experiments were conducted with full scan acquisitions and provided unambiguous NIST library spectral matches for most of the target analytes at the low ECD calibration level, 0.005 or 0.01 ug/mL. To date, chemical ionization using methane and isobutane has not provided the sensitivity of electron impact ionization. Three-point calibration relative response factors using phenanthrene-d10 as the internal standard demonstrate that EI with on-column injection is the preferred configuration. Other data from wide range pesticide calibration, pesticide water sample analysis, and some semivolatile and polychlorinated dibenzo-p-dioxins and furans (PCDD/PCDF) analyses are presented and compared to traditional quadrupole analyses. Results of all of these experiments suggest that ion trap mass spectrometry is a versatile and reliable analytical approach for many Contract Laboratory Program (CLP) sample analysis requirements.

INTRODUCTION

As a result of the exceptional sensitivity and qualitative capabilities of ion trap mass spectrometry, this technique can be expected to play an ever-increasing role in regulatory analysis for many environmental sample types. The only current EPA method that we have reviewed which describes the use of ion trap technology is Method 525 (Rev 2.1, 1988) which requires calibration for many pesticides to 0.1 ng/uL (100 pg injected) for water analysis. We have examined in detail the performance of an ITS40 ion trap for analysis of CLP target pesticides, semivolatiles, and PCDD/PCDF, in several configurations including electron impact (EI), chemical ionization (CI), and splitless and on-column injection.

PESTICIDE ANALYSIS

The CLP method OLM01 for pesticides targets twenty (20) compounds, not including toxaphene or the Aroclors. The Contract Required Quantitation Limits (CRQLs) require detection of 5 or 10 picograms when 1.0 uL injections are performed (Methoxychlor CRQL is 50 pg). The method describes use of electron capture detection (ECD) with two complementary gas chromatography

columns with splitless or on-column injection. QC/QA requirements associated with calibration, GC performance, and extraction/clean-up techniques are included in the method. Several possible advantages of using mass spectrometry instead of the traditional ECD include elimination of the second confirmation GC column, more reliable target compound identification resulting from mass spectral interpretation, and potential identification of non-target compounds.

Most modern quadrupole mass spectrometers provide full scan detection of approximately 1 nanogram of most of the chlorinated CLP target pesticides. Sector instruments provide slightly better full scan detection limits. Quadrupole single ion monitoring (SIM) will provide detection to approximately 100 picograms, while sacrificing the qualitative advantage of full spectral acquisition. Again, single ion monitoring with sector mass spectrometers provide improved detection limits to approximately 1-10 picograms.

The ITS40 ion trap sensitivity specification is 10:1 signal-to-noise at m/z 284 for full scan detection and library searchable spectra acquisition of 10 picograms of hexachlorobenzene with EI/splitless injection. This specification was easily met confirming that this instrument provides approximately 100-fold improved EI full scan sensitivity over quadrupole instruments. The overall full scan sensitivity of the ITS40 for most target analytes is in the range of sector instruments operated in single ion monitoring modes. Although the ITS40 can scan over narrow mass ranges similar to quadrupole or sector SIM scan ranges, the fundamental storage and scanning functions of the ion trap do not provide the same improved detection limits with narrow SIM-like scan windows. Many improvements and developments in the fundamental scanning functions of the ion trap, including improved resolution, tandem MS/MS capabilities, and greater sensitivity can be expected to be available to the average user in the next few years.

Initial experiments to determine the best approach to low level pesticide analysis involved calibration of the ITS40 for the pesticide target compounds in four configurations at target analyte concentrations defined for ECD analysis in OLM01.0 (5-160 ng/mL). In each configuration effort was made to optimize the ion trap performance for maximum sensitivity and spectral integrity, which in the use of chemical ionization required several efforts at optimizing reagent gas pressure. Table 1 lists the average three-point relative response factors using phenanthrene-d10 as the internal standard. Mass spectral base peaks were used for all calculations. Missing values indicate that one or more of the calibration concentrations were not detected with reliable library searchable spectra. Chemical ionization spectra were compared to the Food and Drug Administration (FDA) CI mass spectral compilation, which in many cases did not fit the ITS40 spectra.

As in all of the pesticide experiments a 30 m, 0.25 mm ID, 0.25 um film DB-5ms column (J&W) was employed with helium carrier gas set at a flow velocity of 38 cm/sec. This column was found to provide the lowest bleed compared to the same dimensional DB-5 and DB-5.625 columns. On-column 1.2 uL injection was performed with a Varian SPI injector operated at 60 C (heated to 280 C after 2 minutes) without use of a guard column. The GC program was 80-280 C with a 2 minute initial hold, 8 C/minute ramp, and 10 minute final hold, allowing complete analysis through decachlorobiphenyl in approximately 34 minutes.

TABLE 1. ITS40 Three-Point Average Relative Response Factor Summary

Target Pesticides	EI Splitless	EI On-Column	Isobutane CI On-Column	Methane CI On-Column
alpha-BHC	0.287	0.337		
beta-BHC	0.235	0.287		
delta-BHC	0.227	0.283		
gamma-BHC (Lindane)	0.284	0.289		
Heptachlor		0.039		
Aldrin				
Heptachlor Epoxide	0.142	0.149		0.783
Endosulfan I				
Dieldrin				0.174
4,4'-DDE	0.359	0.337	0.328	0.042
Endrin		0.030		
Endosulfan II				
4,4'-DDD	0.421	0.336	0.564	0.290
Endosulfan Sulfate	0.068	0.100		
4,4'-DDT	0.244	0.259	0.358	0.165
Methoxychlor	0.331	0.322	0.827	0.522
Endrin Ketone	0.065	0.102		
Endrin Aldehyde		0.060		
alpha-Chlordane	0.175	0.354		0.387
gamma-Chlordane	0.176	0.312		0.433
Tetrachloro-m-xylene (Surr)	0.363	0.258		
Decachlorobiphenyl (Surr)	NA	0.406		

14 of 21 target analytes were detected in both EI splitless and EI on-column analysis. Three additional TCLs were detected with on-column EI analysis. From EI splitless to EI on-column we note 10 of 14 increasing analyte response factors with increases ranging from 1.7 to 50.6%, averaging 22.7%.

Chemical ionization with isobutane and methane was largely unsuccessful at detecting the low and mid-level calibration standards. In the best case with methane, 7 of 22 target analytes were detected at all calibration concentrations. Isobutane provided improved detection for those analytes with 3-5 chlorines but sensitivity quickly degraded with those analytes with 6 or more chlorines. Recent instrument upgrades in CI hardware and scanning functions might provide improved sensitivity.

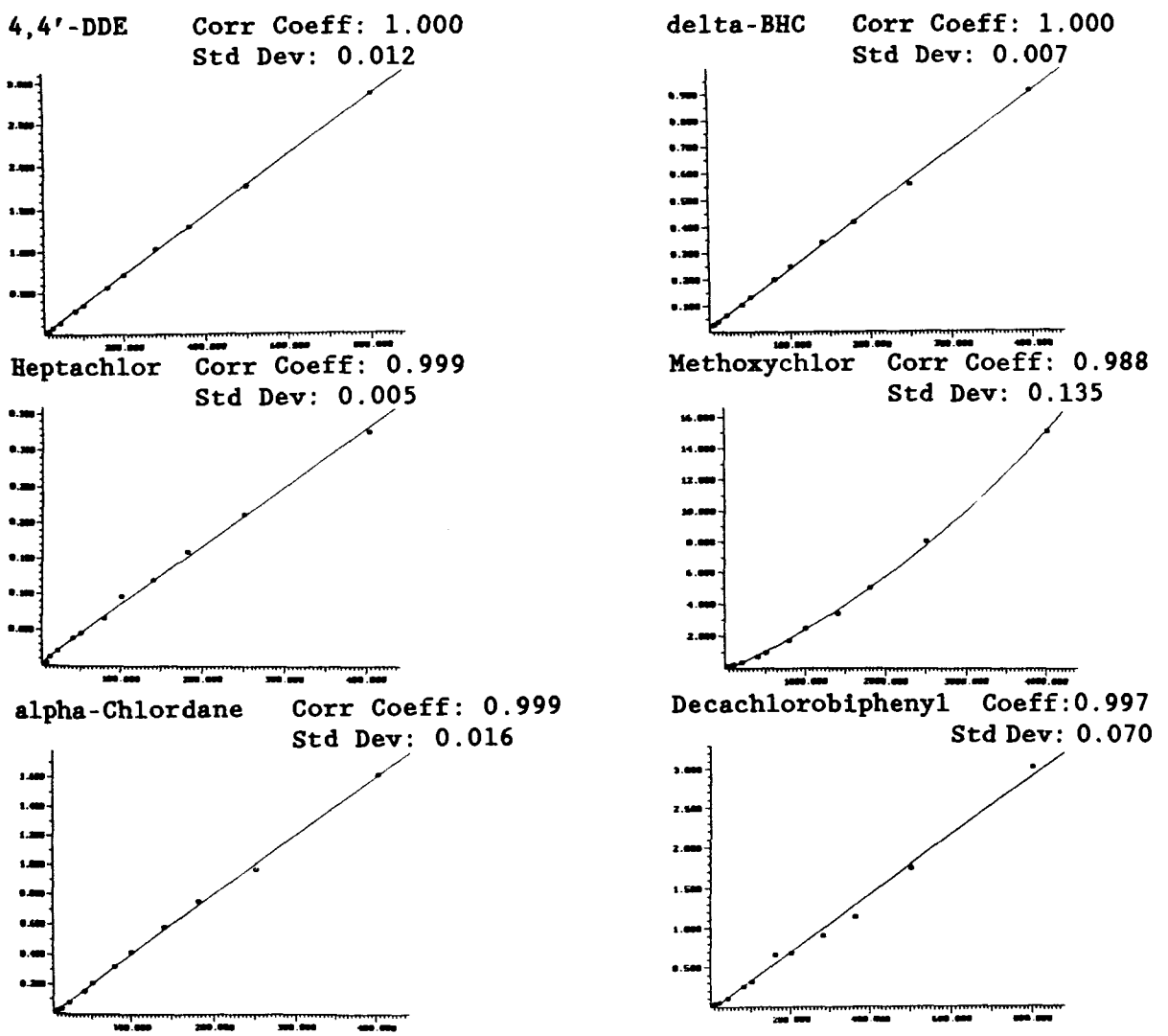
The next set of experiments involved triplicate 12-point calibrations from 0.5X to 80X CRQLs (SAS No. 7147-HQ). These CRQL factors represent from 2.5 or 5.0 to 400 or 800 picograms injected for all analytes except Methoxychlor which was analyzed from 25 to 4000 picograms, respectively. EI/on-column analysis was employed for these analyses with ion trap AGC (Automatic Gain Control) values at 10000, 18000, and 26100, respectively. Table 2 lists the average minimum detection limit calculated from the three lowest detectable concentrations for each compound. Figure 1 illustrates the exceptional linearity for five characteristic analytes. Except for those seven analytes discussed in the following paragraph the correlation

coefficient for all three 12-point calibrations was greater than 0.9. Three compounds, 4,4'-DDD, 4,4'-DDE, and Methoxychlor (*), were detected in all three low level calibration concentrations suggesting that a lower detection limit is possible.

TABLE 2. ITS40 EI/ON-COLUMN ESTIMATED DETECTION LIMITS (picograms on-column)

alpha-BHC	5	Endosulfan II	43
beta-BHC	5	4,4'-DDD	5 *
delta-BHC	5	Endosulfan Sulfate	18
gamma-BHC (Lindane)	5	4,4-DDT	10
Heptachlor	16	Methoxychlor	25 *
Aldrin	10	Endrin Ketone	22
Heptachlor Epoxide	15	Endrin Aldehyde	72
Endosulfan I	37	alpha-Chlordane	8.3
Dieldrin	15	gamma-Chlordane	15
4,4'-DDE	5 *	Tetrachloro-m-xylene (Surr)	5.8
Endrin	93	Decachlorobiphenyl (Surr)	6.7

FIGURE 1. ITS40 12-POINT PESTICIDE CALIBRATION CURVES (0.5X to 80X CLP-ECD CRQLs)



Seven target analytes were not reliably detected at the low concentrations in any of the three calibrations. These included Endosulfan I, Endosulfan II, Dieldrin, Aldrin, Endrin, Endrin aldehyde, and Endrin ketone. These data suggest that although the CRQLs for ECD analysis cannot be met for seven target compounds, the other thirteen compounds can be quantified beyond the range of the OLM01.0 electron capture method.

The final set of pesticide experiments, to date, involved extraction and analysis of two water performance evaluation samples (PES) routinely used in the CLP. These PES have been analyzed in multi-laboratory evaluations to establish advisory intervals for the OLM01.0 pesticide ECD method. The results of these ITS40 analyses and the advisory limits for the ECD method are presented in the following Table 3, using a single pesticide 16X standard and phenanthrene-d10 as the internal standard for the ITS40 quantitation. With two exceptions, Endosulfan I and Endrin, the ITS40 results are within the ECD intervals.

TABLE 3. ITS40 PESTICIDE PERFORMANCE EVALUATION RESULTS
Units: ug/L

PES #1

Target Analytes	ITS40 Result	99% Confidence Interval
alpha-BHC	0.18	0.11 - 0.25
beta-BHC	0.23	0.10 - 0.24
gamma-BHC	0.20	0.11 - 0.25
Heptachlor	0.33	0.087 - 0.44
Aldrin	0.14	0.063 - 0.22
Heptachlor Epoxide	0.29	0.14 - 0.54

PES #2

Target Analytes	ITS40 Result	99% Confidence Interval
alpha-BHC	0.19	0.11 - 0.25
beta-BHC	0.17	0.10 - 0.24
gamma-BHC	0.19	0.11 - 0.25
Heptachlor	0.39	0.087 - 0.44
Aldrin	0.14	0.063 - 0.22
Heptachlor Epoxide	0.28	0.14 - 0.54
Endosulfan I	0.44 *	0.45 - 0.92
Endosulfan Sulfate	0.61	0.56 - 1.3
Endosulfan II	0.96	0.46 - 1.3
4,4'-DDT	1.2	0.46 - 1.4
Endrin	nd *	0.38 - 1.0

* indicates that the ITS40 result is out of the CLP advisory action window for ECD analysis.

SEMIVOLATILE ANALYSES

The CLP semivolatile quarterly blind QB292 was analyzed with the ITS40 with 1:10 dilution of standards and extracts using EI/splitless injection. The results of this analysis, and the accompanying results of quadrupole analysis and EPA performance windows, are presented in Table 4. The ITS40 quantitation is based on a 5 ug/L standard. Owing to the nearly saturated detection of many analytes in the 16 ug/mL standard, in future semivolatile analyses we may dilute the standards and extracts 1:20, depending on trap performance. The most significant difference in the ITS40 semivolatile analyses is the characteristic ion trap DFTPP spectra which with default scanning parameters usually results in a base peak at m/z 442. All of the spectra of the target analytes with these tune conditions result in NIST matchable spectra and the ITS40 quantitation is well within the windows established by pooled quadrupole analyses.

TABLE 4. QB292 SEMIVOLATILE RESULTS AND WINDOWS (Units: ug/L)

Target Analytes	ITS40 Results	INCOS 50B Results	QB Warning Windows
Phenol	45	46	34 - 56
Hexachloroethane	28	26	22 - 43
2,4-Dimethylphenol	37	32	22 - 50
bis)2-Chloroethoxy)methane	17	17	15 - 23
1,2,4-Trichlorobenzene	27	24	22 - 37
Hexachlorocyclopentadiene	49	43	24 - 63
2,4,6-Trichlorophenol	43	28	27 - 43
Pyrene	93	126	80 - 140
Anthracene	3 (J)	4 (J)	NU

PCDD/PCDF ANALYSES

The ITS40 was also calibrated and used for PCDD/PCDF analysis of a severely contaminated soil sample using EI/splitless techniques. This analysis was conducted with full scan acquisition at the calibration concentrations defined in DFLM01.1 (Sept 1991) for quadrupole MID analysis (0.1 - 2.0 ng/uL for 2378-TCDD). The ITS40 full scan results and INCOS 50B MID results are presented in the following Table 5. The advantages realized in these ITS40 analyses include NIST library spectral identification for native PCDD/PCDF which elute without 13C-labelled internal/recovery standards, elimination of MID windows used in quadrupole analysis, and identification of non-target compounds with appropriate sample clean-up. In this case the extract was analyzed before and after carbon-column clean-up resulting in unambiguous identification and estimated quantitation of 37 PCB isomers in the pre-carbon clean-up extract.

The 30m DB-5ms column was found to provide reasonable isomer resolution. The INCOS 50B analysis was also performed with a 30 m column (DB-5.625) of the same dimensions. With the program conditions employed in the ITS40 analyses, (180-280 C at 15 C/min), the total time for analysis through OCDF was less than 32 minutes.

TABLE 5. ITS40 AND QUADRUPOLE PCDD/PCDF ANALYSES, Units: ug/Kg (ppb)

PCDD/PCDF		ITS40 Full Scan Results		INCOS 50 MID	
	(# of Isomers)	(1*)	(2*)	(2*)	RPD in 2*
2378-TCDD		ND	(0.3)	(0.1)	(67%)
Total TCDD	(7)	31	40	34	15%
2378-TCDF		29	39	35	10%
Total TCDF	(12)	120	140	130	7.1%
12378-PeCDD		ND	1.0	(0.9)	(10%)
Total PeCDD	(8)	21	26	22	15%
12378-PeCDF		12	14	12	14%
23478-PeCDF		8.0	9.0	7.5	41%
Total PeCDF	(13)	96	120	90	25%
123478-HxCDD		1.4	2.6	4.4	-69%
123678-HxCDD		3.5	4.2	2.9	31%
123789-HxCDD		2.5	2.8	3.1	-11%
Total HxCDD	(6)	60	74	70	5.4%
123478-HxCDF		27	110	140	-27%
123678-HxCDF		14	37	37	0
234678-HxCDF		13	28	29	-3.6%
123789-HxCDF		7.1	14	19	-36%
Total HxCDF	(13)	120	400	390	2.5%
1234678-HpCDD		11	9.3	7.6	18%
Total HpCDD	(2)	24	17	17	0
1234678-HpCDF		73	54	55	-1.9%
1234789-HpCDF		15	18	20	-11%
Total HpCDF	(4)	120	110	110	0
OCDD		35	30	29	3.3%
OCDF		79	60	65	-8.3%

(1*) - GC/MS analysis performed after silica and alumina column clean-up, before carbon column.
(2*) - GC/MS analysis performed after complete CLP extract clean-up, including carbon column.

Values in parentheses indicate quantitation below CRQL.
RPD = ((ITS40 2* Conc) - (INCOS 50 2* Conc) / ITS40 2* Conc) * 100

TABLE 5 CONTINUED. ITS40 IDENTIFICATIONS IN PCDD/PCDF ANALYSES

Polychlorinated Biphenyls, Estimated Concentrations, Units: ug/kg (ppb)

	ITS40 Results			Aroclor Chlorination Levels		
				% of Total Composition Hutzinger, 1974		
	# Isomers	Est Conc.	%Total	1248	1254	1260
Dichlorobiphenyls	0	nd	0	2	0.5	nd
Trichlorobiphenyls	6	47	4%	18	1	nd
Tetrachlorobiphenyls	9	220	17%	40	21	1
Pentachlorobiphenyls	10	680	53%	36	48	12
Hexachlorobiphenyls	6	260	21%	4	23	38
Heptachlorobiphenyls	4	50	4%	nd	6	41
Octachlorobiphenyls	2	6	<1%	nd	nd	8
Nonachlorobiphenyls	0	nd	0	nd	nd	nd
TOTAL PCBs		1263				

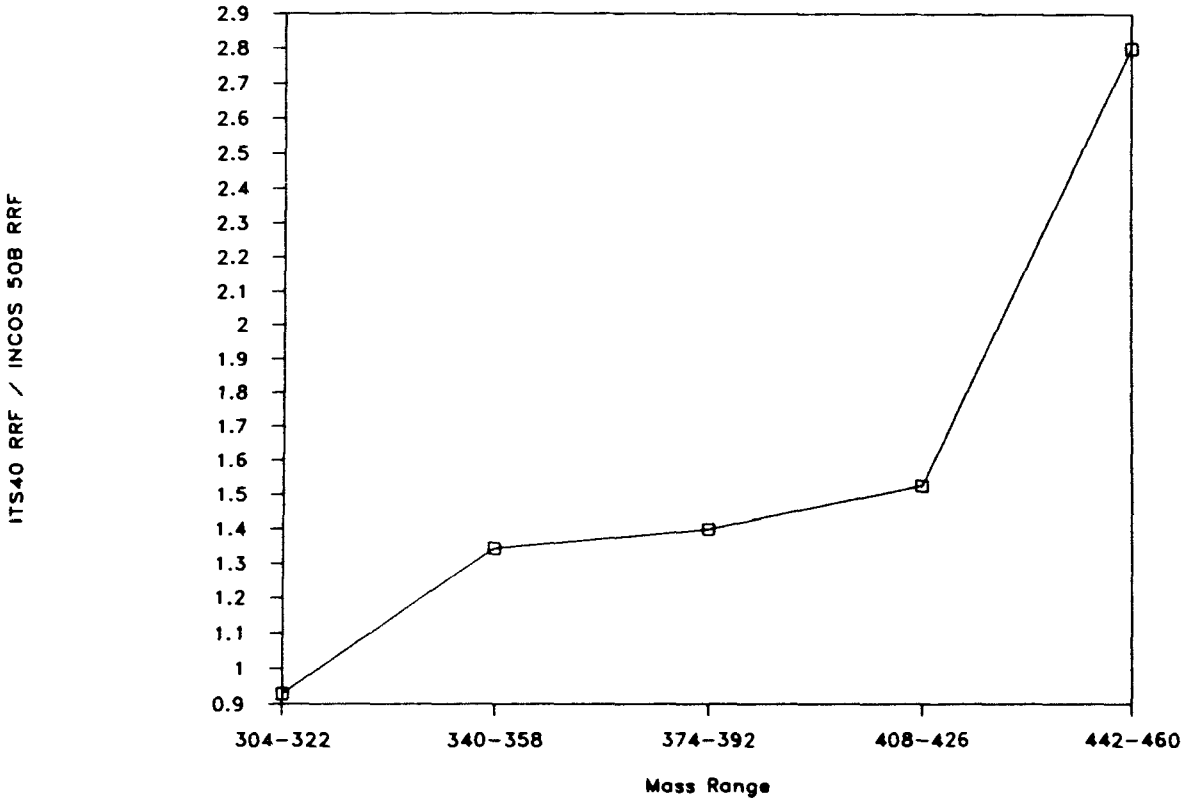
Other Identification, Estimated Concentration, Units: ug/kg (ppb),

Anthracene or Phenanthrene	530

PCB and PAH estimated concentrations are all based on 50 ng of 1234-TCDD-13C used as the internal standard. Unlike the CLP TIC approach, characteristic ions were used for quantitation (e.g. pentachlorobiphenyls m/z 326) with assumed RRFs = 1.0. PCB and anthracene identifications are based on NIST library fit values all >940. The chlorination levels described for the Aroclors were taken from Hutzinger, et.al., 1974, confirmed in our laboratory by analysis of Aroclor standards using the INCOS 50 instrument. Based on these relative chlorination amounts the PCBs found in this soil sample are most likely Aroclor 1254.

The PCDD/PCDF RRFs obtained from the ITS40 calibration were significantly higher than the RRFs from the quadrupole analysis, as illustrated in Figure 2. These differences are a result of the high mass sensitivity of the ITS40 as seen in the semivolatile DFTPP spectra under default scanning parameters. For PCDD/PCDF analysis this high mass sensitivity is a significant advantage over quadrupole analysis.

FIGURE 2. ITS40 PCDD/PCDF RRFs vs QUADRUPOLE RRFs



CONCLUSIONS

The ITS40 ion trap has proven to be a reliable and versatile instrument for pesticide, semivolatile, and PCDD/PCDF analyses, largely due to the approximately 100-fold increase in sensitivity over quadrupole full-scan capabilities. Concern over interferences, which was know to severely degrade the performance of previous trap designs and is a significant issue for the CLP and RCRA programs, appears largely eliminated by current axial modulation designs. Continuing experiments with our instrument will include new approaches to chemical ionization for pesticide analysis which have gained favor in other regulatory environments.

ACKNOWLEDGEMENTS

This work was entirely supported by the CLP National Program Office under Contract Number 68D90041. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Although the research described in this article has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. We wish to thank Finnigan MAT for their continuing invaluable assistance with ITS40 operation, and J&W Scientific for early use of the low-bleed DB-5ms column.

50

EXTENDING THE DETECTION LIMITS OF QUADRUPOLE GC/MS SYSTEMS IN ENVIRONMENTAL ANALYSIS: COMMON PROBLEMS AND NOVEL SOLUTIONS

LINDA C. DOHERTY, Applications Chemist, Scientific Instruments Division, Hewlett-Packard Company, 1601 California Avenue, Palo Alto, California 94304

ABSTRACT

As Environmental Science enters the 1990s, more demands are being placed on existing GC/MS hardware to meet lower detection levels. In order for environmental laboratories to stay competitive, they must apply new advances in technology to routine analyses. Techniques that increase the sensitivity of existing GC/MS systems are discussed. Also, specifications for new generation GC/MS systems are explored.

Among the novel applications that improve the sensitivity of existing GC/MS systems, the ones presented are new GC injection techniques, various MS ionization techniques and alternative GC inlets. Many of these approaches are relatively low cost solutions and can be implemented simply. An example of a new injection technique is electronic pressure controlled large volume injections. Electronic control gives the chemist the ability to program the pressure of the injection port to do high flow injections (burst) followed by constant, low analytical flows. Programming column flow reduces run time, improves resolution and increases retention time reproducibility. GC/MS semi-volatile data acquired with electronic pressure control are shown.

Even with the improvement of existing systems, the need for high sensitivity may necessitate the purchase of a new GC/MS instrument. This has made it critical for instrument companies to develop even more sensitive GC/MS systems. Insights about the key elements of a GC/MS that affect its sensitivity- the GC inlet, MS ion source and detector- are outlined.

Finally, the common problems associated with ultra-trace organic analysis are reviewed. These are the problems that eventually will limit "how low we can go" because they affect the quality of data that is obtained.

INTRODUCTION

Recent developments with the United States Environmental Protection Agency (USEPA) have led to the formation of the Environmental Monitoring Management Council (EMMC) [1]. This council's objectives are to simplify and consolidate methods that exist in the various branches of the EPA. The consolidation of methods will:

- Simplify quality assurance/quality control differences that exist between methods for similar analytes. This will make the analyst job easier, with less confusion.

- eliminate outdated, duplicate methods

- have a permanent structure in place to eliminate duplication of efforts between various branches

By combining methods the three most prominent outcomes are:

- More Analytes

- Lower Detection Limits

- Single Method Independent of Sample Matrix

The result of these outcomes will greatly impact the instrument companies and their customers. Instrument companies will need to improve system (GC/MS) performance with greater dynamic range, faster data review capabilities, and better quantitation software. Also, customers will be impacted. Consolidated methods mean more analytes per method. According to Hites and Budde [2], the technical difficulty of a method increases as the number of analytes does. This means higher technical expertise will be needed at a time when we are observing the opposite. More analytes per method, also means longer analysis times for good chromatographic resolution, which will lead to a decrease in billable samples per shift.

Lower detection limits will require a reduction in contamination and this may mean clean rooms and stringent standard operating procedures. All and all these changes will initially increase expenses. However, the final result should be monetarily favorable to laboratories because QA "re-runs", (samples that have to be analyzed twice because of QA error), should be drastically reduced.

Although it may be sometime before the consolidation of methods is finalized, it is still important for laboratories to stay competitive. This is especially true with the ever increasing importance of sensitivity in analytical measurements. Environmental engineering firms are asking for lower detection limits now. There are two ways to improve GC/MS system performance to meet the needs of the engineers. One is to optimize the existing laboratory GC/MS with new components. These improvements are typically less than $40,000. The second way is to buy a new GC/MS system. This will definitely cost more than $40,000. This paper addresses the optimization of an existing system.

EXPERIMENTS, RESULTS AND DISCUSSION

Figure 1 shows the six areas that will be discussed.

OPTIMIZING THE EXISTING GC/MS

IN THE LABORATORY

GC	MS
• COLUMN TECHNOLOGY	• HIGH ENERGY DETECTORS
• INJECTION TECHNIQUE	• SPECIALIZED MOLECULAR SEPARATORS
• INJECTION SIZE	• IONIZATION TECHNIQUES, SIM

Figure 1. Six areas where newer technology can be applied to existing GC/MS systems.

Column Technology

Today capillary columns are used widely by the environmental sector. Semi-volatiles are normally analyzed with a 0.25 mm ID, 30 meter 5%-phenyl 95%-methyl silicone column. Column manufacturers have come to the aid of chromatographers by introducing this stationary phase with lower bleed. These columns have a significant impact on the chemical noise in a system by reducing column bleed. The signal-to-noise (S/N) ratio is greatly improved, even at high temperature (320° C).

Volatiles have been conventionally separated with packed columns. With the advent of specially designed phases for volatile analysis, 0.53 mm ID (Megabore™) columns being used routinely. The bonded 0.53 mm ID columns greatly improve sensitivity over packed columns. The benefit of the shorter, 30 meter columns is run time, but cryogen (CO_2 or N_2) is required to retain the light gases. Longer columns (75 m and 105 m) are available and have the advantage of not needing cryogen. For GC/MS purposes, a 75 m column is the best choice. This length affords the resolution necessary for the 3-D GC/MS data and only increases the run time by ~4 minutes. Without cryogen, operating costs are significantly reduced.

Injection Technique

The injection technique will be addressed for semi-volatiles only. Since the purge and trap is such an important part of sensitivity in volatile analysis, and is not a part of the GC/MS system, it will be excluded.

The two most common techniques for semi-volatile analysis are splitless and on-column injection. Two areas where splitless injections can be improved are: electronic pressure control (EPC) of the splitless inlet and proper splitless liner choice. On-column injections are the best way to completely transfer sample to the column, but until recently automation and the need for retention gaps have made this technique less than desirable. Now automated injectors for 0.25 and 0.32 mm ID columns are commercially available. Even dirty samples can be run routinely, if a pre-column is used.

Why are splitless injections so hard to optimize? Figure 2 shows eight reasons why! All of these parameters will affect the sensitivity, thermal discrimination and thermal degradation of a sample.

SPLITLESS PARAMETERS

(Why splitless injections are so hard to optimize.)

Inlet Temperature	**Sample Volume**
Liner Design	**Solvent**
Splitless Valve Time	**Injection Speed**
Column Flow	**Sample Volatility**

Figure 2. Various splitless parameters that must be considered.

The proper inlet temperature is needed to volatilize high boiling point compounds without thermally degrading other compounds. Normally, the inlet temperature is a compromise between these two factors. Compounds that can be used to set the highest usable inlet temperature are endrin and benzo[g,h,i]perylene. Endrin's breakdown to endrin aldehyde increases with

increasing inlet temperature and benzo[g,h,i]perylene response decreases with decreasing inlet temperature.

Liner design is one of the most difficult choices simply because of the variety of liners available. The features that are most important are the volume of the liner, whether it is deactivated or not and whether or not to use glass wool. For the highest sensitivity possible, a 4 mm single tapered, deactivated liner with no glass wool is recommended. For large volume injections >2 µl, glass wool is necessary. For dirty samples, glass wool helps to keep the non-volatiles from getting to the column, but too much glass wool can greatly decrease sensitivity and increase adsorption of polar compounds.

Splitless valve time is critical. The time has to be long enough to assure that all of the injected sample reaches the column. A textbook splitless injection has the liner volume swept at least two times. A 4 mm liner has an approximate volume of 1 ml. With a GC/MS flowrate of 1 ml/min, a two minute splitless injection would be necessary. This long splitless time is not common because the initial linear velocity of the carrier gas is usually much high than optimum. This is due to the design of the conventional splitless inlets that are pressure regulated (constant pressure, regardless of oven temperature) and not flow regulated (changing pressure with oven temperature). So, a higher than optimal flow is set initially so that the flow does not go to zero at high temperature. In contrast, electronic pressure control (EPC) of the splitless inlet allows for high pressure initially, followed by more typical GC/MS flowrates that are held constant as the oven temperature increases because the pressure is programmed.

A high initial column head pressure during the injection is also favorable for increased sample volumes. As the injected volume is increased, the required expansion volume for the solvent greatly increases. With higher pressures the volume is reduced ($P_1V_1 = P_2V_2$) and the entire injected volume moves to the column. The higher pressure also decreases the likelihood of highly volatile compounds from escaping out the top of the injection port through the septum purge vent. Solvent choice affects expansion volume, however, methylene chloride is normally used. Finally, it has been found that fast injections tend to give the best results, universally.

The use of electronic pressure control to increase the injection volume size to 5 µl was explored. Figure 3 shows the parameters used Figure 4 is a graphical representation of those parameters. 5 µl injections of a 100 pg/µl 525 standard mix (AccuStandard) with 5 ng/µl of internal standards were run. Notice, in Figure 3, that the initial oven temperature was 90°C. Normally, to take advantage of the solvent effect, an initial oven temperature of 10-20°C below the solvent boiling point is used. The solvent in this case was acetone (BP 56°C). Thus, a typical initial oven temperature would be 45 °C.

ACQUISITION PARAMETERS

INLET:

30 PSI for 1.5 minutes
98 PSI/min to 5.4 PSI then constant flow at 30 cm/sec
PURGE VALVE ON at 1.5 minutes
INJECTION PORT 250°C

GC:

90°C for 2 minutes
35°C/min to 130°C
12°C/min to 180°C
9°C/min to 320°C; 4.35 minute hold

MS:

scan 45-450 amu, A/D = 2
start acquistion at 4 minutes
EM 500 above DFTPP tune
TRANSFER LINE 285°C

Figure 3. The GC/MS parameters used in the large volume injection experiments. An HP 5971A with an HP 5980 Series II GC was used.

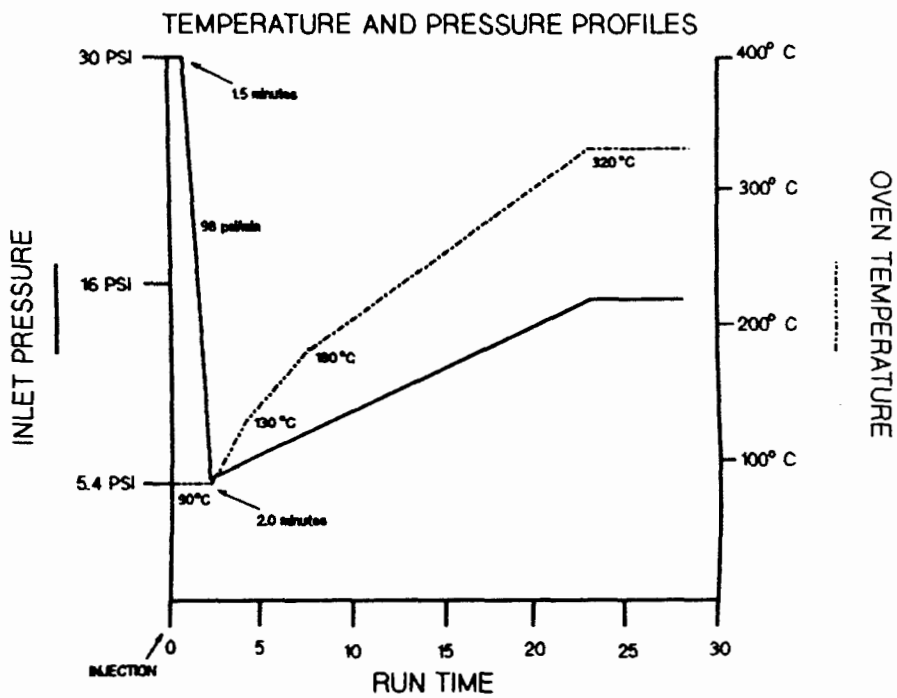


Figure 4. The pressure and temperature profiles for the EPC experiments.

Figure 5 shows what a normal constant pressure (flow decreases with oven temperature) 5 µl injection would look like at 45°C. Only 70% of the total sample is transferred, and the chromatographic peak shape is unacceptable. By raising the initial oven temperature to 90°C, the peak shape improves remarkably, but now only 80% of the sample is transferred. Finally, the optimal temperature of 80°C gave a sample transfer of 90%. These percentages were compared to 100% transfer of sample with a 30 psi initial injection port pressure and constant flow (EPC). Figure 6 shows the optimum conditions for both constant flow and constant pressure. Note that electronic pressure programming (EPP) decreased the run time and increased the resolution. This is especially apparent in the late eluting peaks.

These data show that optimizing splitless injections can improve GC/MS sensitivity with or without EPC, but EPC gives the best results. These data confirm that larger volume injections are possible with optimization. So, at the GC end, the proper choices of column, liner and pressure control can greatly improve the amount of sample that is transferred to the mass spectrometer.

Once the sample is transferred to the mass spectrometer how can the MS be optimized? There are three areas:

- Detectors
- Jet Separators
- Alternative Ionization Techniques and SIM

Detectors

Detector manufacturers are improving the continuos dynode detectors to decrease noise (shot noise, dark current, neutral noise) and improve the dynamic and liner range. Many of these detectors fit into existing mass spectrometers. High energy dynode (HED) detectors are also available. These detectors improve sensitivity as mass-to-charge ratio (m/z) of the ion increases. The rule of thumb is: divide the m/z valve by 100 and that is the improvement you will see. For example, if the ion has an m/z equal to 500, the HED would improve the sensitivity by a factor of 5. The HED works by increasing the energy of the ion as it reaches the detector. The energy is directly proportional to its mass. The heavier the ion, the slower to is. By increasing its velocity before it reaches the detector, it has a greater chance of producing secondary electrons in the multiplier and being detected.

Jet Separators

Jet separators have been around since glass columns were interfaced to mass spectrometers. The old glass jets were designed for packed column flows (30

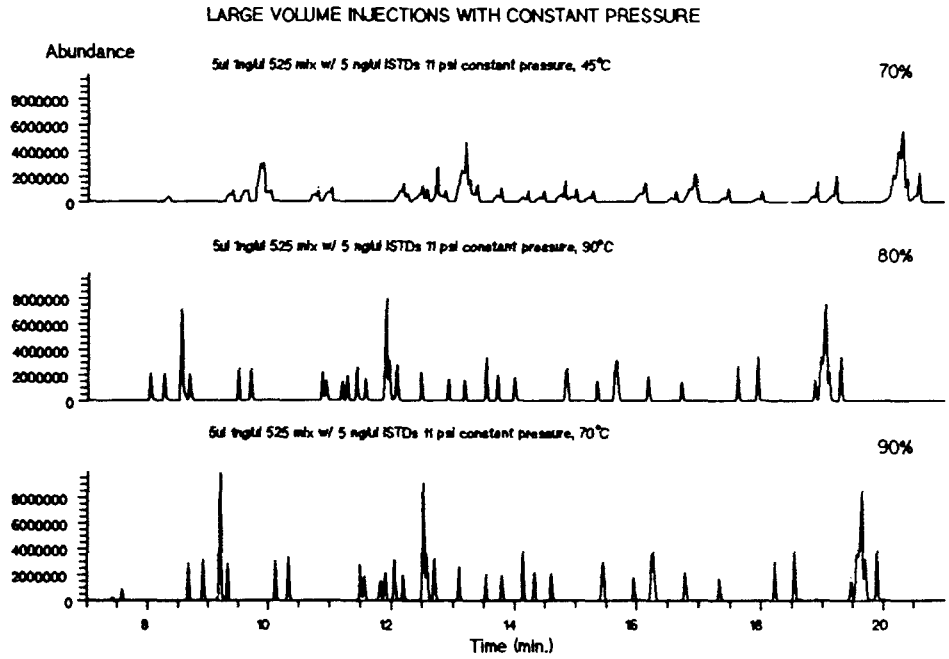


Figure 5. Total ion chromatograms of a 525 standard mix showing the importance of initial oven temperature.

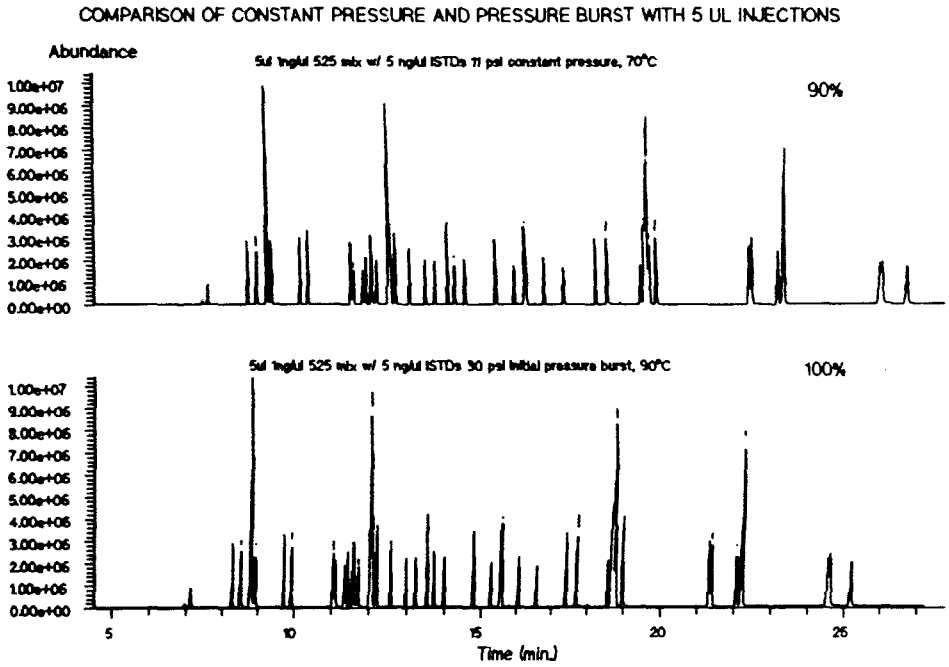


Figure 6. Two total ion chromatograms comparing constant pressure and constant flow with EPC.

ml/min). As the 0.53 mm ID columns became more widely used modifications were made to the glass jet (e.g., make-up gas) to provide 30 ml/min through the jet. This actually diluted the sample stream! Now jets have been developed for lower flows. These new jet designs increase sensitivity over the conventional glass jets.

Alternative Ionization Techniques and SIM

The third way to improve sensitivity is to change from electron impact (EI) to alternate ionization modes. Figure 7 outlines three very common chemical ionization techniques. These three techniques have been especially useful for increasing pesticide sensitivity. Positive chemical ionization (PCI) gives primarily a protonated molecular ion. This combines all of the ion current into a single mass, increasing signal. Drawbacks to PCI are that all compounds have varying proton affinity and the sensitivity is class dependent. For example chlorotriazines (simazine, atrazine) show no improvement over EI [3].

Electron capture negative ionization (ECNI) is very specific and sensitive. It only works for electrophilic compounds and is best used with selected ion monitoring (SIM) because all the useful ion current is found in the molecular ion. A drawback of ECNI is that many compounds are not electrophilic. Also, a GC electron capture detector response for a certain compound may not give an equivalent response by ECNI. By far, the biggest problem with ECNI is instrument variation. Differences in mass spectrometer design (different manufacturer, different design) greatly influence spectra produced [4]. This makes direct comparisons of results, lab to lab, impossible.

Another negative chemical ionization technique is negative ion chemical ionization (NICI). This example is chloride attachment. Once again, it may increase sensitivity but the variation of chloride adduct formed is compound dependent [3].

In all cases, no standard libraries exist and methods developed would have to be based on a certain compound class. This is contradicts the method consolidation movement. The importance of scanning does not hold here either. Since chemical ionization is a "soft ionization" technique, it produces mostly molecular weight information. SIM with CI gives the highest sensitivity. The movement toward these kinds of analyses will come with lower detection requirements. These techniques will also require more highly skilled chemists.

Although there are ways to improve the performance of existing GC/MS systems, it is important to investigate new mass spectrometers. New mass spectrometers yield improved system performance. The mass spectrometer

IONIZATION TECHNIQUES

POSITIVE CHEMICAL IONIZATION (PCI)

reduces fragmentation thus increases sensitivity

$$CH_4^{+\bullet} + CH_4 \longrightarrow CH_5^{+} + CH_3^{\bullet}$$

$$CH_5^{+} + M \longrightarrow (M+H)^{+} + CH_4$$

ELECTRON CAPTURE NEGATIVE IONIZATION (ECNI)

very sensitive, highly specific

$$e^{-} + M \longrightarrow M^{-}$$

NEGATIVE ION CHEMICAL IONIZATION (NICI)

changes selectivity, may increase sensitivity

$$Cl^{-} + M \longrightarrow (M + Cl)^{-}$$

Figure 7. Alternative chemical ionization techniques that improve sensitivity, especially for pesticides.

ULTIMATE SYSTEM LIMITATIONS

SYSTEM BACKGROUND

COLUMN, TRAP BLEED

INTEGRATION

SAMPLE ADSORPTION

MEMORY EFFECTS

LABORATORY AIR BACKGROUND

UBIQUITOUS PHTHALATES

SPE QUALITY

Figure 8. Limitations in obtaining the highest sensitivity possible.

may have a newly designed ion source that increases ionization efficiency. The detector may have lower noise, greater collection efficiency and better linear range. The data system may be faster, with better application software and more advanced GC control. A different type of mass spectrometer may be desired. An ion trap, magnetic sector (for dioxins) or triple quadrupole are common examples. Also, a new mass spectrometer may be needed if alternate ionization modes are of interest.

With all the possibilities for improving system performance and GC/MS sensitivity, there are ultimate limitations. Figure 8 lists some. System background (air leaks, pump oil) and column, trap bleed are difficult to eliminate and are the background chemical noise. Better vacuum systems, cleaner pump oils and lower bleed phases are solutions, but there is a limit to how clean a system can be. Data system integration of low level, noisy data needs to improve to speed up sample throughput. Manual integration of low level samples is tedious. Sample adsorption that may lead to sample loss (especially at low levels) and memory effects exist. Care in sample pre-screening is one way to minimize memory effects. For low level volatiles, laboratory air is a major concern and the volatiles should be kept separate from the semi-volatiles. Phthalates are everywhere [5] and extra sample preparation steps are necessary if phthalates are target analytes. Finally, as solvent waste consumption is minimized, alternative sample preparation with solid phase extraction cartridges has been encouraged. Unfortunately, SPE cartridge quality has been poor. These cartridges tend to increase contamination. Another alternative is the EMPORE™ disk from Varian Associates. These Teflon disks with the solid phase bonded greatly reduce contamination.

CONCLUSION

Many solutions are available now to improve the performance of current instrumentation. Investing time into learning how to use on-column injections, instead of splitless, is becoming more realistic with the introduction of automated injectors for 0.25 and 0.32 mm ID columns. Larger splitless injections are also possible with a small amount of method development. It is also important to keep up with current column technology to decrease the chemical noise introduced by high bleed columns.

If a new mass spectrometer is on the horizon, consider the total system performance (GC, MS and data system). Also, since good automated laboratory practices (GALPs) are becoming important, choose new systems that help provide GALP compliance.

All instruments require people to run them. Remember, there is nothing more important than proper training. Without it, all of the solutions will be difficult or impossible to implement. Chemists must be trained so they can

comfortably compete. Better training leads to better quality work. Quality is definitely the key to any lab's success in the 1990s.

REFERENCES

[1] Friedman, David: *Environmental Lab*, **4**, (1992), 20.

[2] Hites, Ronald and Budde, William: *Environmental Science and Technology*, **25**, (1991), 998.

[3] Barcelo, Damia: *Trends in Analytical Chemistry*, **10**, (1991), 323.

[4] Stemmler, Elizabeth et al.: *Analytical Chemistry*, **60**, (1988), 781.

[5] Lopez-Avila, Viorica: *Journal of the Association of Official Analytical Chemists*, **73**, (1990), 709.

51

ENVIRONMENTAL APPLICATIONS OF PARTICLE BEAM LC/MS

Daniel R. Doerge, Research Chemist, Division of Biochemical Toxicology, National Center for Toxicological Research, Division of Biochemical Toxicology, Jefferson, Arkansas 72079.

ABSTRACT. The introduction of particle beam (PB) interfaces has held great promise for LC/MS analysis because typical EI spectra can be obtained from thermally labile, nonvolatile compounds. This paper will detail the use of PB-LC/MS for the analysis of selected environmental toxicants.

Analysis of polycyclic aromatic hydrocarbons (PAH) and their metabolites in water and sediments from the Alaska oil spill was performed by PB-LC/MS using a C18 silica separator column. Spectra of PAH were essentially identical to those in the NIST library. Detection limits (LOD) were highly dependent on PAH volatility: sub-nanogram LOD were obtained for 5-ring PAH but the more volatile 3- and 4-ring PAH had higher detection limits due to losses in the particle beam momentum separator. The EI fragmentation patterns obtained from PB LC/MS were sufficient for structure elucidation of oxygenated metabolites of PAH which often lack the volatility and thermal stability required for analysis by GC/MS. These studies suggest that PB LC/MS is complementary to GC/MS for the analysis of PAH and metabolites.

Detection of pesticides in groundwater is a national priority reflected in the National Pesticide Survey (NPS). The polar nature of these compounds makes them potential groundwater contaminants and also more amenable to LC separation. A shortcoming of most LC methods is the lack of an MS confirmation step. The use of PB LC/MS to confirm and quantitate NPS analytes showed that ca. one half of the compounds could be sensitively detected (LOD ca. 0.4-20 ng). This sensitivity is sufficient, in many cases, for the confirmation of ppb levels of pesticides in ground water using conventional cleanup and concentration procedures.

Ethylenethiourea (ETU) is a goitrogenic and carcinogenic metabolite of EBDC fungicides which are used on ca. one third of all fruits and vegetables in the United States. The low volatility of ETU has hampered GC analysis and LC methods have employed electrochemical (EC) and UV detection. Analysis of ETU by PB LC/MS in several crops commonly treated with EBDC's gave LOD's (5 ppb, 1.25 ng) that were comparable to those obtained using LC/EC with the added specificity of MS confirmation. The primary quantitation method was external standard calibration but when ^{13}C-ETU was used as an internal standard, no evidence for coelution enhancement was observed.

The use of PB LC/MS as a tool to perform quantitative isotope dilution MS was investigated. Although coelution of single-labelled internal standards with varying amounts of native analytes showed large coleution enhancement, no enhancement was seen when multiply labelled (≥3) internal standards were used. This suggested that chemical effects (e.g., complex formation) did not affect particle formation and transmission efficiency. Spectral overlap and detector nonlinearity were determined to be the cause of the observed coelution enhancements. Isotope dilution PB LC/MS was used to quantitate the concentration of caffeine in coffee and atrazine in spiked groundwater. These results suggest that PB LC/MS has no inherent limitations for use in isotope dilution methods as they have been previously performed by GC/MS.

INTRODUCTION

Particle beam (PB)-LC/MS has proven useful for the analysis of many thermally labile or involatile molecules, including environmental toxicants (1), primarily because of the typical EI spectra obtained. This facilitates comparisons with reference library compendia (e.g., NIST) even though these spectra have been generated by GC or direct insertion probe interfaces. Qualitative target compound identification is possible because of the structural information revealed through fragmentation. In addition, the presence of multiple ions in the mass spectra facilitate quantitative applications. This paper describes the use of PB-LC/MS for both qualitative compound identification and quantification using potential toxicants in water, soil and foods.

EXPERIMENTAL

The VG Trio 2A mass spectrometer used in these studies was equipped with the LINC PB interface and a Perkin Elmer series 10 isocratic LC pump or a Hewlett Packard 5890 GC. A source temperature of 200°C was used for all studies except PAH analysis where 250°C was used. The gas flow through the desolvation chamber was maintained at 30°C and a Hildebrand double grid nebulizer (40 psi He head pressure). Typical operating pressures are: 5, 0.8, 3×10^{-5} mbar at the first stage momentum separator, the second stage momentum separator and the ion source housing, respectively. Positive ion spectra were obtained using EI conditions (70 eV) and full scan conditions (50-650 m/z in 1 sec). The mass spectrometer was tuned and calibrated daily with PFTBA.

POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AND METABOLITES

The use of PB-LC/MS for the analysis of PAH was investigated using a number of 3-6 ring compounds. These compounds displayed both linear and concave-upward calibration plots often seen for many analytes when using PB-LC/MS (2). This phenomenon is likely related to the linearity of detector response as discussed below. Mass spectral response sensitivity was dependent on source block temperature with a maximum in sensitivity seen at ≥250°C. This higher source temperature requirement probably reflects the need for compound volatilization when the particle beam impinges upon the heated block (3). The detection limits (LOD, S/N = 3/1) for a series of PAH were determined for five 3-5 ring PAH using flow injection analysis (FIA). LOD decreased with ring number and correlated inversely with PAH volatility as measured by boiling point. Figure 1 shows that subnanogram detection limits were obtained for the 5-ring PAH's but that LOD increased rapidly with increasing volatility to 25 ng for anthracene (3-rings). LOD for more volatile PAH were in the μg range. This relationship probably reflects the losses of volatile compounds in transmission through the momentum separators in the PB interface. These data suggest that PB/LC/MS can be an important adjunct

to GC/MS analysis of PAH, especially the higher molecular weight congeners. The low volatility of high molecular weight compounds that could complicate GC analysis can enhance the analytical sensitivity of PB-LC/MS methods.

PB-LC/MS was also used in the qualitative identification of oxygenated metabolites of PAH based on fragmentation-derived structural information. Figure 2 shows the mass spectrum of dibenzanthracene-7,14-quinone. Fragmentation was characterized by sequential loss of 28 daltons (-CO) from the molecular ion (308 m/z). This pattern was also observed for quinone metabolites of benzanthracene and benzo[a]pyrene. The fragmentation of 7-hydroxyB[a]P showed a prominent $[M-29]^+$ peak (-CHO). In addition, the relative intensities for the various 28 mass unit losses were distinct for regioisomers of benzanthracene. These data suggest that PB-LC/MS could be valuable in the identification of unknown PAH metabolites. An important aspect of these findings is that diagnostic mass spectra are obtained from underivatized samples that are often not amenable to analysis by GC/MS (4).

PB-LC/MS was used to identify and quantitate PAH and potential oxygenated metabolites in water and soil samples obtained in Prince William Sound, Alaska following the Exxon Valdez oil spill. The combination of on-line UV (255 nm) and MS detection was used to correlate UV-absorbing peaks with mass spectra of PAH. The spectra of PAH consisted of a prominent molecular ion and were matched with NIST library spectra. Table I shows the values obtained from oiled and non-oiled regions. More PAH were found in samples from the oiled region (both soil and water) but the water sample from a non-oiled region also showed PAH. No identifiable metabolites from these PAH were found in these samples.

PESTICIDES IN GROUNDWATER

It is the polar nature of some pesticides that makes them potential groundwater contaminants. This property also can make LC separations more practical that GC. However, a limitation on the use of multiresidue LC methods is the lack of LC/MS confirmation procedures (5).

The use of PB-LC/MS as a qualitative confirmation tool and as a sensitive and selective detection system was investigated using ca. 100 analytes from the U.S. EPA National Pesticide Survey (NPS) of pesticides in groundwater (6). The fragmentation produced under EI conditions was sufficient for matching with NIST library spectra in many cases. However, in some cases the spectra differed from the library entries but had interpretable differences. Some of the compounds were not included in the library. In all cases, user defined libraries of target compounds could be compiled for use in identification of unknowns. The existence of intense and characteristic ions in the spectra facilitated the

use of PB-LC/MS as a sensitive and selective detection method for analysis of pesticides in groundwater. This technique was able to detect ca. one half of the NPS analytes at 0.5-25 ng per injection (7). Pesticide classes giving the best response were the triazines, phenylureas, carbamates/carbamoyloximes and organophosphates. Over the range of volatilities encountered in selected NPS analytes, no association between detection limit and volatility was observed. The techniques described were used to confirm the presence of diuron and atrazine in Hawaiian groundwater samples at ca. 1 ppb.

QUANTITATION USING ISOTOPICALLY LABELED INTERNAL STANDARDS

Environmental decomposition of ethylene-bis-dithiocarbamates fungicides (EBDC's) leads to the presence of trace levels of ethylenethiourea (ETU) in many food crops (8). ETU causes thyroid enlargement (goiter) and thyroid cancer when given to rodents in large doses (8). The low volatility has made LC separations preferable and the required sensitivity has made electrochemical detection most popular (9). While these methods possess the required sensitivity, they cannot provide the selectivity and specificity of MS detection.

LC was used to separate ETU from crop matrices when fortified into several fruit crops at 10-20 ppb (2.5-5 ng injected) and the LOD was 5 ppb (1.25 ng) (10). The MS response was linear from 0-10 ng ETU and the method of standard addition was used to quantitate ETU residues in commercial papaya samples. Because of the interday and intraday fluctuations in MS responses, the use of ^{13}C-ETU as an internal standard (IS) was investigated. Under these conditions, no enhancement of IS signal (10 ng) upon coelution with native analyte (10 ng) was observed. This was in contrast to previous reports where such effects were observed (1,11). These workers concluded that enhancement of transmission of IS occurred in the presence of increasing amounts of native analyte because of complex formation leading to larger particle sizes.

The origin of the coelution effect was investigated with pairs of singly labeled IS/native compounds (12). As previously described, significant enhancement of the IS signal was observed upon coelution with increasing amounts of native analyte (see Figure 3). These experiments were conducted as an isotope dilution experiment i.e., addition of a constant amount of IS to varying amounts of native analyte. In these experiments no "self-CI" effects were observed over the concentration range used. Other experimental parameters (e.g., temperature of desolvation chamber, mobile phase composition, nebulizer type) affected the magnitude of the coelution enhancement. However, when the data were plotted in the form of an isotope dilution experiment (i.e. ^{12}C/^{13}C response ratio vs. ^{12}C/^{13}C concentration ratio), identical plots were obtained. This sugested that an experimental artifact equally affecting native and IS signals was involved. This was tested using GC/MS since no coelution enhancement has been reported for a capillary interface.

Figure 4 shows that for identical concentration ratios, large coelution enhancement occurs with the PB Interface but none are observed for the GC. However, the isotope dilution plots are identical. This confirmed that transmission effects through an interface were not involved. Moreover, these results suggest that there are no limitations on the use of PB-LC/MS for isotope dilutions as they have been previously performed by GC/MS.

These hypotheses were further tested using $^{13}C_1$- and $^{13}C_3$-labeled IS compounds to determine the effect of spectral overlap on the coelution phenomenon. Figure 5 shows that under conditions where large enhancement of the $^{13}C_1$ signal occurs, no effect on $^{13}C_3$ signal occurred. This suggested that spectral overlap of native and IS signals was required to observe the coelution effect and that detector nonlinearity was the cause. This was confirmed by repeating the GC/MS experiment with a high split ratio in order to reduce total signal output to the levels encountered in the PB experiment. Under these conditions, large coelution effects were observed. These results show that detector nonlinearity and spectral overlap are the cause of coelution enhancement under the conditions of these experiments.

Isotope dilution MS analysis of caffeine (IS = $^{13}C_1$-IS, Table II) in coffee and atrazine in fortified groundwater (d_5-IS, Figure 6) was performed. The precision and accuracy of these studies indicate that PB-LC/MS can be an important procedure for the quantitative analysis of thermally labile or nonvolatile compounds.

REFERENCES

1. Behymer, T.D., Bellar, T.A. and Budde, W.L. *Anal. Chem.* 62, 1686-1690 (1990).

2. Kim, I.S., Sassinos, F.I., Stephens, R.D., Wang, J. and Brown, M.A. *Anal. Chem.* 63, 819-823 (1991).

3. Jones, G.G., Pauls, R.E. and Browner, R.C. *ibid* 63, 460-463 (1991).

4. Jacob, J., Karcher, W., Grimmer, G., Schmoldt, A. and Hamann, M. in **Polynuclear Aromatic Hydrocarbons** (M. Cooke and A.J. Dennis, Eds.), Battelle Press (1986), pp. 417-426.

5. Miles, C.J. *J. Chrom.* 592, 283-296 (1992).

6. U.S. Environmental Protection Agency, in **National Survey of Pesticides in Drinking Water Wells**, U.S. Government Printing Office, Washington, D.C. (1990) EPA-570/9-90-015.

7. Miles, C.J., Doerge, D.R. and Bajic, S. *Arch. Env. Contam. Toxicol.* 22, 247-251

(1992).

8. U.S. Environmental Protection Agency, *Federal Register* 52, 27172-27177 (1987).

9. Doerge, D.R. and Yee, A.B.K. *J. Chrom.* 586, 158-160 (1991).

10. Doerge, D.R. and Miles, C.J. *Anal. Chem.* 63, 1999-2001 (1991).

11. Bellar, T.A., Behymer, T.D. and Budde, W.L. *J. Am. Soc. Mass Spectrom.* 1, 92-98 (1990).

12. Doerge, D.R., Burger, M.W. and Bajic, S. *Anal. Chem.* (in press, 1992).

Table I. Quantitation of PAH in Soil and Water Samples from Alaska Oil Spill Sites.

FRACTION	ANALYTE	CONCENTRATION IN EXTRACT (LOD)
BAY-S[a], F2[b]	B[e]P	20 μg/ml (0.5 ng)
	Chrysene	2 μg/ml (5 ng)
	Triphenylene	22 g/ml (5 ng)
BAY-W, F2	B[e]P	0.3 μg/ml (0.5 ng)
	Chrysene	3 μg/ml (5 ng)
LIPS-W, F3	B[e]P	0.1 μg/ml (0.5 ng)
	B[a]P	0.2 μg/ml (0.5 ng)

[a]Samples designated BAY and LIPS were obtained in a heavily oiled waterway, and an unaffected waterway, respectively (S = soil and W = water samples).
[b]Samples were processed by sequential extraction using hexane-benzene (F2) and methylene chloride-ethyl acetate-methanol (F3). Quantitation was obtained from one point calibrations.

Table II. Analysis of Caffeine Content in Coffee.

Sample	Molecular Ion Data[a] (ng)	Fragment Ion Data (ng)
Decaffeinated + 40 ng	40.8	37.9
duplicate injection	41.0	38.3
Decaffeinated + 40 ng	40.9	36.7
duplicate injection	40.4	37.5
AVERAGE	40.8 ± 0.3	37.6 ± 0.7
LC/UV	40.4 ± 0.1	
Regular	44.7	44.2
duplicate injection	45.1	46.8
Regular	48.4	48.4
duplicate injection	46.2	43.4
AVERAGE	46.1 ± 1.7	45.7 ± 2.3
LC/UV	42.9 ± 0.6	

[a]Data were collected with the PB interface as described in Figure 4 using native and 3-$^{13}C_1$-caffeine. Peak areas for the molecular ions (194 and 195 m/z, respectively) or the major fragment ion (109, 110 m/z, respectively).

FIGURE LEGENDS

Figure 1. PAH Detection Limits Depend on Volatility.
Detection limits were determined using FIA (75% acetonitrile/water) for anthracene, pyrene, chrysene, benzo[e]pyrene, benzo[a]pyrene and dibenzanthracene in order of decreasing LOD. PAH boiling points were obtained from Lange's Handbook of Chemistry.

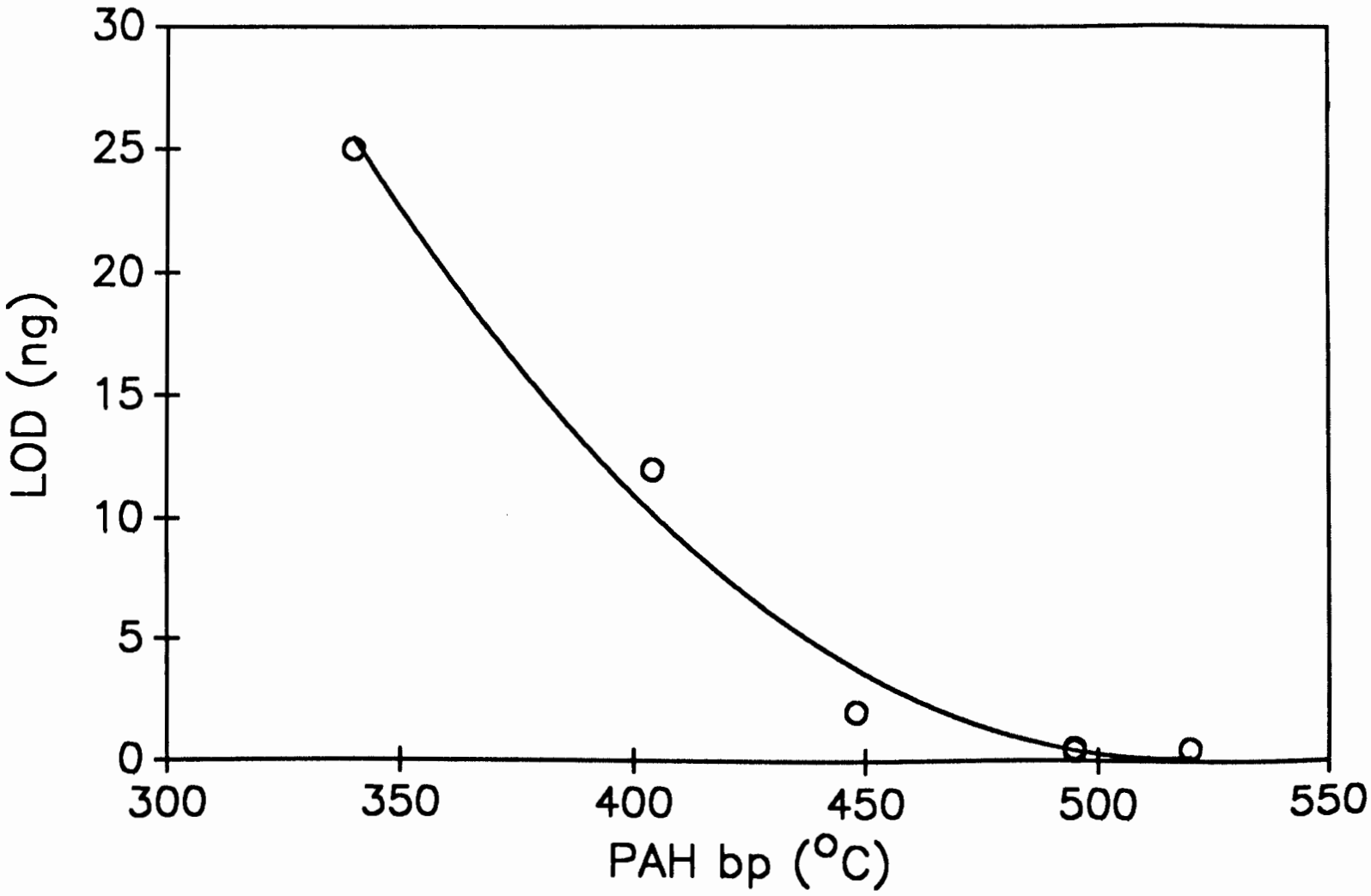
Figure 2. EI Mass Spectrum of Dibenzanthracene-7,14-quinone.
The spectrum was obtained using FIA (75% acetonitrile/water, 0.5 ml/min) of a 100 ng sample.

Figure 3. Coelution Enhancement for IS Signal by Native ETU.
The signal enhancement for 10 ng of 2-^{13}C-ETU (peak area of 103 m/z) was determined in the presence of varying amounts of coeluting native ETU using FIA (50% acetonitrile/water). Enhancement factor = ^{13}C signal *with* coelution ÷ ^{13}C signal *without* coelution.

Figure 4. Isotope Response Ratio Plots and Enhancement Factors for PB-LC/MS and GC/MS Analysis of Caffeine.
Ratios and enhancement factors were determined for coeluting 3-$^{13}C_1$ caffeine in the presence of varying amounts of native caffeine with sample introduction via PB or GC interfaces.

Figure 5. Coelution Enhancement for 3-$^{13}C_1$- and 1,3,7-$^{13}C_3$-Caffeine.
The signal enhancement was determined as described in Figure 3 using 25 ng IS using FIA (20% acetonitrile/water).

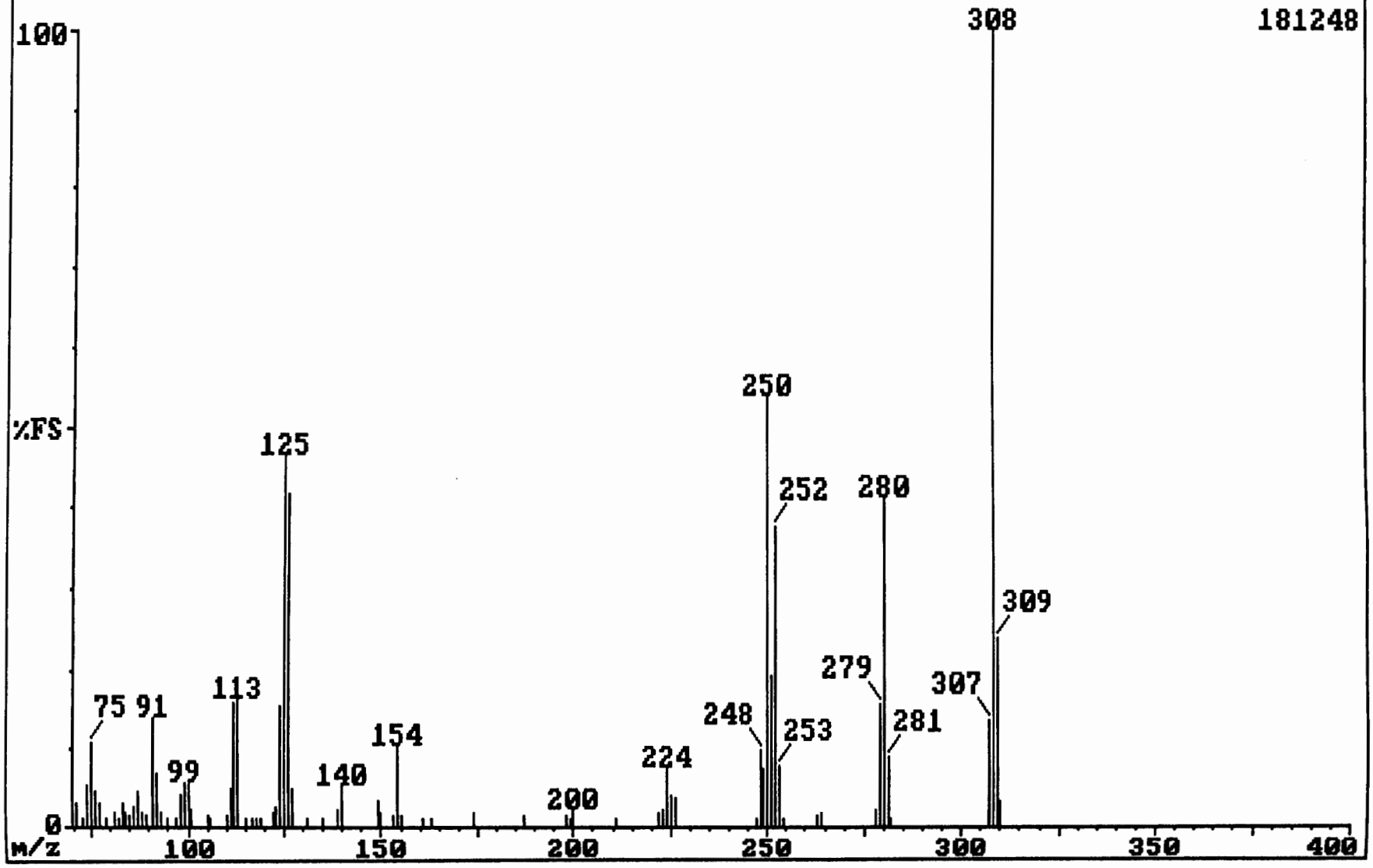
Figure 6. Isotope Dilution Calibration Plot for Analysis of Atrazine in Groundwater.
Samples were chromatographed using a Perkin Elmer 0.46 x 3 cm C18 column (3 micron particle size) with a flow rate of 0.5 ml/min and mobile phase of 75% acetonitrile/water. Response ratios were calculated using either the molecular ion or the major fragment ion for native (215, 205 m/z) and d_5 (220, 205 m/z) atrazine and plotted vs. the amount of native atrazine present with constant addition of 25 ng d_5-atrazine (correlation coefficient = 0.995). Data points shown represent averages with standard deviations shown as error bars.

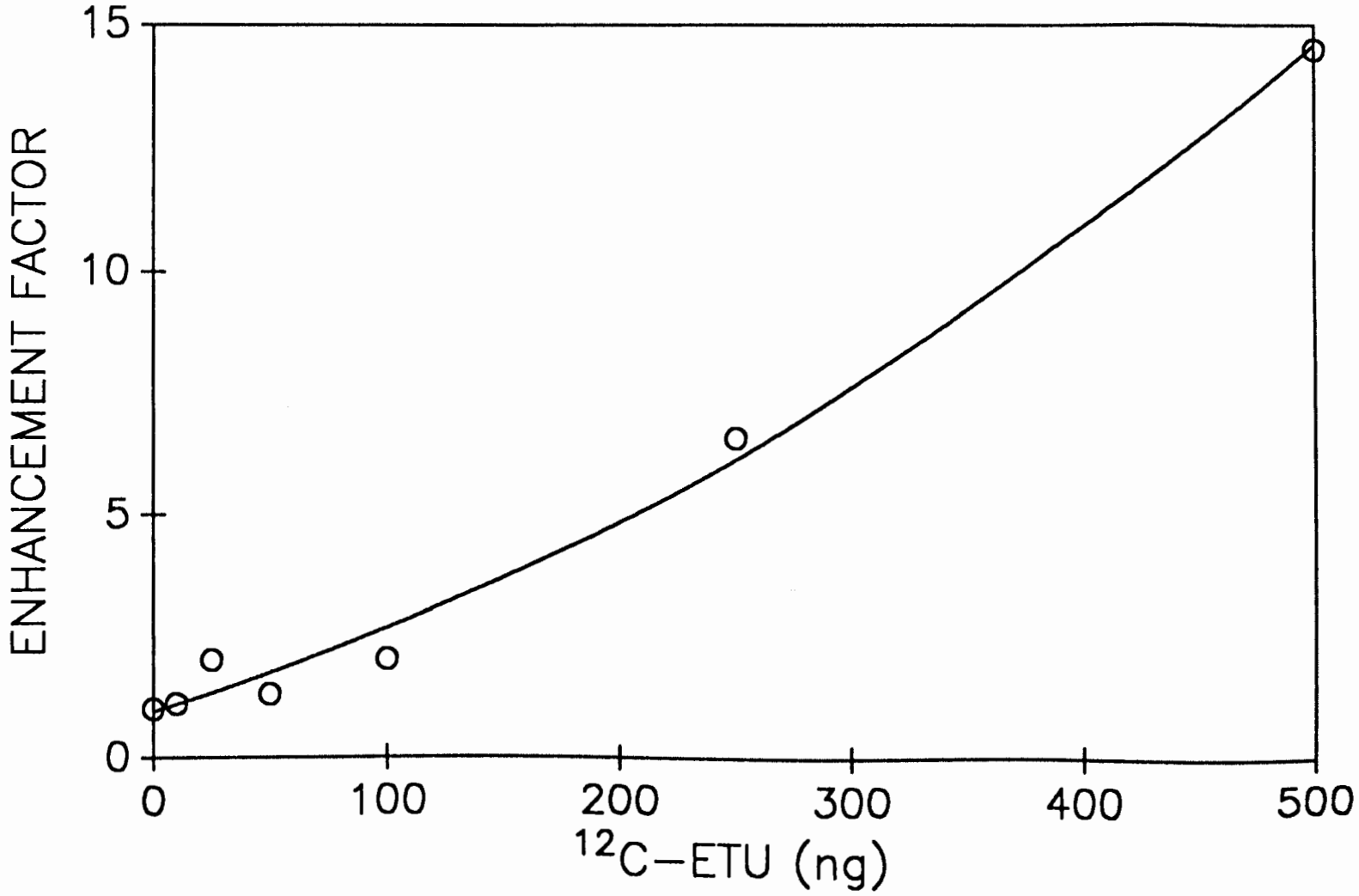

30
25
20
15
10
5
0
LOD (ng)
300
350
400
450
500
550
PAH bp (°C)

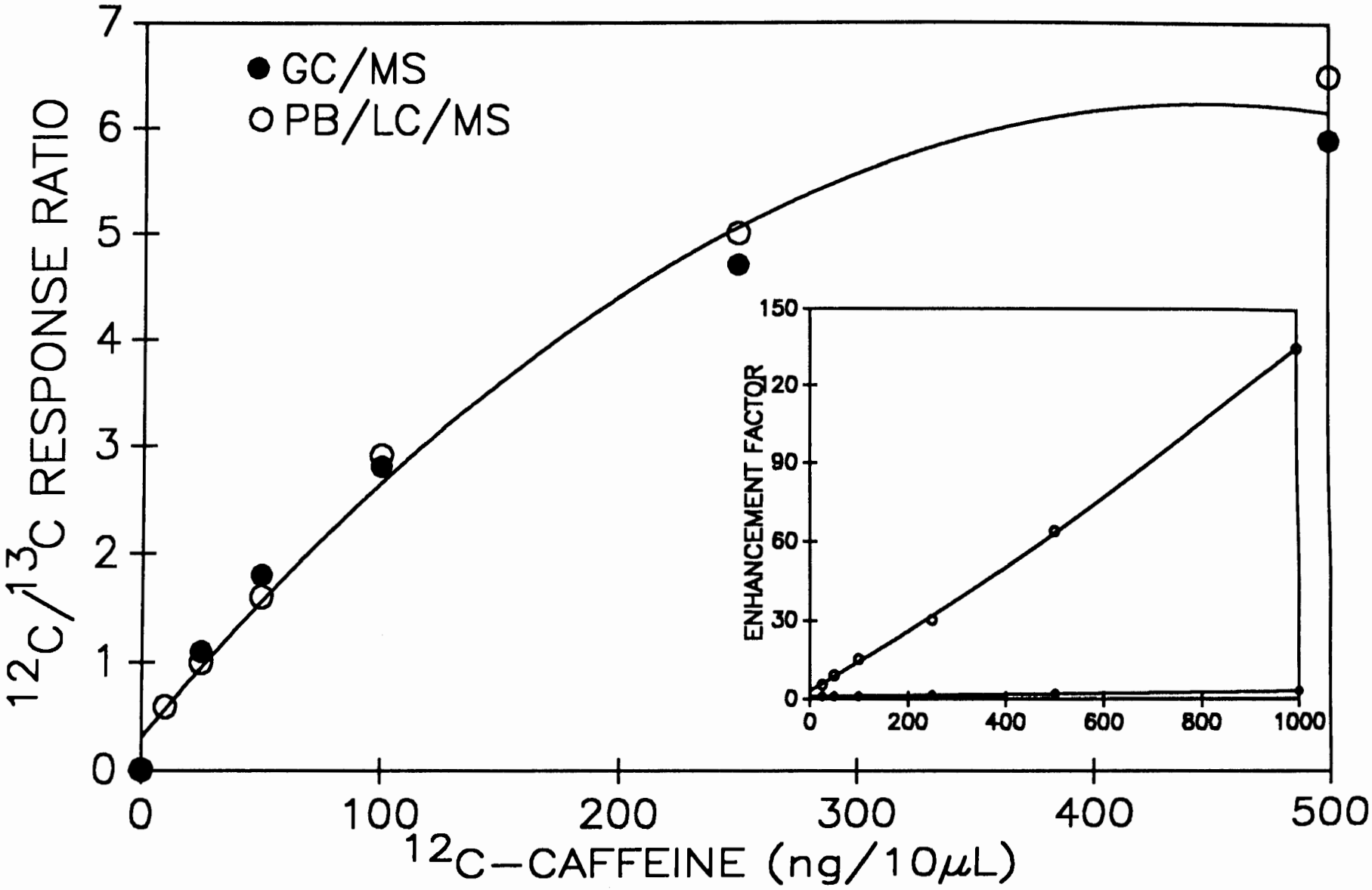
UH ENV MASS SPE
LINC EI+

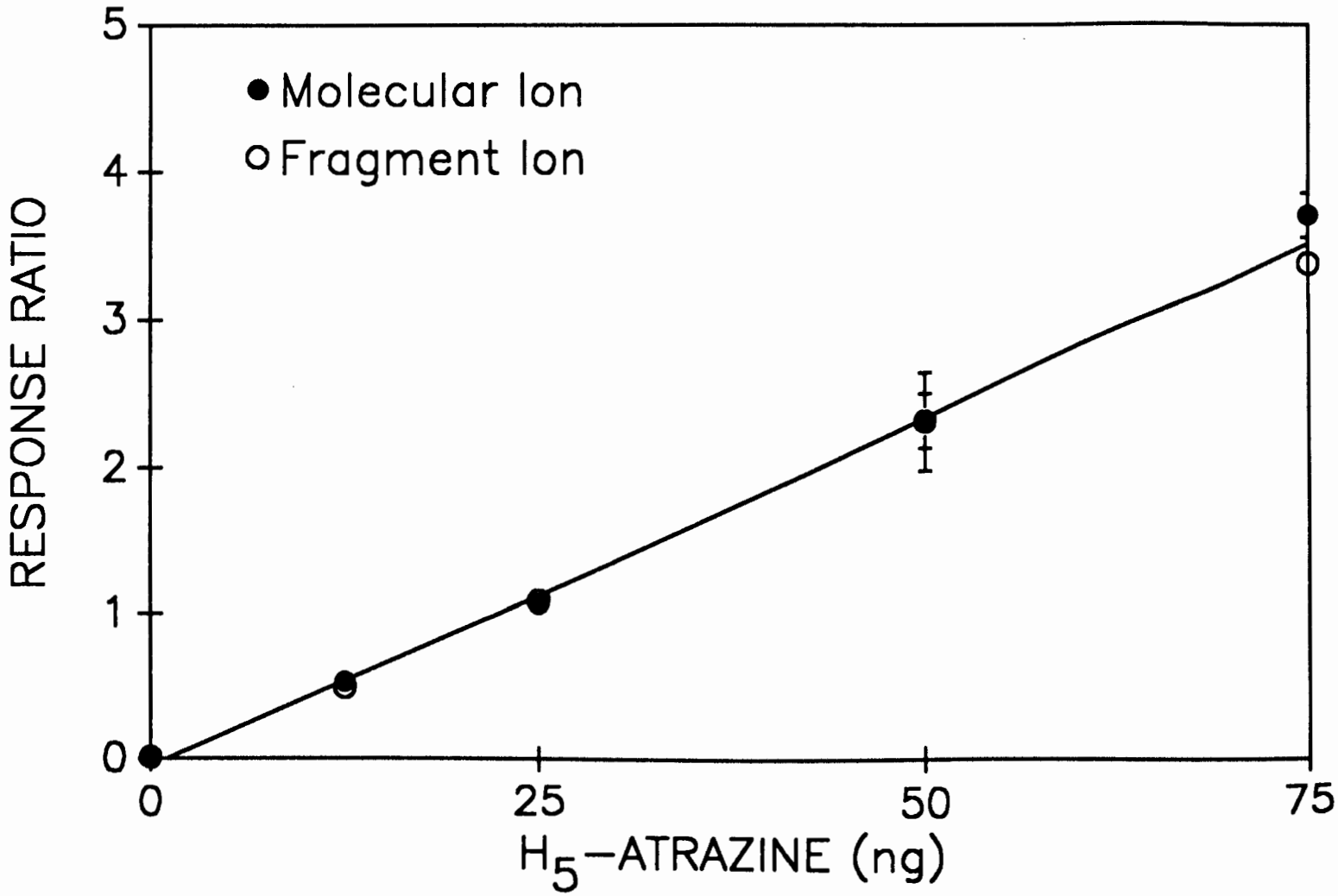
12/24/91
15:40

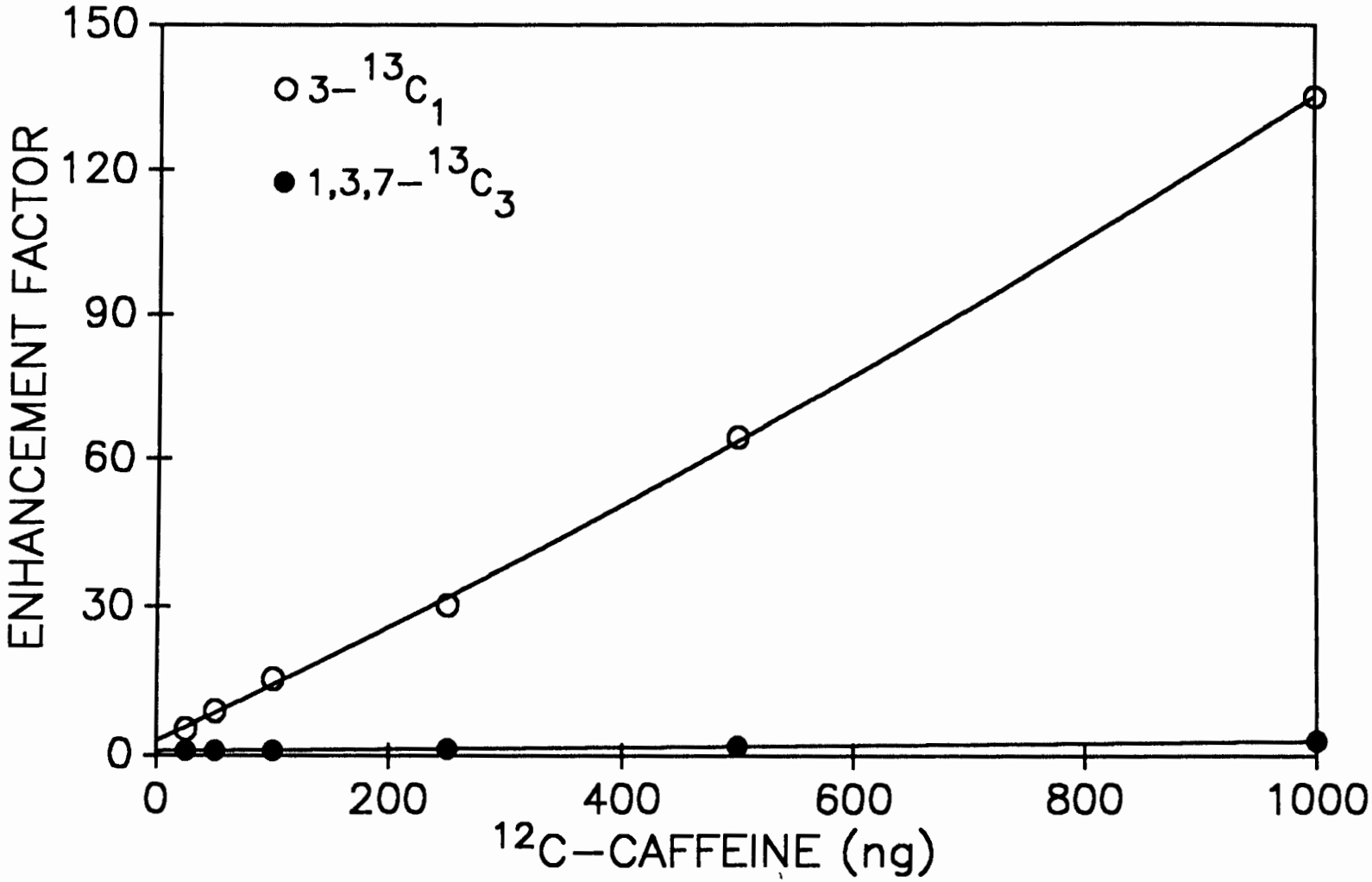
DBA1'20 (0.335) COMBINE:(15 to 32)-(((1 to 12)+(41 to 65))*1.000)




ENHANCEMENT FACTOR
15
10
5
0
0
100
200
300
400
500
12C–ETU (ng)


GC/MS
PB/LC/MS
$^{12}C/^{13}C$ RESPONSE RATIO
^{12}C–CAFFEINE (ng/10μL)
0
1
2
3
4
5
6
7
0
100
200
300
400
500
ENHANCEMENT FACTOR
0
30
60
90
120
150
0
200
400
600
800
1000


Molecular Ion
Fragment Ion
RESPONSE RATIO
0
1
2
3
4
5
0
25
50
75
H5–ATRAZINE (ng)


150
120
90
60
30
0
ENHANCEMENT FACTOR
○ 3–$^{13}C_1$
● 1,3,7–$^{13}C_3$
0
200
400
600
800
1000
^{12}C–CAFFEINE (ng)

52

The Determination of Semi-Volatile Organic Compounds in Analytical Extracts Using Split Injection Technique with an Ion Trap GC/MS.

Robert Brittain, Norman Kirshen, and Elizabeth Almasi,
Varian Chromatography Systems, 2700 Mitchell Drive, Walnut Creek, CA 94598, 510-939-2400 / FAX 510-945-2335

ABSTRACT

The determination of semivolatile organic compounds in analytical extracts of waste water or hazardous waste following EPA Method 8270 requires the screening of a large number of target compounds at low PPB to PPM levels. This translates to extract concentrations of approximately 0.1 to 1000 ng/mL. Hot splitless injection has traditionally been required to deliver sufficient analyte to the mass spectrometer for full-scan confirmation and quantitation. But, this injection technique can lead to problems such as polar analyte losses, imprecision, and discrimination. It also causes the more rapid contamination of injector inserts and capillary columns which have to be replaced regularly. When using the split injection technique with the more sensitive ion-trap MS several of these problems can be reduced while obtaining much improved chromatography.

This study employed a 25:1 split injection. The chromatography was superior to that obtained with other injection techniques. The multi-ramp temperature program used throughout the study was selected with the DryLab GC(R) software from LC Resources, Inc. The following QC acceptance criteria were investigated using the EnviroPro data reporting package: maximum %RSD for initial calibration, minimum average RRFs, continuing calibration checks, internal standard area reproducibility, and retention time precision. These criteria met both 8270 and CLP guidelines. Finally, this approach was applied to the analysis of two samples, one an NIST Standard Reference Material (Coal Tar Extract, 1597) and the other a TCLP extract showing many phenolic analytes in a high level hydrocarbon matrix. The results obtained from the NIST Standard compared very well with the published results.

53 ANALYSIS OF PESTICIDES IN GROUNDWATER USING ATMOSPHERIC PRESSURE CHEMICAL IONIZATION (APcI)/MS

Daniel R. Doerge, Research Chemist, National Center for Toxicological Research, Division of Biochemical Toxicology, Jefferson, AR 72079 and Steve Bajic, Development Department, VG BioTech, Altrincham, WA14 5Z, U.K.

ABSTRACT. The inherent chemical differences between classes of analytes has been a limitation for environmental LC/MS analysis because no single LC interface/ionization technique is sufficient. For this reason, a more universally applicable LC/MS interface/ionization technique possessing high sensitivity and ease of use has been sought. The atmospheric pressure ionization (API)/MS technique of electrospray (ES) has proven invaluable in the analysis of large biomacromolecules (≥1.5 kD) and in some cases, smaller molecules. The major limitation for ES is the low LC flow rate amenable to efficient ionization (2-5 µL/min or 20-100 µL/min for pneumatically assisted ES). Although microbore LC and the newer techniques of nanoscale chromatography and capillary zone electrophoresis can be successfully coupled to ES, the wide-spread use of conventional bore LC columns in environmental labs makes it desirable to perform API/MS under higher flow rate conditions (ca. 1 mL/min).

Interfaces which effect API using a corona discharge have recently been introduced for analysis of thermally labile and nonvolatile compounds of environmental interest. Since this technique involves the gas phase ionization of analyte molecules by reagent gas ions, it has been termed atmospheric pressure chemical ionization (APcI). This paper describes the use of APcI/MS for analytes in the EPA National Pesticide Survey (NPS) of groundwater contaminants. Seventeen analytes from the NPS were selected from five different pesticide classes: 1) Triazines 2) Phenylureas 3) Carbamates 4) Organophosphates 5) Miscellaneous. Positive ion spectra were obtained for all compounds using nitrogen as the source gas except p-nitrophenol which was observed as negative ions produced using dioxygen. Varying flow rates and mobile phase composition were used to separate analytes using a typical LC column (Perkin Elmer 0.46 x 3 cm, C18, 3µ deactivated silica) or in flow injection analysis. Spectra typically consisted of the protonated molecular ion ($M+H^+$) or deprotonated negative ion ($M-H^-$) but application of a potential difference in the intermediate pressure region produced voltage-dependent fragmentation of all carbamates and alachlor. Detection limits (LOD) from full scans ranged from 0.8-10 ng and these LOD were reduced to pg levels by employing selected ion monitoring. The MS response was highly linear (cc ≥ 0.99) over the entire range of concentrations tested (LOD to 100 ng) for all compounds tested. Mobile phase composition had minimal effects on MS response for any class of analyte over the range tested (50-100% acetonitrile). The MS response for diazinon was not affected by flow rate between 0.25 and 1.0 mL/min but decreased ca. 50% at 1.25 mL/min.

These results show that APcI/MS is a versatile, practical, and highly sensitive technique. The sensitivity is not affected by chemical differences over a wide range of analyte types suggesting that this is a more universal detection system that other LC/MS techniques (e.g., thermospray, particle beam). The low detection limits, high degree of linearity and the ability to produce diagnostic fragments by use of cone voltage or collision-induced dissociation in an MS/MS experiment are important elements required for the identification, confirmation and quantitation of analytes in groundwater and other environmental matrices.

INTRODUCTION

The chemical differences between classes of pesticides has limited the universal application of a single LC/MS technique for multiresidue analysis. While thermospray (TSP) and particle beam (PB) interfaces have been successfully applied to pesticide residue analysis, significant gaps in sensitivity have emerged. For these reasons, the development of a more universally applicable yet highly sensitive LC/MS technique would be a valuable addition to pesticide analytical labs for the development of multiresidue methods that could employ a single ionization/introduction mode.

Atmospheric pressure ionization (API) MS has been widely applied to analysis of large biomolecules (e.g., proteins, peptides, nucleic acids) with molecular weights of > 1.5 kDa using electrospray (ES) (1). However, classical ES and pneumatically assisted ES require LC flow rates of 2-5 µL/min or 20-100 µL/min, respectively. This requirement has limited the application of API/MS to pesticide residue analysis because such LC methods have employed conventional-bore columns (4.6 mm) and flow rates of ca. 1.0 mL/min. Recent development of interfaces that effect API using a corona discharge have facilitated analysis of small molecules (<1 kDa) that are thermally labile or nonvolatile (2). This technique produces ionization of analyte molecules via atmospheric pressure gas-phase ion-molecule reactions with solvent reagent ions produced from the corona discharge in the ion source volume. For this reason, the technique is called atmospheric pressure chemical ionization (APcI). This form of ionization is extremely "soft" in nature and yields primarily protonated molecular ions $(M+H)^+$ or deprotonated molecular ions $(M-H)^-$ in the positive ion and negative ion modes, respectively. In addition, structural information can be obtained using cone voltages to effect collision-induced dissociation of the sample ions in the intermediate pressure region (ca. 1 mbar) between the API source and the MS source housing. Moreover, this technique is amenable to flow rates between 0.2-2 mL/min without the need for flow splitting.

This paper describes the use of APcI/MS for the analysis of multiple classes of compounds included in the U.S. Environmental Protection Agency (USEPA) National Pesticide Survey (NPS) of pesticides in groundwater (3). A major limitation of current LC methods is the lack of MS confirmation procedures, especially those capable of identifying multiresidue contaminants. The results of this study show that APcI/MS has high sensitivity for all pesticide classes tested and much smaller differences in sensitivity between classes when compared with results from TSP and PB interfaces.

EXPERIMENTAL

Mass Spectrometer Conditions. The mass spectrometer used in these studies was a Trio 2000 single quadrupole instrument equipped with a VG BioTech dual ESI/APcI source (Fisons VG BioTech, Altrincham, U.K.). Mass spectra were collected in full scan (m/z 100-400 in 1 sec) or selected ion monitoring (SIM, dwell = 0.08 sec, span = 0.2 amu). The source temperature was maintained at 130°C and the cone voltage was 34V unless specified. Ions were generated using dinitrogen (positive ions) or dioxygen (negative ions) as the bath gas (see below). Sensitivity was checked periodically by injecting a reference compound whose responses remained consistent.

Interface Description. Referring to the schematic diagram in Figure 1, the entire LC mobile phase flow enters the probe inlet and is transferred to the nebulization/desolvation region via a 100 µm i.d. fused quartz capillary. The liquid flow is then pneumatically formed into an aerosol by the action of a high velocity concentric dinitrogen gas flow

between the fused silica and an 0.5 mm i.d. stainless steel capillary. The nebulizer gas flow and an additional concentric sheath gas flow carry the aerosol through a 45 mm heated desolvation tube with an internal diameter of 2 mm. Heat from a 75W desolvation heater is transferred to the aerosol droplets via the hot nitrogen gas flow which partially converts the mobile phase (and hence sample) into the gas phase. Prior to ionization, the resulting flow from the probe is carried towards the counterelectrode by a dinitrogen carrier, or bath gas, at a flow of typically 300 l/hr. In order to prevent condensation in the source volume and corona voltage flash-over when high aqueous content mobile phases are employed, the source is typically maintained at 140°C. A "cone of ionization" is formed between an axially-located nickel-plated carbon steel corona pin and the 2 mm exit aperture of the counterelectrode by the application of a potential difference of ca. 2kV (at a fixed pin/aperture distance of 2 mm). For positive ions, the corona pin and counterelectrode are typically maintained at voltages of +2.5kV and +0.5kV, respectively. Primary ions created in the corona discharge rapidly react with abundant mobile phase molecule in the gas phase to produce terminal (reagent) ions. Sample molecules introduced into the source react with the reagent ions and then exit the counterelectrode. At the adjustable off-axis sampling cone, the gas containing the sample and reagent ions expands into an intermediate pressure region (ca. 1 mbar) which is pumped by two $18m^3$/hr rotary pumps. Prior to this expansion, the atmospheric pressure ions can only drift under the influence of the applied electric field, i.e. no significant translational energy can be gained above thermal energy. However after expansion into the intermediate pressure region, where the mean-free-path of an ion increases, ions can gain an excess of energy between collisions. In practice, this energy is obtained by applying a potential to the sampling cone (typically 10-100V) with the skimmer held at ground potential. From a practical viewpoint, the application of a cone voltage serves to decluster solvated molecular ions and furthermore provides a method of obtaining structural information, i.e. by a process analogous to collision-induced dissociation (CID). Finally, the ions that pass through a skimmer aperture are focused into the quadrupole analyzer via a 2-lens source optics arrangement.

LC Conditions. Samples were introduced into the interface using an LKB isocratic pump for flow injection analysis (FIA) with 100% acetonitrile as mobile phase or through a Perkin Elmer C18 silica column (0.46 x 3 cm, 3μ particle size). An 0.45 μ stainless steel filter was installed between the LC column and the interface.

Pesticide Analytical Standards. Pesticides standards were obtained from the USEPA repository (Research Triangle Park, NC) or from the respective manufacturer and were of at least 97% purity.

RESULTS AND DISCUSSION

The pesticides listed in Table I were selected from 5 classes: triazines, phenylureas, carbamates, organophosphates and some other miscellaneous compounds on the NPS list of pesticides in groundwater. This selection permitted intra- and inter-class comparisons of sensitivity, ionization, fragmentation, etc. The results shown in Table I indicate that APcI/MS gives high sensitivity detection of all compounds with a minimum of differences in detection limits (LOD) between classes. Low nanogram LOD's were observed for all compounds in scan mode and these were reduced to picogram levels by using SIM mode. The LOD's determined in scan mode varied ca. 10-fold while those in SIM mode varied ca. 100 fold. These low LOD's coupled with the limited variability across these diverse chemical classes suggests that APcI/MS may be a more universally applicable MS detection system for use in confirmation and detection of pesticides in environmental

samples. The high degree of linearity of response is shown for selected analytes in Figure 2.

The ions shown in Table I were either $(M+H)^+$ or $(M-H)^-$ in positive or negative ion modes, respectively. These results are consistent with reactions of reagent ions consisting primarily of protonated mobile phase ions and clusters, in positive ion mode and presumably O_2^- and solvent clusters in negative ion mode[illegible].

Cone Voltage-Dependent Fragmentation. Only the carbamate pesticides and alachlor showed fragment ions in the presence of higher cone voltages. The application of successively higher voltages resulted in the progressive diminution of $(M+H)^+$ ion intensity with increases in the intensities of diagnostic fragment ions (see Table II). For example, aldicarb sulfoxide showed three ions: 223, 166 and 148 m/z. These ions correspond to $(M+H)^+$, protonated oxime and protonated nitrile fragments, respectively. Table II shows the effect of cone voltages on the relative intensities of these ions. In principle, the voltage could be adjusted to produce any desired degree of fragmentation desired. In this way, the desired amount of fragmentation required for confirmation and quantitation is available from a single quadrupole mass spectrometer. Alternatively, this information could be obtained in an MS/MS experiment with analytes that are recalcitrant to fragmentation via cone potentials.

Effect of Mobile Phase. The effect of mobile phase composition and flow rate on analyte sensitivity was examined for ranges typically encountered in pesticide analysis. The effects were monitored using 4 different classes of pesticides to determine if compound-specific changes in sensitivity occurred. Figure 3 shows that the responses from 4 different classes of pesticides were not affected below ca. 0.75 mL/min. However, when flow rate was further increased, responses decreased to about 50% response at 1.25 mL/min. These flow rates are readily compatible with those used in the many commercially available conventional bore LC columns [illegible]. Little effect of mobile phase composition on MS response was noted between 50-100% acetonitrile (data not shown). Although not studied in detail, it was observed that increasing the water content does cause some reduction in analyte responses, especially with 100% aqueous solvents. The invariance of response for the range of compound classes tested suggests that APcI/MS may be amenable to the use of gradient LC separations. However, it was observed that some losses in sensitivity occurred upon changing mobile phase flow rate or composition. The MS responses could be restored to original levels by adjustment of the off-axis skimmer. These observations suggest that this is an important experimental parameter for optimizing the sampling of gaseous ions as they expand into the MS analyzer.

APcI/MS Analysis of Triazine Herbicides in Water. A multiresidue LC method for the analysis of 4 triazine herbicides often found in groundwater was developed. Figure 4 shows the results from a conventional bore LC separation using full scan conditions on 50 ng samples of each herbicide. Detection limits estimated using SIM were 1-2 ng on-column and the major noise component was due to LC pump pulsations.

Comparison of APcI LOD's with TSP and PB Interfaces

Table III shows the LOD for APcI (this work) and values obtained from the literature from studies that used TSP and PB interfaces for the analysis of pesticides. The full scan sensitivity for these selected pesticides varied over an order of magnitude for APcI, 50-fold for TSP and >300 for PB. Thus, although TSP[illegible] or PB[illegible] interfaces provide adequate sensitivity for some analytes, APcI provides the optimal combination of high sensitivity

with broad specificity. These results suggest that APcI/MS is more suited to multiresidue pesticide analysis than the more established TSP and PB methodologies for analysis of groundwater contamination.

REFERENCES

1. Smith, R.B., Loo, J.A., Edmonds, C.G., Barinaga, C.J. and Udseth, H.R. *Anal. Chem.* 62, 882-899 (1990).

2. Gilbert, J.D., Hand, E.L., Yuan, A.S., Olah, T.V. and Covey, T.R. *Biol. Mass Spectrom.* 21, 63-68 (1992).

3. U.S. Environmental Protection Agency in **National Survey of Pesticides in Drinking Water Wells**; Phase 1 Report:1990; Offices of Water and Pesticide Programs. EPA-570/9-90-015.

4. Miles, C.J. *J. Chrom.* 592, 283-296 (1992).

5. Miles, C.J., Doerge, D.R. and Bajic, S. *Arch. Env. Contam. Toxicol.* 22, 247-251 (1992).

6. Voyksner, R.D. and Haney, C.A. *Anal. Chem.* 57, 991-996 (1985).

7. Voyksner, R.D., Bursey, J.T. and Pellizari, E.D. *ibid* 56, 1507-1514 (1984).

FIGURE LEGENDS

Figure 1. Schematic Diagram of the APcI Interface.

Figure 2. Calibration Plots for Selected Pesticides.
The MS response was determined from average peak areas (n=3) of varying amounts of the analytes using FIA (acetonitrile).

Figure 3. Effect of Mobile Phase Composition on APcI Response for Diazinon.
Diazinon (50 ng) was introduced using FIA at the indicated mobile phase compositions. The data shown are means (n=3) with standard deviations as error bar.

Figure 4. Multiresidue Triazine Herbicide LC Analysis Using APcI Detection.
The indicated herbicides (50 ng each) were analyzed under full scan conditions as described in the Exeprimental Section using 60% acetonitrile (isocratic) as mobile phase at 0.5 mL/min.

Table I. APcI LC/MS Analysis of Pesticides, Figures of Merit.

Pesticide	Ion	LOD Scan (ng)	LOD SIM	Linearity[1]
Atrazine	216	2.5	0.2	0.998
Ametryn	228	1	0.2	0.999
Cyanazine	241	1	0.5	0.999
Hexazinone	253	4	1	0.999
Fluometuron	233	0.8	0.1	0.994
Diuron	233	4	0.2	0.960
Neburon	275	2.5	0.2	0.995
Linuron	249	4	0.1	0.999
Propanil	218	8	0.5	0.992
Aldicarb Sulfoxide	223[2]	7	0.5	0.998
Carbofuran	222[2]	2.5	0.15	0.998
Carbaryl	202[2]	5	0.5	0.999
Diazinon	305	1	0.01	0.999
Fenamiphos	304	8	0.2	0.999
Alachlor	270[2]	8	0.2	0.996
p-Nitrophenol	138[3]	10	0.2	0.996

[1]Correlation coefficient of the calibration curve from the detection limit to 100 ng.
[2] Cone voltage-dependent fragmentation observed
[3] $(M-H)^-$ Ion

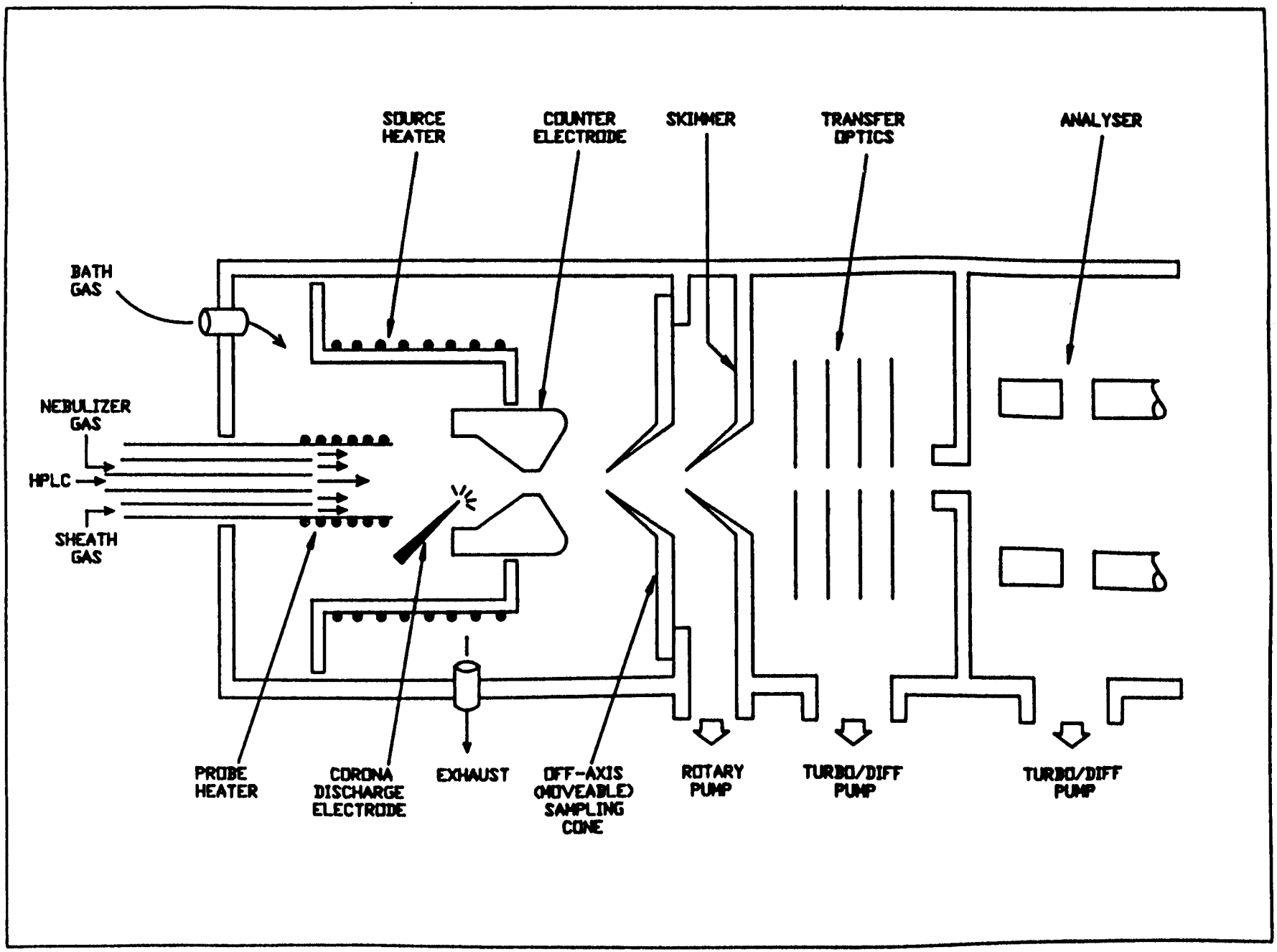
Table II. Cone Voltage-Dependent Fragmentation of Aldicarb Sulfoxide.

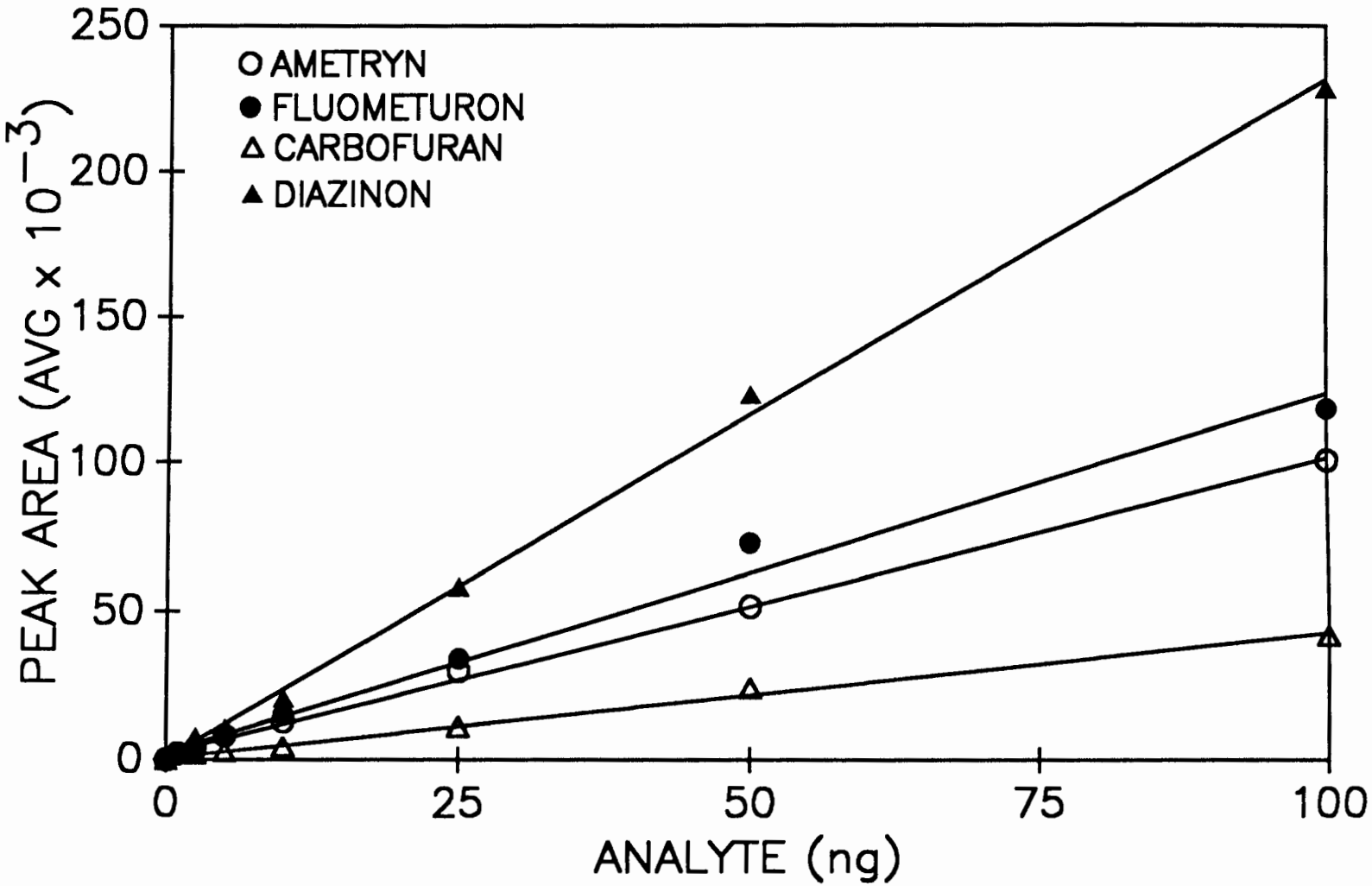
Cone Voltage	Ion	Intensity
24 Volt	223 m/z	100%
	166	0
	148	0
34	223	100
	166	40
	148	40
44	223	40
	166	70
	148	100

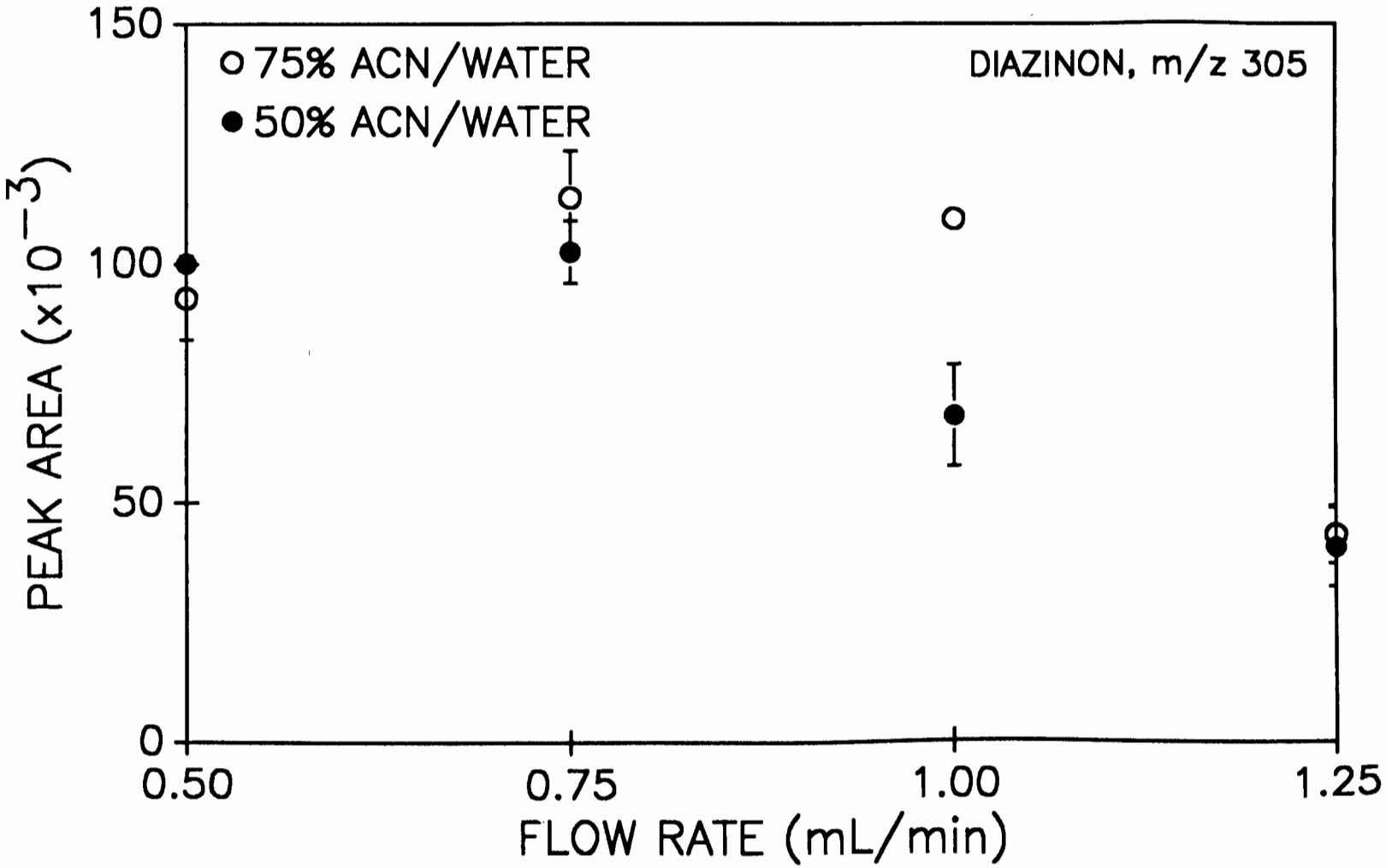
Table III. Comparison of APcI, TSP and PB Interfaces for the Analysis of NPS Pesticides.

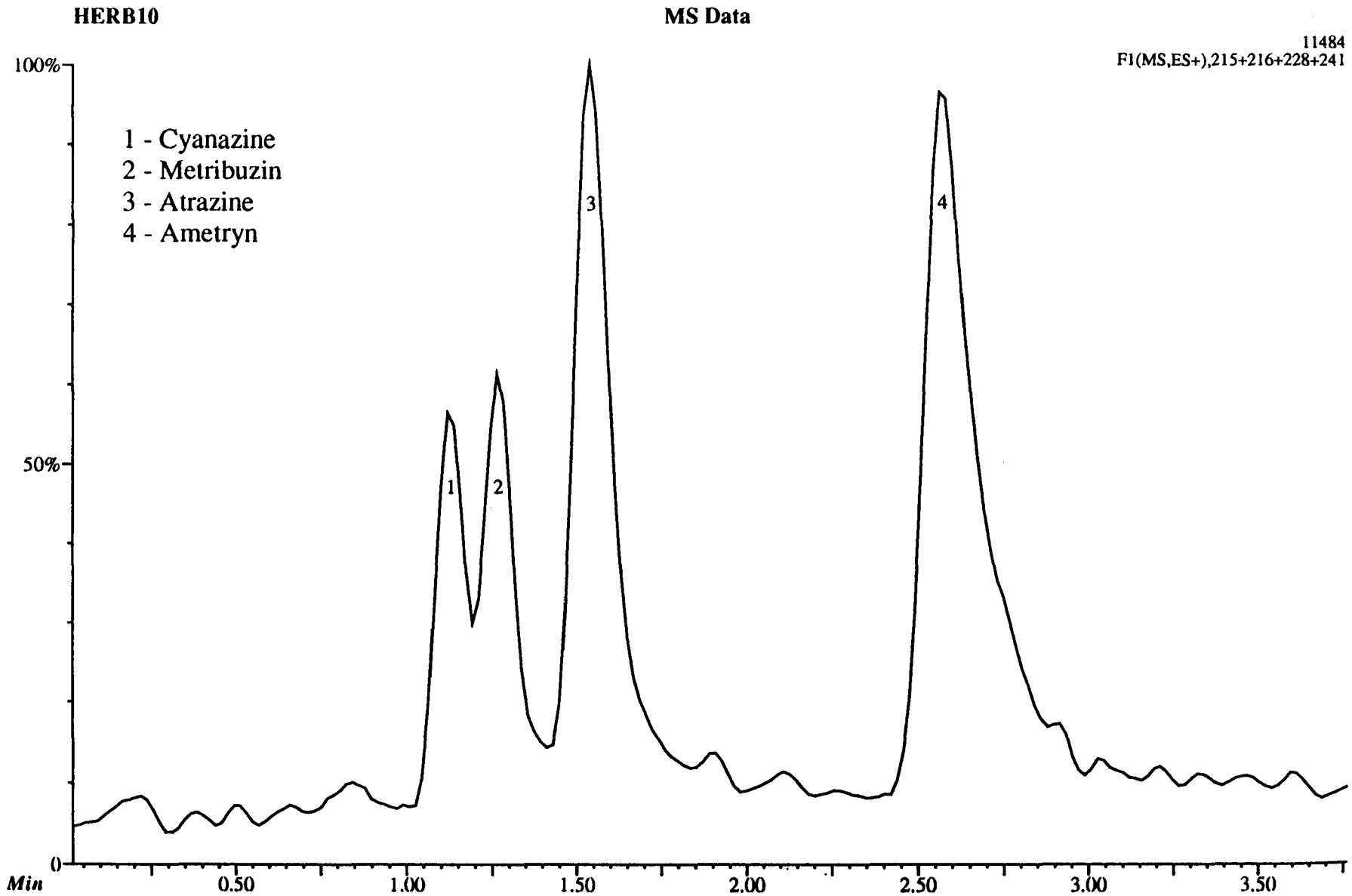
Pesticide	LOD-APcI (ng)	LOD-TSP (ng)	LOD-PB (ng)[1]
Atrazine	2.5	20[2]	19
Ametryn	1.0	20-60[2]	11
Cyanazine	1.0	--	2.0
Hexazinone	4.0	20-60[2]	0.4
Fluometuron	0.8	--	1.4
Diuron	4.0	50-80[3]	0.4
Neburon	2.5	--	3.4
Linuron	4.0	4-8[3]	4.4
Propanil	8.0	--	0.6
Aldicarb Sulfoxide	7.0	--	4.0
Carbofuran	2.5	1-4[3]	9.0
Carbaryl	5.0	3-5[3]	6.0
Diazinon	1.0	--	--
Fenamiphos	8.0	--	4.2
Alachlor	8.0	10-20[3]	68
p-Nitrophenol	10.0	--	12

[1]Reference 5
[2]Reference 6
[3]Reference 7


SOURCE HEATER
COUNTER ELECTRODE
SKIMMER
TRANSFER OPTICS
ANALYSER
BATH GAS
NEBULIZER GAS
HPLC
SHEATH GAS
PROBE HEATER
CORONA DISCHARGE ELECTRODE
EXHAUST
OFF-AXIS (MOVEABLE) SAMPLING CONE
ROTARY PUMP
TURBO/DIFF PUMP
TURBO/DIFF PUMP


AMETRYN
FLUOMETURON
CARBOFURAN
DIAZINON
PEAK AREA (AVG x 10^{-3})
250
200
150
100
50
0
0
25
50
75
100
ANALYTE (ng)


150
100
50
0
PEAK AREA (x10^{-3})
○ 75% ACN/WATER
● 50% ACN/WATER
DIAZINON, m/z 305
0.50
0.75
1.00
1.25
FLOW RATE (mL/min)


HERB10
MS Data
11484
F1(MS,ES+),215+216+228+241
100%
50%
0
1 - Cyanazine
2 - Metribuzin
3 - Atrazine
4 - Ametryn
1
2
3
4
Min
0.50
1.00
1.50
2.00
2.50
3.00
3.50

54 THE USE OF SUPERCRITICAL FLUID EXTRACTION/GC-MS FOR THE QUANTITATIVE DETERMINATION OF PAHs IN SOIL

Joseph M. Levy Manager of Technology and Customer Support, Suprex Corporation, 125 William Pitt Way, Pittsburgh, PA 15238, Telephone: 412-826-5200, FAX: 412-826-5215

ABSTRACT

Supercritical fluid extraction (SFE) has a broad range of applicability, especially with regards to environmental problems. SFE has achieved a significant amount of attention due to the benefits of eliminating toxic, liquid solvent usage, reduction in sample preparation time and an increase in the overall analytical reliability of determinations. On-line SFE/GC-MS is a powerful technique to accurately analyze and quantitate environmental analytes. In addition, the off-line transfer of SFE effluents to collection vials adds a considerable amount of flexibility in characterizing complex matrices since a full compliment of analytical tools can be used (i.e. GC, LC, IR, NMR and UV). Moreover, the advantages of SFE can be further augmented by the development of automation for greater sample throughput which can be especially important for environmental applications.

This paper will discuss the use of on-line and off-line SFE/GC-MS methodologies for the determination polynuclear aromatic hydrocarbons (PAH) in soil. Details of method development will be presented demonstrating how EPA method 8270 was followed except for the replacement of Soxhlet sample preparation with SFE. This discussion will also focus on the experimental verification of optimized SFE variables to achieve efficient and quantitative extractions of the target analytes in the soil. An example is shown in Table 1 where an off-line SFE/GC comparison was made between the extraction of PAHs from soil at different pressures, indicating that higher pressures were necessary for the complete recovery of the PAHs, especially the four and five ring. The use of various pre-extraction strategies (i.e. matrix manipulation, modifier addition, adsorbent use) for the enhancement of extraction efficiencies will also be outlined.

Table I: Off-Line SFE/GC-MS of PAH Contaminated Soil: Pressure Variation SFE: 65°C, 40 minutes, flow 0.9 ml/min (compressed) GC: methyl 25 m x 0.2 mm I.D., 60°C (2.0 min) to 280°C (30 min) at 7°C/min.

Compound	Acceptance Range (PPM)	Concentration Levels (PPM) 250 atm	350 atm	400 atm
Naphthalene	24.2-40.6	23	23	25
Acenaphthylene	14.7-23.5	20	•	22
Acenaphthene	527-737	566	601	614
Fluorene	414-570	445	471	458
Phenanthrene	1270-1966	1682	1978	1911
Anthracene	373-471	357	439	400
Fluoranthene	1060-1500	1028	1459	1571
Pyrene	744-1322	703	1153	1269
Benzo(a)Anthracene	214-290	74	235	284
Chrysene	271-323	74	251	314
Benzo(b,k)Fluoranthene	130-174	<1.0	107	155
Benzo(a)Pyrene	80.1-114.3	<1.0	64	89

55

SUPERCRITICAL FLUID EXTRACTION (SFE) of TOTAL PETROLEUM HYDROCARBONS (TPHs) with ANALYSIS by INFRARED SPECTROSCOPY

Mark L. Bruce, Director of Research and Development, and Marvin W. Stephens, Technical Director, Wadsworth/ALERT Laboratories, Division Of Enseco, Inc., 4101 Shuffel Dr. N.W., North Canton, Ohio 44720

ABSTRACT

Infrared spectroscopy is an attractive analysis procedure for the screening of petroleum hydrocarbons in solid matrices because of its low cost and rapid sample throughput. Coupled with off-line supercritical fluid extraction (SFE), this method provides a rapid monitoring procedure with almost a 100 fold reduction in the amount of solvent used as compared to the present Soxhlet method. This method uses supercritical carbon dioxide as the extraction solvent to remove the target components from a solid sample and deposit them into a solid phase adsorbent trap. The trap is rinsed with 3 mL of tetrachloroethene which has replaced Freon-113® in this application. Extraction conditions are 400-500 atmospheres, 25-30 minutes dynamic step, 8 mL/min supercritical CO_2 flow and an oven temperature of 150°C. Dry and wet soil samples have been successfully extracted with this method. Many dry samples can be extracted in less than 20 minutes.

INTRODUCTION

According to EPA estimates there are three to five million underground storage tanks in the United States (1). Approximately 100,000 of these tanks are believed to be leaking. In addition, as many as 300,000 more tanks are predicted to begin leaking in the next five years (1). At present, semivolatile petroleum hydrocarbons are extracted by Soxhlet, sonication, or Soxtec® using an organic solvent followed by gas chromatographic or infrared analysis.

Freon-113® is used when the analysis is performed by infrared spectroscopy. It is a known ozone depleter (2), making it unacceptable as a laboratory solvent. According to M.P. McCormick of Langley Center's Aerosol Research Branch, polar stratospheric clouds provide a surface on which chlorofluorocarbons (CFCs) can react to free the chlorine to react with ozone (2). In accordance with the Montreal Protocol on Substances that Deplete the Ozone Layer and the Clean Air Act Amendments of 1990 (CAA), CFCs will be phased out by the year 2000. Recent White House decisions have moved many solvent phase-out deadlines to 1995.

Extraction of hydrocarbons from soil samples was one of the first applications of analytical SFE with carbon dioxide. Numerous researchers have worked with these analytes in this matrix. Petroleum hydrocarbons can be extracted from soil, that has been proven. The question now is, "Can the extraction be performed in the typical environmental lab with all its constraints?" Routine environmental work requires rugged methods that are easy to use properly. The cost (economic, environmental and health) must be low. Yet the sample throughput must be high and the extraction time short enough to meet client needs. These additional nonanalytical constraints significantly narrow the SFE choices. Most SFE parameters are directly or indirectly affected by these constraints such as; sample size, solvent, pressure, temperature, flow rate and extraction time.

Numerous solvents were examined for use in the IR analysis. Freon-113® can be replaced in this application by several solvents: hexafluorotetrachlorobutane, tetrachloroethene and FC-77. Each of these solvents has advantages and disadvantages.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Supercritical Fluid Extractor
- Suprex, PrepMaster, AccuTrap
- 5 mL extraction vessel
- Restrictor, prototype VariFlow restrictor (adjustable from 0.1 to 8 mL/min)

Infrared Spectrophotometer
- Perkin-Elmer, 710
- Buck Scientific Oil in Water Analyzer
- 10 mm, 3 mL quartz cell

Reagents and Standards
- Freon-113®, EM Science
- Fluorinert® FC-77, 3M
- Isooctane, Mallinckrodt
- Xylenes, Mallinckrodt
- Hexadecane, EM Science
- Kaolin, Baker Analyzed
- CO_2, SFC grade with 1500 PSIA Helium headspace with dip tube, Scott Specialty Gases
- Tetracholorohexafluorobutane, Horiba or Halocarbon
- Tetrachloroethene, Aldrich

RESULTS & DISCUSSION

The development for this method was conducted in two areas, 1) the search for a suitable collection/analysis solvent, and 2) the optimization of supercritical fluid extraction parameters. The approaches and representative results are discussed below.

Collection Solvent

The search for an appropriate collection solvent was broken down into four stages. In the first stage, the catalogs of seven chemical vendors were examined for potential solvents. This search resulted in about 70 possible collection solvents. The desirable solvent characteristics are listed in Table 1.

Table 1. Desired Solvent Characteristics

- no C-H bonds
- high hydrocarbon solubility
- high purity
- liquid at ambient temperature
- nonflammable
- nontoxic
- not an ozone depleter
- not a greenhouse gas
- not a long term health hazard target cost <$5/sample

In the second stage, vendors were contacted for additional product information regarding the potential collection solvents as to their hydrocarbon solubility, IR spectra, and material safety data. This information was used to eliminate all but 8 solvents. Small amounts of these solvents were obtained for further testing.

The third stage was to confirm conclusions drawn from the information provided by the vendors. All solvents were tested for hydrocarbon contamination by measuring the C-H stretch region of the infrared spectrum (2900-3100 cm^{-1}). Even with background correction, the concentration of hydrocarbon contamination of the possible collection solvents was prohibitively high for all solvents except the Fluorinerts® FC-77 and FC-72, tetrachlorohexafluorobutane and tetrachloroethene.

Using Freon-113® as a solubility reference, it was estimated that the solubility limit of diesel fuel in FC-77 and FC-72 is approximately 5000 mg/L. The low molecular weight fraction of the diesel fuel appeared to be preferentially more soluble than the higher molecular weight components when compared to the Freon-113® standard. High molecular weight hydrocarbons such as motor oil have very low solubility in FC-77. Tetrachlorohexafluorobutane (TCHFB) and tetrachloroethene (Perc) exhibited hydrocarbon solubility characteristics similar to Freon-113.

In stage four, the EPA independently selected tetrachloroethene as the analysis solvent. FC-77 did not have adequate solubility for all hydrocarbons. Tetrachlorohexafluorobutane has excellent analytical and Health & Safety characteristics, however, it is a chlorofluorocarbon that if released into the ozone layer could deplete it. Tetrachloroethene does present some long term health concerns but special laboratory precautions and using small solvent volumes should reduce the risk to analysts. Table 2 summarizes the solvent options.

Table 2. Solvent Short List

Characteristic	Freon-113	FC-77	TCHFB	Perc
TPH solubility	yes	diesel only	yes	yes
Carcinogenic	no	no	no	yes
Ozone depletion	yes	no	?	no
Boiling point (°C)	48	97	134	121
Vapor pressure (mm Hg)	334	42	12	19

Optimization of Extraction Parameters

The goal at this stage of the method development was to optimize the extraction parameters so that this method could be used with as broad a spectrum of environmental matrices and hydrocarbon mixtures as practical. Due to the lack of standard reference materials (SRMs) with known "native" TPH concentrations, spiked analyte and unknown "native" analyte samples were used in the development of this method. Using the recovery of spiked analytes to prove quantitative extraction of "native" analytes is tentative at best and very misleading at worst. Spiked compound matrix interactions may be much weaker than "native" analytes which have had months or years to adsorb on and into the matrix. Kaolin, Fullers earth and montmorillonite clay types were used to produce worst case matrix spike recovery data. Each is a highly absorptive, fine particle matrix with a high surface area. Spiked clay samples were tumbled over night to homogenize the sample and enhance the absorbance of the spiked compounds. Water was added to some samples prior to extraction to produce wet clay samples.

The wet sample test is vital since SFE has well documented problems with water. Also many environmental "soil" matrixes have large percentages of water. Figure 1 shows the % moisture found in 650 "solid" samples. The typical sample was 20% moisture but a significant number of samples had moisture content above 50%. A rugged extraction method should handle at least 95% of the sample load. Figure 2 plots the cumulative frequency of %moisture for the same sample set. To reach the 95th percentile the extraction must handle up to 60% moisture.

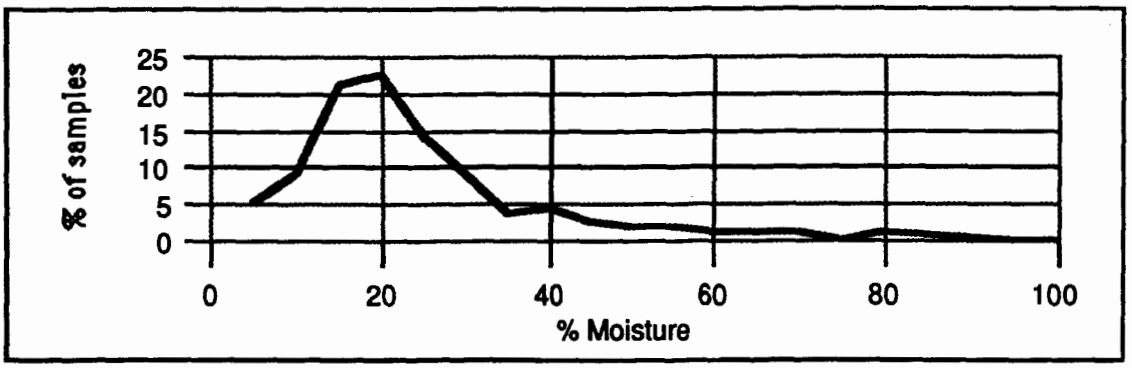


Figure 1. Percent Moisture Distribution

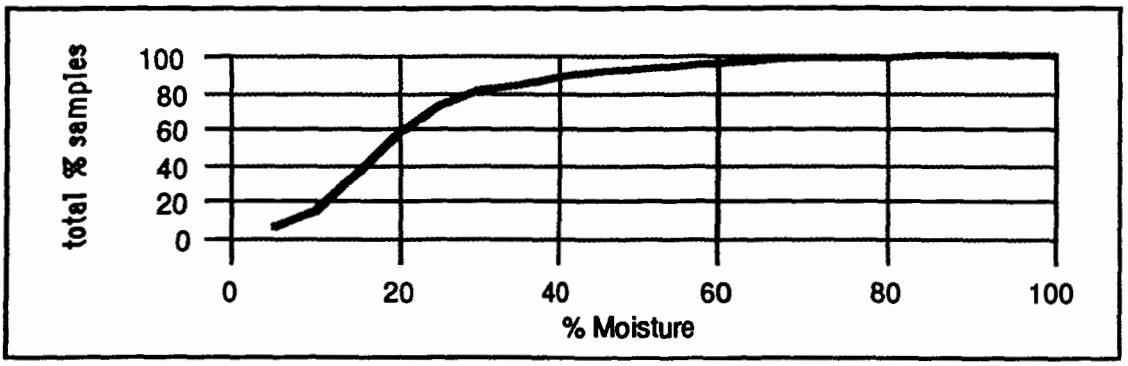


Figure 2. Cumulative Frequency of %Moisture

Under some extraction conditions the water is released from the sample and impinges upon the restrictor. If a conventional fused silica capillary tube is used as the restrictor the liquid water may drastically reduce flow, thus aborting the extraction. Heating the restrictor improves its resistance to water plugging but this is not a rugged solution to the problem. A variable restrictor was developed specifically for this problem. The VariFlow® restrictor (from Suprex) is a simple, low cost and "water proof" variable restrictor. Water plugging tests have shown that several milliliters of water can be pushed through the restrictor without degrading restrictor performance. The overall SFE system is shown in Figure 3.

Data Analysis Tools

Two primary data analysis tools were used, factorial design and extractograms. Factorial design allows the experimenter to vary several extraction conditions during a systematic set of experiments. Statistical calculations estimate the effect of each parameter (factor) and the interactions between factors. Thus, each extraction parameter is optimized and its importance is determined. Figure 4 plots the effect of varying 5 common SFE factors. The

native hydrocarbons in a 2g Kaolin sample were extracted using various combinations of the conditions listed in Table 3. The TPH concentration was about 20 mg/kg. The restrictor was a 60 cm fused silica capillary tube. Analytes were collected directly in 5 mL of FC-77. Figure 4 shows that the high value for pressure, oven temperature, static step time and dynamic step time yields greater TPH recovery than the low value. The low value for the restrictor produces higher TPH recovery.

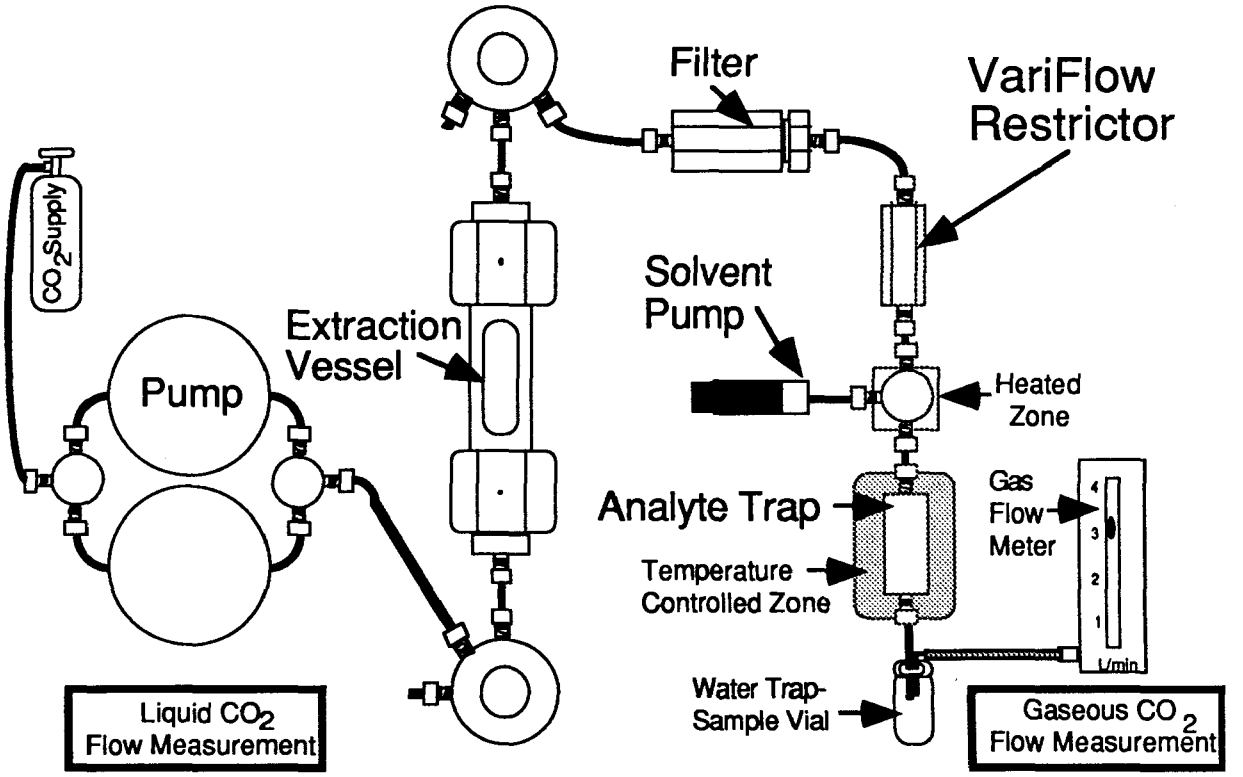


Figure 3. SFE System Diagram

Table 3. Factorial Design Parameters

Factor	Low Value	High Value	Best results with
Pressure	200 atm	400 atm	high
Oven Temperature	60°C	120°C	high
Static time	0 min	10 min	high
Dynamic time	10 min	20 min	high
Restrictor I.D.	32 µm	40 µm	low

The extractogram is a profile of extracted components versus time. Extractograms are generated by splitting off a small portion of the CO_2 stream and directing it to a flame ionization detector which responds well to petroleum hydrocarbons.

As expected the largest quantity of analytes are extracted near the start of the dynamic step. After peaking, the amount of extracted analyte exponentially declines. Eventually the FID returns to the baseline indicating that analyte extraction has ceased.

Dry Soil Matrixes

Supercritical fluid extraction of hydrocarbons from dry soil samples with unmodified carbon dioxide has been reported often. Mild extraction conditions are usually sufficient to achieve acceptable analyte recovery.

Extraction of environmental matrixes requires the use of large sample quantities to ensure that the aliquot is representative of the entire sample. SFE works best with small samples. Sample aliquots of 3 g have been chosen as a reasonable compromise between these two requirements.

Wadsworth/ALERT participated in a recent EPA interlaboratory study to evaluate draft Method 3560. Petroleum hydrocarbons were extracted from relatively dry soils. Extraction conditions were, 340 atm, 80°C, 1.2 mL/min CO_2, 30 min dynamic, analyte trap - solvent vial with 3 mL of tetrachloroethene. IR analysis was performed by Midwest Research Institute, Mountain View, CA.

Table 4. Dry Sample Recovery Data from the EPA Interlaboratory Study

Soil Number	% Recovery	Analyte
1	75	614 mg/kg native TPH
2	92	2050 mg/kg native TPH
3	90	32600 mg/kg native TPH
4	79	10000 mg/kg spiked TPH
5	blank soil	
6	87	10000 mg/kg spiked TPH
7	97	10000 mg/kg spiked TPH

Factorial design experiments were used in an attempt to optimize the extraction conditions and shorten the 30 minute extraction time required by draft EPA method 3560. It was thought that higher pressure, temperature and flow rate would shorten the extraction time.

The first fractional factorial used 3 g of ERA TPH #1 Lot 91019 as the sample. This QC sample consists of vacuum pump oil spiked onto a clean, dry soil. A VariFlow restrictor was used for flow control and the analytes were trapped on a solid phase absorbent. The absorbent was eluted with 3 mL of tetrachlorohexafluorobutane. Extraction time was determined from the extractograms. The factors and levels tested are shown in Table 5 below. The effect of each factor is shown in Figure 6.

The most prominent effect is that the static step lengthened the extraction by 4 minutes for this sample. Pressure, temperature and flow rate had small or negligible effects. The two extractograms in Figure 7 illustrate the difference between extractions with and without the 5 minute static step.

The static step was eliminated and another factorial experiment was designed to examine the effects of pressure, temperature and flow rate. The second factorial design also used 3 g of ERA TPH #1 Lot 91019 as the sample. Flow control and analyte trapping were the same. The total extraction time was the sum of oven warm-up time and dynamic step. The factors and levels tested are shown in Table 6 below. The effect of each factor is shown in Figure 8. The extractor oven needs about 4 minutes to heat from 20°C to 150°C. The dynamic step did not begin until the temperature had reached the set point, thus a 4 minute static step was essentially added to the extraction. Since the elevated temperature did not

shorten the required dynamic time, the net effect of elevated temperature was a longer extraction time. Once again pressure and flow rate had no effect. The two extractograms in Figure 9 illustrate the difference between extractions with the temperature at 80°C and 150°C.

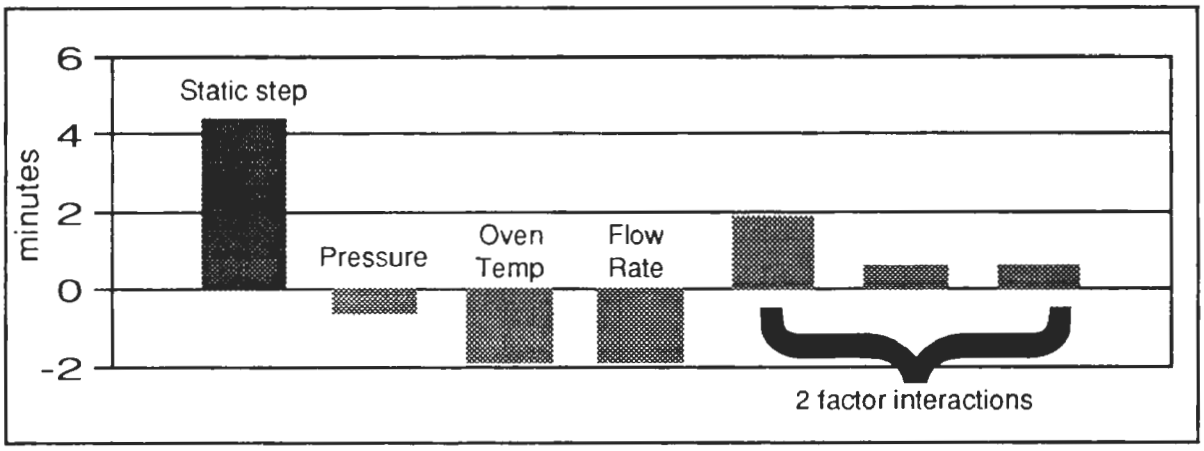


Figure 6. Dry Sample Factorial Design #1 Results

Table 5. Factorial Design #1 Parameters

Factor	Low Value	High Value	Best results with
Static time	0 min	5 min	low
Pressure	340 atm	450 atm	no effect
Oven Temperature	80°C	140°C	high*
Flow Rate	600 mL/min CO_2 gas	2000 mL/min CO_2 gas	high

* Oven warm-up time was not considered during this experiment.

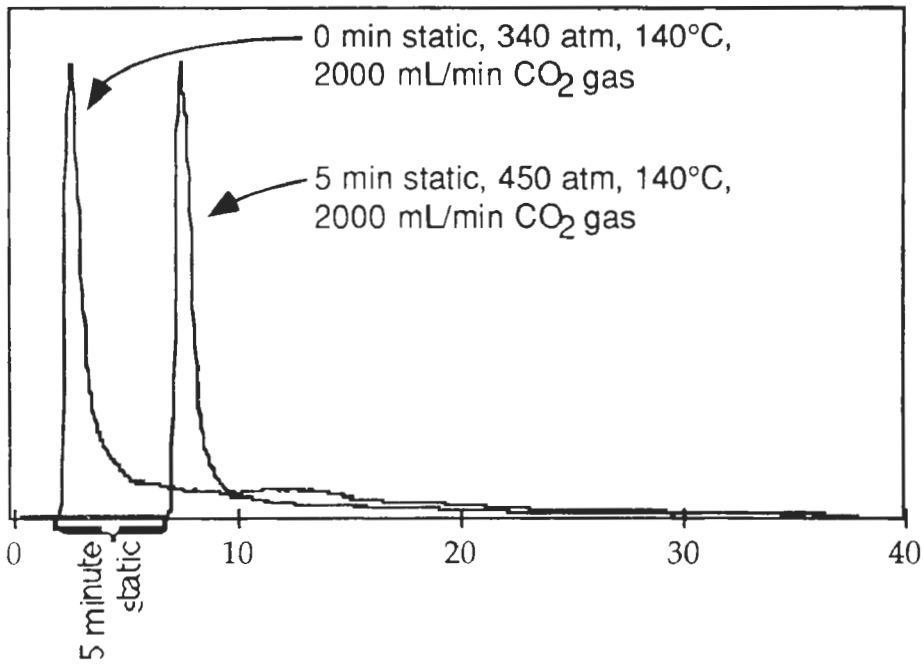


Figure 7. Extractogram Comparison - With and Without the Static Step

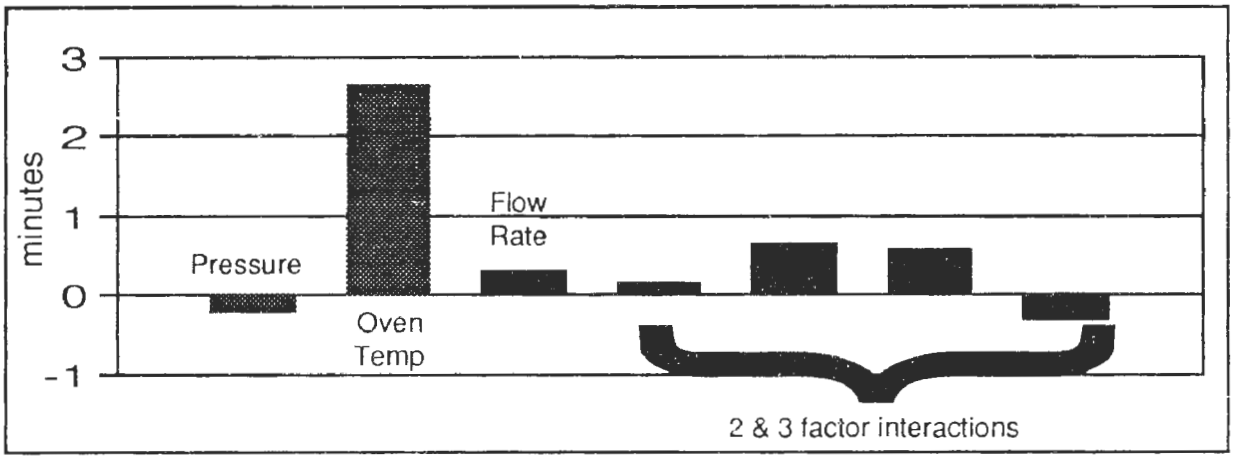


Figure 8. Dry Sample Factorial Design #2 Results

Table 6. Factorial Design #2 Parameters

Factor	Low Value	High Value	Best results with
Pressure	340 atm	500 atm	no effect
Oven Temperature	80°C	150°C	low
Flow Rate	600 mL/min CO_2 gas	3000 mL/min CO_2 gas	no effect

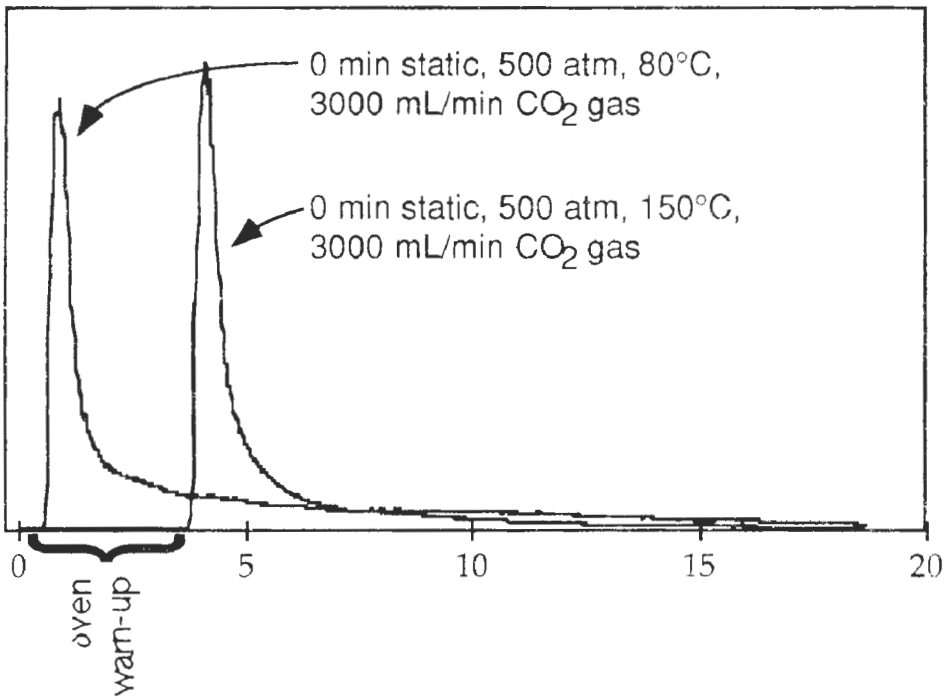


Figure 9. Extractogram Comparison - 80°C and 150°C

Wet Soil Matrixes

Wet matrixes present several problems for SFE. First, the moist soil particles stick together reducing sample exposure to the supercritical fluid. This may be solved by mixing an absorbent with the sample. Second, if the water is released from the sample during the extraction, the restrictor may plug. Restrictor plugging has been reduced or eliminated by the use of heated or variable restrictors. Lastly, the water may modify both the matrix and the supercritical fluid to help or hinder analyte extraction. Currently the modifier phenomenon is not as well understood.

Extractions of very wet soil samples (>30% moisture) at 340 atm, 80°C, 1.2 mL/min for 30 minutes have produced poor and erratic analyte recovery with some samples. NIST round robin samples were extracted wet and dry. Elevated temperature and flow were used to drive off the water and allow the extraction to proceed *normally* afterward. One gram soil and clay samples were extracted at 500 atm, 150°C, 10 min static, 10 min dynamic, 2000 mL/min CO_2 gas flow. The analyte trap was 0.5 g of Varian EnvirElut solid phase adsorbent. SFE Diesel recoveries compared well with Soxhlet extraction.

Wet clay was studied with a factorial design experiment to determine the effects of pressure, temperature and flow rate. Fuller's earth was spiked with motor oil (10,000 mg/kg). Water was added to make it 50% moisture. Four grams were used for each extraction. The dynamic extraction time was fixed at 25 minutes and percent recovery was measured. The factors and levels tested are shown in Table 7. Up to 1 mL of water was released from the wet clay and passed through the VariFlow restrictor. No plugging was encountered. The water then passed through the solid phase absorbant trap and was directed to a waste container. Since the trap was at ambient temperature, the water did not cause any problems. The effect of each factor is shown in Figure 10. Oven temperature and CO_2 flow rate had very dramatic effects. Higher temperature and flow increased percent recovery by about 25% each. Other experiments show that a 30 minute dynamic step is necessary to achieve 100% recovery with this sample. Those extractions that recovered the most motor oil also released the most water from the sample. Apparently the water *insulates* the sample from the supercritical fluid. Removing the water allows the extraction to proceed *normally*.

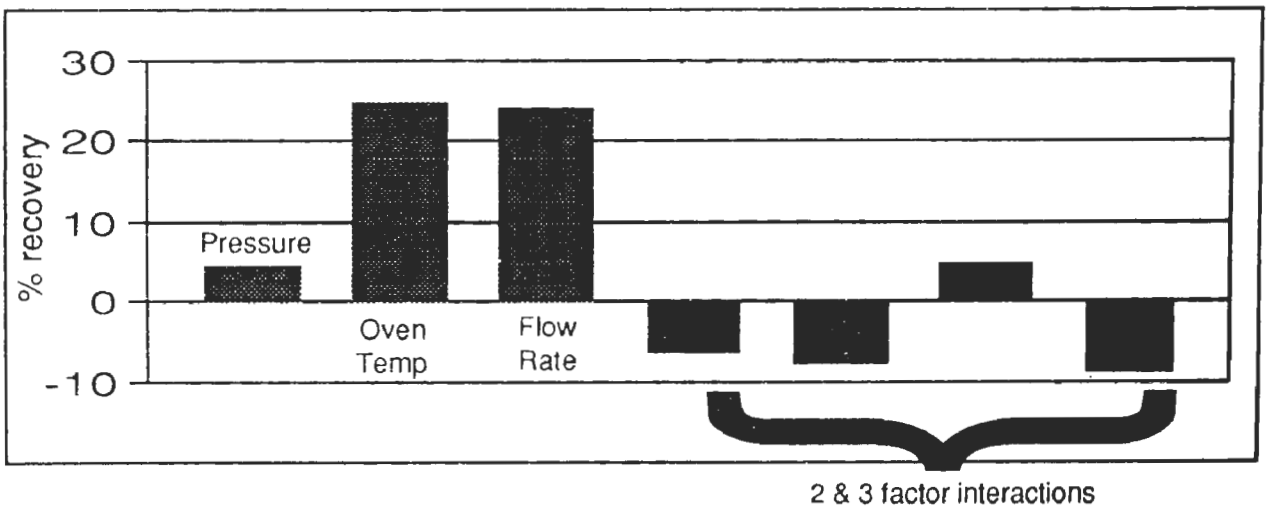


Figure 10. Wet Sample Factorial Design Results

Table 7. Wet Sample Factorial Design Parameters

Factor	Low Value	High Value	Best results with
Pressure	340 atm	450 atm	no effect
Oven Temperature	120°C	150°C	high
Flow Rate	2000 mL/min CO_2 gas	4000 mL/min CO_2 gas	high

SUMMARY

Tetrachloroethene and tetrachlorohexafluorobutane are acceptable analytical alternative solvents for Freon-113. The EPA has selected tetrachloroethene because it is not a chlorofluorocarbon. Hydrocarbons can be extracted accurately and reproducibly from many dry soil matrixes with *mild* extraction conditions. Extraction of many wet soil types requires high temperature, high flow rate,*waterproof* restrictor and a *waterproof* analyte trap.

ACKNOWLEDGEMENTS

3M, John Ruffing
Horiba Jim Vance
Midwest Research Institute, Viorica Lopez-Avila, Richard Young
Motter & Son Inc., William Motter
Rocky Mountain Analytical Laboratory, Marshall Tilbury
Suprex, Doug Koebler, Phil Hunsucker, Joel Fontaine, Joe Levy, Ray Houck, Jerry Wisser, Lori Dalatta, Athos Rosselli
Varian, Rex Hawley, Max Erwine
Wadsworth/ALERT, Edward Bruner, Katie Ritz, Leslie VanKuren, Chuck Jacobs, Bob Scafate, Brian Haueter, Russ Sommer, Brad Custer, Doug Stimson, Connie Schussler, Mike Paessun, Kim Davis

"Surely You have outdone Yourself!" I shouted to my partner in the lab.
George Washington Carver (complimenting his Lord on the many mysteries hidden in the peanut)

REFERENCES

1) Industrial Safety & Hygiene News, 01/88.

2) NASA's Innovators, NASA Tech Briefs Vol.15, No.4, 1991, pp.114.

56

USING A VACUUM CENTRIFUGE AS AN ALTERNATIVE TO KUDERNA-DANISH DISTILLATION, ROTARY EVAPORATORS AND NITROGEN BLOW DOWN

Bruce N. Colby and C. Steve Parsons, Pacific Analytical, 6349 Paseo Del Lago, Carlsbad, California 92009

Abstract: The vacuum centrifuge offers an alternative to Kuderna-Danish distillation, rotary evaporation and nitrogen blowdown as a means for reducing the solvent volume of environmental sample extracts. A vacuum centrifuge has been tested for reducing solvent volume in the analysis of 49 organochlorine pesticides and for 2,3,7,8-TCDD and 2,3,7,8-TCDF analyzed according to Method 8290. It provides a particularly effective mechanism for removing low volatility solvents such as toluene and acetonitrile, does not emit large quantities of solvent into the atmosphere and is easy and efficient to operate.

INTRODUCTION

Nearly all environmental methods for the determination of semivolatile organic compounds involve some form of solvent extraction. The resulting extracts are typically reduced in volume by about a factor of about 250 prior to sample cleanup and analysis. In general solvent volume is reduced using some combination of Kuderna-Danish (K-D) distillation, rotary evaporation and nitrogen blow down. Each of these techniques has advantages and disadvantages with respect to how well it performs and under what circumstances. K-D for example, is very effective with low boiling solvents such as methylene chloride (bp 40°C) and hexane (bp 69°C) but it is impractical when used with higher boiling solvents such as toluene (bp 111°C) or acetonitrile (bp 82°C).

When reducing the solvent volume of an environmental sample extract, several criteria must be taken into account. These include the required time and skill level required of the bench of the chemist, the potential for cross contamination of samples, the cost and space requirements of the equipment, the types and quantities of waste generated and any impact the process might have on the recovery of target analytes under investigation. As part of an ongoing effort to improve laboratory operations, a vacuum centrifuge was evaluated with respect to these considerations. Emphasis was given to the reduction of low volatility solvents, in particular acetonitrile and toluene, because these have proven the most challenging from a laboratory efficiency standpoint.

EXPERIMENTAL

The vacuum centrifuge tested was a Labconco Centrivap. It utilizes a 5 position sample head which rotates at 1800 rpm. Each position holds a 50 mL sample tube. It is evacuated using an Edwards 5.0 mechanical pump which generates a vacuum of 750 mm

Hg. All solvent vapors removed from the extracts are cryogenically trapped so solvents are neither lost into the laboratory air nor vented up a hood.

An acetonitrile solution containing 39 organochlorine pesticides (Table 1) at 0.1 ug/mL was tested first. Five 10 mL aliquots were reduced in the Centrivap as follows. After placing the sample vials in the centrifuge head, the vacuum pump and rotor were turned on. After 15 minutes, the device was stopped and the solvent level was checked. If solvent remained, another 15 minute cycle was initiated. This process was repeated until the samples had been taken to dryness. The total time required was 55 minutes. After solvent reduction, 10 mL of toluene was added to each sample tube, then the tube was capped and votexed for 30 sec. A 1 mL aliquot was placed in an autoinjector vial for analysis by GC-ECD (HP 5890). An aliquot of blank solvent was concentrated and analyzed in the same manner. Percent recoveries were calculated for each analyte.

A toluene solution was spiked with 2,3,7,8-TCDD and 2,3,7,8-TCDF at 0.1 ng/mL. Five 10 mL aliquots were reduced in the Centrivap as described for acetonitrile. After solvent reduction, 1 mL of toluene was added to each sample tube, then the tube was capped and votexed for 30 sec. A 10 uL aliquot was then transferred to a micro-autosampler and 10 uL of internal standard solution was added. The contents of the vial were analyzed by HRGC/HRMS (VG 70VSE). An aliquot of blank solvent was concentrated and analyzed in the same manner. Percent recoveries were calculated for both analytes.

RESULTS AND DISCUSSION

Acetonitrile is particularly useful solvent for extracting pesticides from soils, sediments and sludges and from tissues. However, because it boils at 82°C, it is not practical to carry out solvent volume reduction via Kuderna-Danish (K-D) distillation using a water bath as the heat source. It is possible to use a heating mantle in place of the water bath but the higher temperatures causes some of the pesticides to decompose. Consequently, acetonitrile has always been reduced in volume via nitrogen blow down or rotary evaporator. Nitrogen blowdown is very time consuming and produces a waste stream which contaminates the atmosphere. Rotary evaporation is less time consuming, does not contaminate the atmosphere but is prone to cross contamination if the solvent flashes. It is also expensive and space intensive if multiple units are required to achieve thruput.

When acetonitrile was reduced in volume using the Centrivap, the time requirement is very similar to that of rotary evaporation but multiple samples can be processed at one time. Also, because of the centrifugal forge created by spinning the sample, flashing is not a problem. Further, because no heat is used, decomposition of the thermally labile pesticides is not encountered.

The recoveries experienced for chlorinated pesticides (Table 1) indicated that six of the more volatile analytes, dichlorbenil, alpha-BHC, PCNB, gamma-BHC, heptachlor and aldrin, were being partially lost, most likely through vaporization. These six analytes also

generated precisions which were two to three times worse than those of the other analytes. In an attempt keep the six problem compounds in the sample vial, a 10 uL aliquot of a keeper solvent was added prior to reduction. Nonane and cyclohexanol were tested as keepers. The average recovery values were little changed as a consequence of adding the keeper solvents but precision improved for most of the more volatile analytes (Table 2). No target analytes were detected in any of the blanks.

Experiments are currently underway to determine the effectiveness of less powerful vacuum pump (higher pressure) as a means to control losses with the more volatile analytes.

The other solvent tested, toluene, is used for extracting chlorinated dioxins (PCDDs) and furans (PCDFs) from solid media. It boils at 111°C so K-D using a water bath is out of the question. Heating mantles could be used to generate the required temperature but, even though the PCDDs and PCDFs do not thermally decompose to any noticeable degree at this temperature, the potential for creating dioxin contaminated wastes as a consequence of glassware washing keeps K-D from being desirable. Consequently, the rotary evaporator has been the technique of choice.

When the vacuum centrifuge is used to remove toluene from dioxin containing extracts, excellent recovery and precision were encountered (Table 3). No dioxins or furans were detected in the blank and after six months of operation with dioxin sample preparations, no cross contamination or blank levels have been noted.

SUMMARY

The vacuum centrifuge is an effective and efficient means for removing high boiling solvents such as toluene and acetonitrile from sample extracts. It is particularly useful for dioxin analysis where waste generation and cross contamination are minimized. It is less effective for applications involving more volatile analytes such as some of the early eluted organochlorine pesticides.

Table 1 - Pesticide Percent Recoveries

Pesticide	R1	R2	R3	R4	R5	Mean	%sd
Dichlorbenil	33	14	8	46	42	29	15.1
Ethalfluralin	88	93	95	101	101	96	5.0
Ben/Trifluralin	89	97	97	106	103	98	5.9
BHC, alpha-	85	77	74	53	42	66	16.1
PCNB	57	35	76	29	23	44	19.7
Vegadex	87	95	96	87	88	91	4.0
BHC, gamma-	90	89	84	74	66	81	9.2
Profluralin	89	100	100	103	102	99	5.0
Heptachlor	71	43	76	49	51	58	13.0
Pronamide	90	96	97	97	102	96	3.8
Aldrin	73	36	73	49	51	56	14.5
Chlorothalonil	99	94	99	99	99	98	2.0
Alachlor	101	98	100	117	113	106	7.7
Vinglozolin	85	95	99	100	98	95	5.5
BHC, delta-	98	103	98	95	98	98	2.6
Dacthal	101	88	98	97	96	96	4.3
Heptachlor Epoxide	99	85	94	94	90	92	4.7
Triadimefon	93	117	109	111	110	108	8.0
Endosulfan I	100	89	96	96	94	95	3.6
Chlordane, gamma-	99	99	96	95	97	97	1.6
Chlordane, alpha-	98	95	97	97	98	97	1.1
DDE	100	84	96	96	97	95	5.5
Dieldrin	103	91	98	98	97	97	3.8
Endrin	101	101	102	100	102	101	0.7
Perthane	99	93	95	103	96	97	3.5
Folpet	105	96	101	100	104	101	3.2
Oxadiazon	103	97	101	101	105	101	2.7
Nitrofen	93	113	101	92	94	99	7.9
Dyrene	97	98	101	103	104	101	2.7
Chlorobenzilate	103	91	98	99	103	99	4.4
Endosulfane II	104	97	102	99	102	101	2.5
DDD	102	92	100	102	104	100	4.2
Oxyfluorfen	121	119	117	113	127	119	4.6
DDT	105	101	102	102	102	102	1.4
Endosulfan Sulfate	103	98	100	101	104	101	2.1
Methoxychlor	102	101	103	103	104	103	1.0
Iprodione	107	94	97	100	100	100	4.3
Tetradifon	107	101	106	106	105	105	2.1
Bifenox	100	100	102	102	102	101	1.0

Table 2 - Precision (%sd) With and Without Keeper Solvents

Pesticide	Acetonitrile	w/Nonane	w/Cyclohexanol
Dichlorbenil	59.0	45.2	9.9
Ethalfluralin	5.8	4.9	11.8
Ben/Trifluralin	6.6	9.9	5.1
BHC, alpha-	27.1	25.5	6.2
PCNB	50.1	34.9	5.4
Vegadex	5.0	6.8	10.4
BHC, gamma-	12.8	9.7	7.4
Profluralin	5.7	2.3	6.3
Heptachlor	25.1	13.8	7.7
Pronamide	4.4	3.6	5.5
Aldrin	28.7	14.1	5.7
Chlorothalonil	2.3	6.3	8.8
Alachlor	8.1	7.5	5.2
Vinglozolin	6.4	6.3	8.8
BHC, delta-	2.9	2.0	4.7
Mean	16.7	12.8	7.3

Table 3 - Chlorinated Dioxin and Furan Recoveries

Analyte	R1	R2	R3	R4	R5	Mean	%sd
2,3,7,8-TCDD	100	102	117	96	102	103	7.7
2,3,7,8-TCDF	100	113	120	106	101	108	7.8

57 AN INTERLABORATORY EVALUATION OF A METHOD TO EXTRACT TOTAL PETROLEUM HYDROCARBONS FROM SOLID SAMPLES USING SUPERCRITICAL CARBON DIOXIDE

ORGANIC

Werner F. Beckert, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119, and Viorica Lopez-Avila, Midwest Research Institute, California Operations, Mountain View, California 94043.

ABSTRACT

EPA SW-846 Method 9073 for the determination of total recoverable petroleum hydrocarbons (TPHs) specifies infrared (IR) analysis of extracts prepared from the samples using Freon-113. Soil samples are subjected to Soxhlet extraction with Freon-113, according to Method 9071A, followed by silica gel cleanup of the extract to remove interferences. Since production and use of Freon-type materials are being phased out, a new extraction method is needed. The replacement solvent may not be of the Freon-type, and it also must not contain any C-H bonds or other bonds that would interfere with the IR determination of the petroleum hydrocarbons. Furthermore, since the parameter of total recoverable petroleum hydrocarbons is operationally defined by the method (i.e., Method 9073), the new solvent should show the same or very similar extraction efficiencies for TPHs.

We and others have reported that carbon dioxide, under supercritical conditions(supercritical fluid extraction - SFE), is a good extraction medium for hydrocarbons from soil samples. We have demonstrated for a limited number of solid matrices that extraction of TPHs from soil samples with supercritical carbon dioxide gives recoveries that are similar to those obtained with Freon-113 using Soxhlet extraction. The SFE collection solvent found to be most suitable as a replacement for Freon-113 was tetrachloroethylene, which is transparent in the IR region of interest.

This new method is now being subjected to a multilaboratory evaluation study. Fifteen volunteer laboratories are participating in this study. They will each extract nine solid samples, three of them in triplicate, and mail the fifteen extracts to the lead laboratory, MRI - California Operations, for IR analysis. Both carbon dioxide and tetrachloroethylene will be provided to the participating laboratories to assure that all laboratories are using solvents of the same quality.

The results of the studies will be evaluated according to standard procedures, and the results will be reported at the symposium.

58

CONCENTRATION OF WATER SOLUBLE VOLATILE ORGANIC COMPOUNDS FROM SOLID SAMPLES BY AZEOTROPIC MICRODISTILLATION

Mark L. Bruce, Director of Research and Development, Rita Tomayko, GC Specialist and Marvin W. Stephens, Technical Director, Wadsworth/ALERT Laboratories, Division Of Enseco, Inc., 4101 Shuffel Dr. N.W., North Canton, Ohio 44720

ABSTRACT

Azeotropic distillation has been used to effectively concentrate alcohols and other water soluble volatile organic compounds from aqueous samples. This method has been modified for use with solid samples. Water extraction of the solid sample is combined with distillation of the volatile components from the aqueous extract. The distillation also functions as a cleanup. Most nonvolatile and semivolatile sample components will not be transferred to the distillate. This greatly reduces the contamination of the GC injection port and chromatographic column. Total extraction and distillation time is less than 15 minutes. Concentration factors are typically one order of magnitude with a 5 g sample.

INTRODUCTION

Currently methanol and other water soluble volatile organic compounds in solid matrixes are extracted with water then analyzed by direct injection of the sample extract or purge-and-trap, followed by gas chromatographic separation and detection. For many compounds the method detection limits are not low enough to meet client needs. The overall method response of the alcohols in particular is poor for direct aqueous extract injection and purge-and-trap.

A microdistillation system was developed to address the shortcomings of direct aqueous extract injection and purge-and-trap. The Wadsworth MicroVOC^3 was developed at Wadsworth/ALERT Laboratories and currently is manufactured and sold by Shamrock Glass of Seaford, Delaware. VOC^3 is an acronym for Volatile Organic Compound Concentration and Cleanup. The microVOC^3 has been described in detail previously (1,2). The system is shown in Figure 1.

Fractional factorial experimental designs have been used extensively through the optimization process. Factorial design is a statistical procedure which estimates the effect of each factor as well as interactions. EPA SW-846 Method 8015 (modified) was used for analysis.

INSTRUMENTATION, EQUIPMENT AND SUPPLIES

Gas Chromatograph/Data System
- Hewlett Packard 5890 equipped with a flame ionization detector

Gas Chromatography Columns
- Quantitation: RTX-Volatile, 30 m X 0.53 mm I.D.

Hardware
- Wadsworth MicroVOC^3 System®, Shamrock Glass (see Figure 1.)
  - Round bottom flask, 100 ml , 14/20 joint
  - Fractionation column, 14/20 joint, 1.6 cm O.D., 1.3 cm I.D., 60 cm in length
  - Pipe insulation, polyurethane foam, $1^1/_2$" O.D., $^5/_8$" I.D., 55 cm in length

Glass beads, 5 mm O.D.
Keck clamps, for 14/20 ground glass joint
Glass reducing union, 14/20 ground glass joint to 6 mm O.D. tube
Stainless steel reducing union, $^1/_{16}$" to $^1/_4$"
Air condenser, Teflon® tubing, $^1/_{16}$" O.D., $^1/_{32}$" I.D. (40 cm in length)
GC autosampler vials
Autosampler vial inserts, 100 µl, calibrated
Graduated cylinder, 50 ml
Support stand with rod, 1 meter
Three-finger clamp
Heating mantle, Glas-Col, 115 volts, 230 watts, STM 400
Temperature controller, Glas-Col PL115-Cordtrol, 115 volts, 600 watts
Porous carbon boiling chips, VWR cat # 26397-409

Reagents and Standards
Ethanol, Everpure, 200 proof
Methanol, B&J Brand, purity 99.9%
1-Propanol, Baxter, purity 99%
2-Methyl-1-propanol, Aldrich, purity 99.9%
1-Butanol, Aldrich, purity 99.8%
1,4 Dioxane, Aldrich
Acetonitrile, Aldrich, purity 99.9%
Propionitrile, Aldrich, purity 99%
Acrolein, Aldrich, purity 97%
Acrylonitrile, JT Baker, purity 99%
Ethyl Acetate, Aldrich, purity 99%
Reagent water, deionized

METHOD SUMMARY

The azeotropic microdistillation method is summarized in Figure 2. A 5 g aliquot of sample is transferred to a round bottom flask. Internal standard(s) are added to the sample followed by 40 mL of reagent water. The distillation apparatus is assembled using Keck clamps at both ground glass joints after insuring that the fractionation column and air condenser are completely dry and at room temperature. The sample is heated to the boiling point. The first 100 µl of distillate are collected in a microvial for analysis by GC-FID. All calibration standards are distilled in the same manner as samples to compensate for system bias since the absolute recoveries of analytes are typically less than 50%. This calibration procedure is analogous to purge-and-trap calibration procedures.

METHOD OPTIMIZATION

The key parameters to optimize were sample weight, reagent water volume and heat input (ie the reostat setting). Initial experiments evaluated the benefit of performing the initial water extraction at a low heat input setting and followed by a quick distillation similar to the method for aqueous samples.

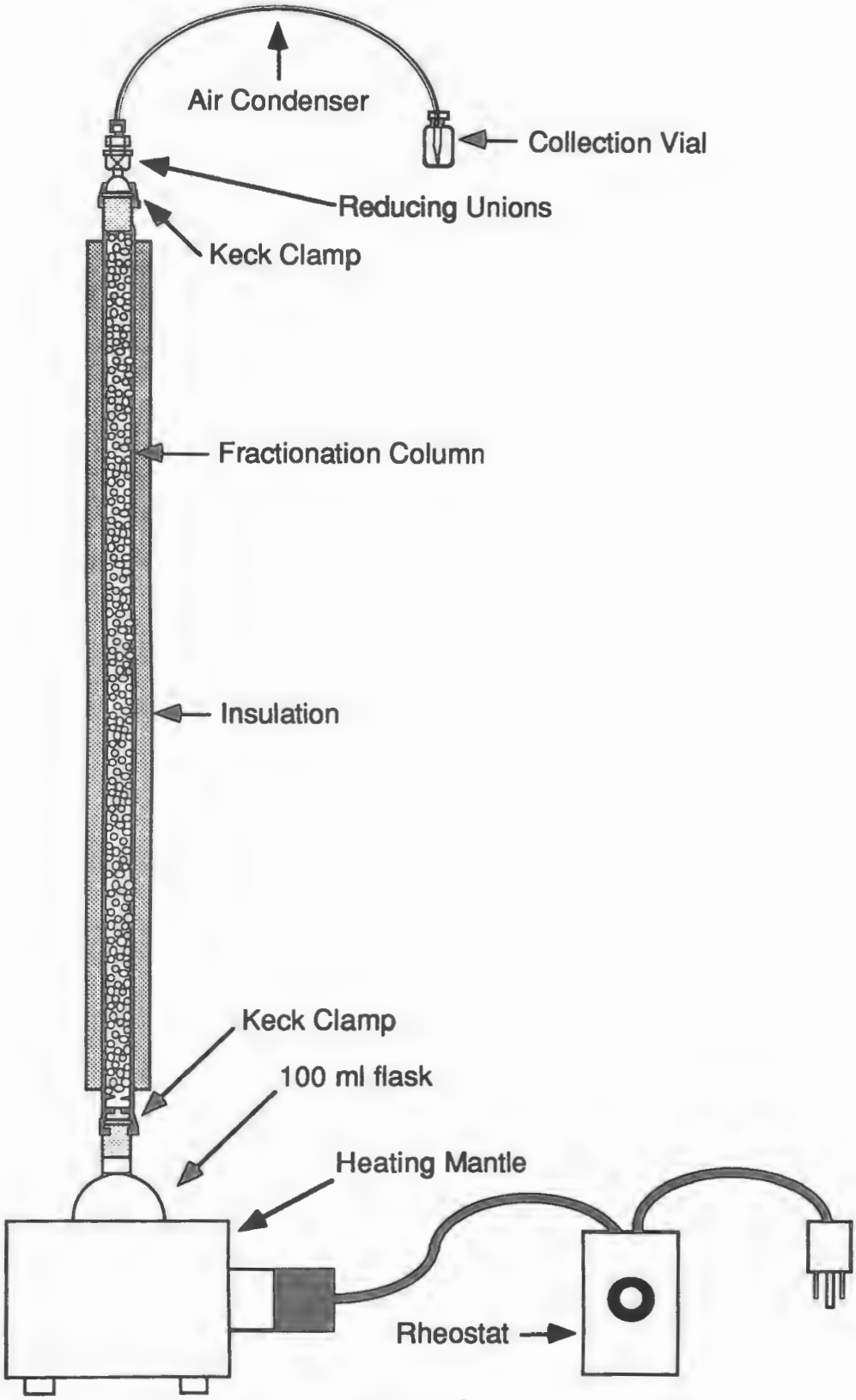


Figure 1. MicroVOC^3 distillation system

The initial factorial design set of experiments with methanol spiked loam and clay samples indicated that 20 mL of water was better than 40 mL. Also a hotter water extraction was better. The second set of factorial experiments showed better performance with 10 mL of water and a higher boiling rate. Methanol spiked incinerator ash samples were used. The third factorial set demonstrated that 10 mL of water was not enough for some very absorptive matrixes such as dry incinerator sludge. The fourth factorial design used "native" methanol in both incinerator sludge and ash. The water volume effect was exactly the opposite of what had been measured before with matrix spiked methanol. More water (40 mL vs 15 mL) was much better. As expected "native" analytes behaved differently than spiked analytes. Apparently extracting the methanol from the solid matrix was more difficult than distilling the methanol from the water extract. Thus, using more water improved the extraction more than it hurt the distillation. Heating at the higher heat input setting was also more efficient. Presumably the higher temperature improved the water extraction step. Final optimized parameters will be presented.

Data for the following compounds will be presented: methanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 1,4-dioxane, acetonitrile, propionitrile, acrolein, acrylonitrile and ethyl acetate. Various solid matrixes have been studied. New internal standards are being investigated since ethanol (the internal standard from the aqueous version of the method) has been added to the analyte list.

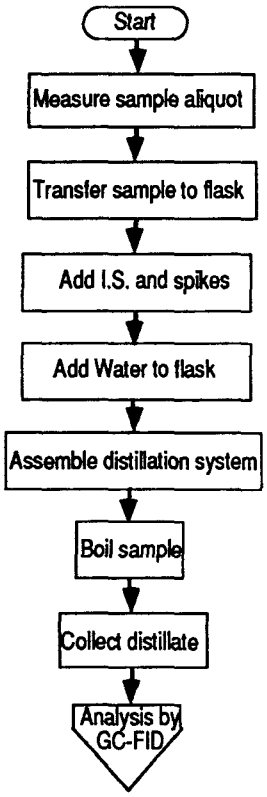


Figure 2.
Method Summary

CONCLUSION

The microdistillation system (Wadsworth MicroVOC[3]) has been used extensively for aqueous matrixes. The water method has been modified for use with solid matrixes. Small sample aliquots are required (5 g). Analyte concentration factors are about one order of magnitude when a 5 g sample aliquot is used. The total extraction and distillation time is less than 15 minutes.

REFERENCES

1) Bruce, M.L., Lee, R.P., Stephens, M.W., Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation, Seventh Annual Waste Testing and Quality Assurance Symposium Proceedings Vol II, p. 2, 1991

2) Bruce, M.L., Lee, R.P., Stephens, M.W., Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation, ES&T, 26 (1), pp. 160-163, 1991.

59 GC/MS IDENTIFICATION OF ARTIFACTS FORMED DURING SAMPLE PREPARATION USING EPA METHODS 625 AND 8270

Paul H. Chen, William A. VanAusdale, W. Scott Keeran and Dwight F. Roberts, Analytical Services Division, Environmental Science and Engineering, Inc., P.O. Box 1703, Gainesville, Florida 32602-1703

ABSTRACT

In EPA Methods 625 and 8270 samples are generally analyzed for the target compound list (TCL) components by an automated data system and for non-TCL components by a library search. Non-TCL components identified and reported as tentatively identified compounds (TIC) are rarely verified and sometimes incorrect information is reported. This incorrect information includes incorrect compound identification, contamination in the lab or during sampling, and artifacts produced during sample preparation. The purpose of this study was to identify the artifacts formed during sample preparation using EPA Methods 625 and 8270. During our analysis of thousands of samples we have identified thirty-three artifacts formed by the following reactions: I. Oxidation of phenolic surrogates and phenolic target analytes: Three oxidation products of phenolic surrogates were reported by us two years ago at this symposium. We report here the identification of oxidation products of some phenolic target analytes. The compounds identified include benzoquinone, chlorobenzoquinone, 2,6-dichlorobenzoquinone, 2,6-dichlorohydroquinone, and tetrachlorohydroquinone. II. Halogenation or nitration of phenolic surrogates: The compounds identified include 2- and 4-chlorophenols-d4, 2- and 4-bromophenols-d4, 2-nitrophenol-d4, 4-chloro-2-fluorophenol, 4-bromo-2-fluorophenol, and 4-nitro-2-fluorophenol. III. Reaction of preservative cyclohexene in methylene chloride with halogens to form halogenated cyclohexanols, cyclohexanes, and cyclohexenes: Ten of these artifacts were identified, five of them were major compounds and were reported elsewhere. Five minor compounds identified in this study are 3-chlorocylohexene, 3-bromocyclohexene, 2-chlorocyclohexanol, 1,2-dichlorocyclohexane, and 1-bromo-2-iodocyclohexane. IV. Autoxidation of cyclohexene: Cyclohexene oxide (7-oxabicyclo[4.1.0]heptane), 2-cyclohexen-1-ol, and 2-cyclohexen-1-one are often present in the extract. 1-Formylcyclopentene and 1,2-cyclohexanediol are found sometimes. V. Reaction of cyclohexene with methylene chloride degradation products: 2-Chlorocyclohexanol was identified. VI. Aldol condensation of acetone: 4-Hydroxy-4-methyl-2-pentanone and 4-methyl-3-penten-2-one were found. If these compounds are found in the sample, they should be labeled as artifacts and not considered as contaminants in the site with a possible exception of 4-hydroxy-4-methyl-2-pentanone and 4-methyl-3-penten-2-one which might be present in the sample before extraction.

INTRODUCTION

EPA Methods 625 (1) and 8270 (2) are widely used in environmental laboratories for the analysis of semivolatile organics by GC/MS. In these methods samples are generally analyzed for the target compound list (TCL) components by an automated data system and for non-TCL components by a forward library search of a published mass spectral data base (3). The results of TCL components analysis are generally accurate. However, non-TCL components identified and reported as tentatively identified compounds (TIC) are rarely verified and sometimes incorrect information is reported. This incorrect information includes incorrect compound identification, contamination in the lab or during sampling, and artifacts produced during sample preparation. Though artifacts should be reported to the client, it is important that they should be labeled as artifacts and not considered as contaminants in the site. Artifacts formed during extraction of brine samples with cyclohexene-inhibited methylene chloride were reported by Campbell et al. (4) and Fayad (5). We reported earlier (6,7) artifacts formed by oxidation of phenolic surrogates during acid extraction of water samples using EPA Method 625. The purpose of this study was to identify the artifacts formed during sample preparation using EPA Methods 625 and 8270.

EXPERIMENTAL SECTION

Sample Preparation. Water samples were extracted at pH>11 and then at pH<2 with methylene chloride according to EPA Method 625 (1). Soil samples were extracted with methylene chloride in Soxhlet extractors according to EPA SW-846 Method 3540/8270 (2). Before extraction, each sample was spiked with 1.0 mL of surrogate spiking solution which contains 100 µg/mL each of acid surrogates (2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol) and 50 µg/mL each of base/neutral surrogates. Methylene chloride extract was concentrated to 1 mL with Kuderna-Danish concentrator and analyzed by GC/MS.

GC/MS Analysis. Samples were analyzed on a HP 5988 GC/MS system. The column used was a 30m x 0.25 mm i.d. DB-5 (0.25µm coating) fused silica capillary column (J&W Scientific, Folsom, CA). The column temperature was held isothermal at 40°C for 4 minutes and then programmed at 10°C per minute to 280°C, and held isothermal at this final temperature for 12 minutes. The mass spectrometer was scanned from 35 to 500 amu per half second. The extract was spiked with a mixture of six internal standards before GC/MS analysis according to CLP protocol (3). A forward library search was performed for non-TCL compounds on a Wiley/NBS data base which contains 139000 different spectra (8). Compounds were tentatively identified by library searches or by elucidation of the com-

pound structure from its mass spectrum if no match was found in the library. The tentatively identified compounds were confirmed by the agreement of mass spectra and retention times between the sample component and the authentic compound.

RESULTS AND DISCUSSION

Three oxidation products of phenolic surrogates were reported by us two years ago at this symposium (6). The mass spectra of these three compounds are reproduced in Figures 1A to 1C. We report here the identification of oxidation products of some phenolic target analytes. The compounds identified include p-benzoquinone, 2-chloro-p-benzoquinone, and 2,3,5,6-tetrachlorohydroquinone which are oxidation products of phenol, 2-chlorophenol, and pentachlorophenol, respectively. The mass spectra of these three oxidation products are shown in Figures 1D to 1F. These compounds were found in some matrix spike samples which were spiked with five phenolic matrix spike compounds according to CLP protocol (3). When the samples which contained the oxidizing agents (7) were spiked with the complete list of 14 phenolic target analytes (3), 2,6-dichloro-p-benzoquinone and 2,6-dichlorohydroquinone were also found. The mass spectra of these two compounds are displayed in Figures 1G and 1H. These two oxidation products are probably from the oxidation of 2,4,6-trichlorophenol.

The three acid surrogates used in the EPA methods for the semivolatile organics analysis are phenolic compounds. The phenolic group activates the aromatic ring toward electrophilic substitution at ortho and para positions of the ring. Therefore, it is not surprising to find some artifacts formed during extraction by halogenation or nitration of the phenolic surrogates. The artifacts found in the samples are 2-chlorophenol-d4, 4-chlorophenol-d4, 2-bromophenol-d4, 4-bromophenol-d4, 2-nitrophenol-d4, 4-chloro-2-fluorophenol, 4-bromo-2-fluorophenol, and 4-nitro-2-fluorophenol. Their mass spectra are shown in Figures 2A to 2H.

Methylene chloride is the solvent used in the extraction of samples for both EPA Methods 625 and 8270. Cyclohexene is added to methylene chloride by the manufacturer (Burdick & Jackson) as a preservative and scavenger (4,5). The brand of methylene chloride we used (B&J Brand™) is most widely used in the environmental labs. A number of artifacts are formed by autoxidation (9) of cycloexene and by the reaction of halogens with cyclohexene in the presence of halogens or halides and oxidizing agents in the samples. The most common artifact formed by autoxidation during sample preparation using cyclohexene -inhibited methylene chloride is cyclohexene oxide (7-oxabicyclo[4.1.0]heptane).

2-Cyclohexene-1-ol and 2-cyclohexen-1-one, and to a lesser extent, 1-formylcyclopentene and 1,2-cyclohexanediol are also often found in the extract. The mass spectra of the artifacts from autoxidation of cyclohexene are shown in Figures 3A to 3E.

A number of halogenated cyclohexanols, cyclohexanes, and cyclohexenes are found in samples which contain halogens or halides and extracted with cyclohexene-inhibited methylene chloride. These artifacts are usually formed during extraction at acidic conditions (7). The most common artifact found is 2-iodocyclohexanol. In addition to 2-iodocyclohexanol, 1-chloro-2-iodocyclohexane, and to a lesser extent, 2-bromocyclohexanol are sometimes found in the samples. In high salinity or brine samples, we found large amounts of 2-bromocyclohexanol, 1-bromo-2-chlorocyclohexane, 2-iodocyclohexanol, 1,2-dibromocyclohexane, and 1-chloro-2-iodocyclohexane (7) (see Figure 4 for the mass spectra of these compounds). Similar findings were reported by Campbell et al. (4). A much smaller amount of 3-chlorocyclohexene, 3-bromocyclohexene, 2-chlorocyclohexanol, 1,2-dichlorocyclohexane, and 1-bromo-2-iodocyclohexane was also found in the brine sample. 2-Chlorocyclohexanol was sometimes formed by the reaction of cyclohexene with the degradation products of methylene chloride. This is supported by the presence of a substantial amount of 2-chlorocyclohexanol in some methylene chloride which has not been used in the extraction of samples.

If acetone is present in the sample, the aldol condensation product of acetone, 4-hydroxy-4-methyl-2-pentanone, and its dehydration product, 4-methyl-3-penten-2-one, are often formed during extraction. These two compounds may also be present in samples before extraction. The mass spectra of these two artifacts are shown in Figure 5. Extraction of soil by sonication (SW-846 Method 3350) using acetone/methylene chloride as a mixed solvent generates a number of other aldol condensation products in addition to the two artifacts mentioned above.

In summary, thirty-three artifacts formed during sample preparation were reported in this study. We plan to put the mass spectra of these compounds in a library which can be searched routinely. If these compounds are found in the sample extracted with cyclohexene-inhibited methylene chloride, they will be labeled as artifacts and would not be considered as contaminants in the site with possible exception of 4-hydroxy-4-methyl-2-pentanone and 4-methyl-3-penten-3-one which might be present in the sample before extraction. Among the thirty-three artifacts, the mass spectra of the following thirteen compounds are not in the 1989 Wiley/NBS Registry of Mass Spectra Data (8): p-benzoquinone-d4, 2-fluoro-p-benzoquinone, 2,6-dibromohydroquinone, 2,6-dichlorohydroquinone, 4-chlorophenol-d4, 2-bromophenol-d4, 4-bromophenol-d4, 4-chloro-2-fluo-

rophenol, 4-bromo-2-fluorophenol, 4-nitro-2-fluorophenol, 2-iodocyclohexanol, 1-bromo-2-iodocyclohexane, and 1-chloro-2-iodocyclohexane.

ACKNOWLEDGMENTS

We thank P. Dumas and his department for extracting the samples and D. Schindler and C. Diaz for their assistance in GC/MS analysis.

REFERENCES

1. EPA 40 CFR Part 136 Fed. Regist., 1984, 49 (No. 209).

2. USEPA Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition, 1986.

3. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, 1988.

4. Campbell, J. A.; LaPack, M. A.; Peters, T. L.; Smock, T. A. Environ. Sci. Technol. 1987, 21, 110.

5. Fayad, N. M. Environ. Sci. Technol. 1988, 22, 1347.

6. Chen, P. H.; VanAusdale, W. A.; Roberts, D. F. Proceedings of Sixth Annual Waste Testing and Quality Assurance Symposium, 1990, Vol. II, 142.

7. Chen, P. H.; VanAusdale, W. A.; Roberts, D. F. Environ. Sci. Technol., 1991, 25, 540.

8. McLafferty, F. W.; Stauffer, D. B. The Wiley/NBS Registry of Mass Spectral Data, Wiley: New York, 1989.

9. Pryor, W. A. Free Radicals, McGraw-Hill: New York, 1966; p. 288.

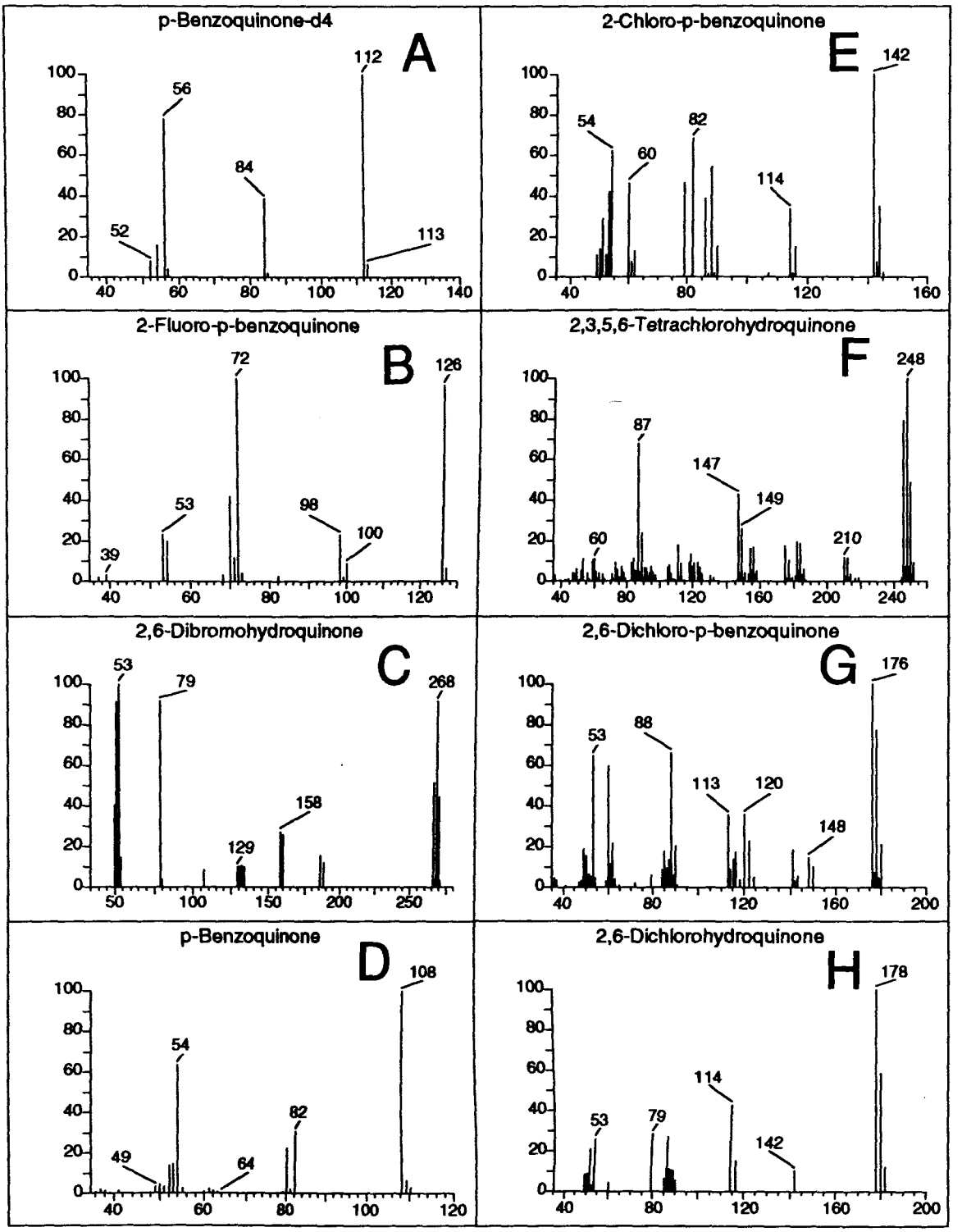


Figure 1. Mass spectra of artifacts from oxidation of phenolic surrogates and target analytes.

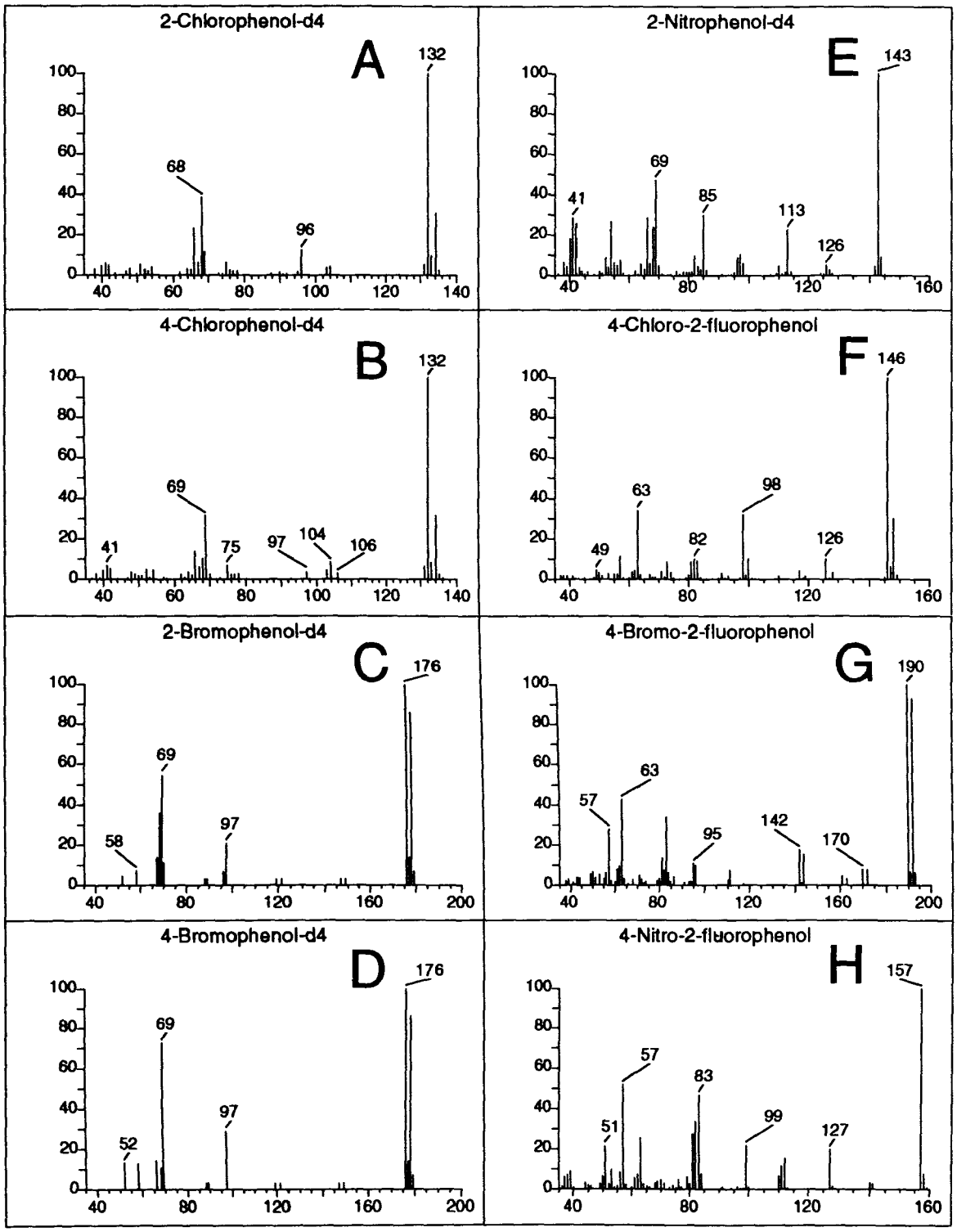


Figure 2. Mass spectra of artifacts from halogenation or nitration of phenolic surrogates.

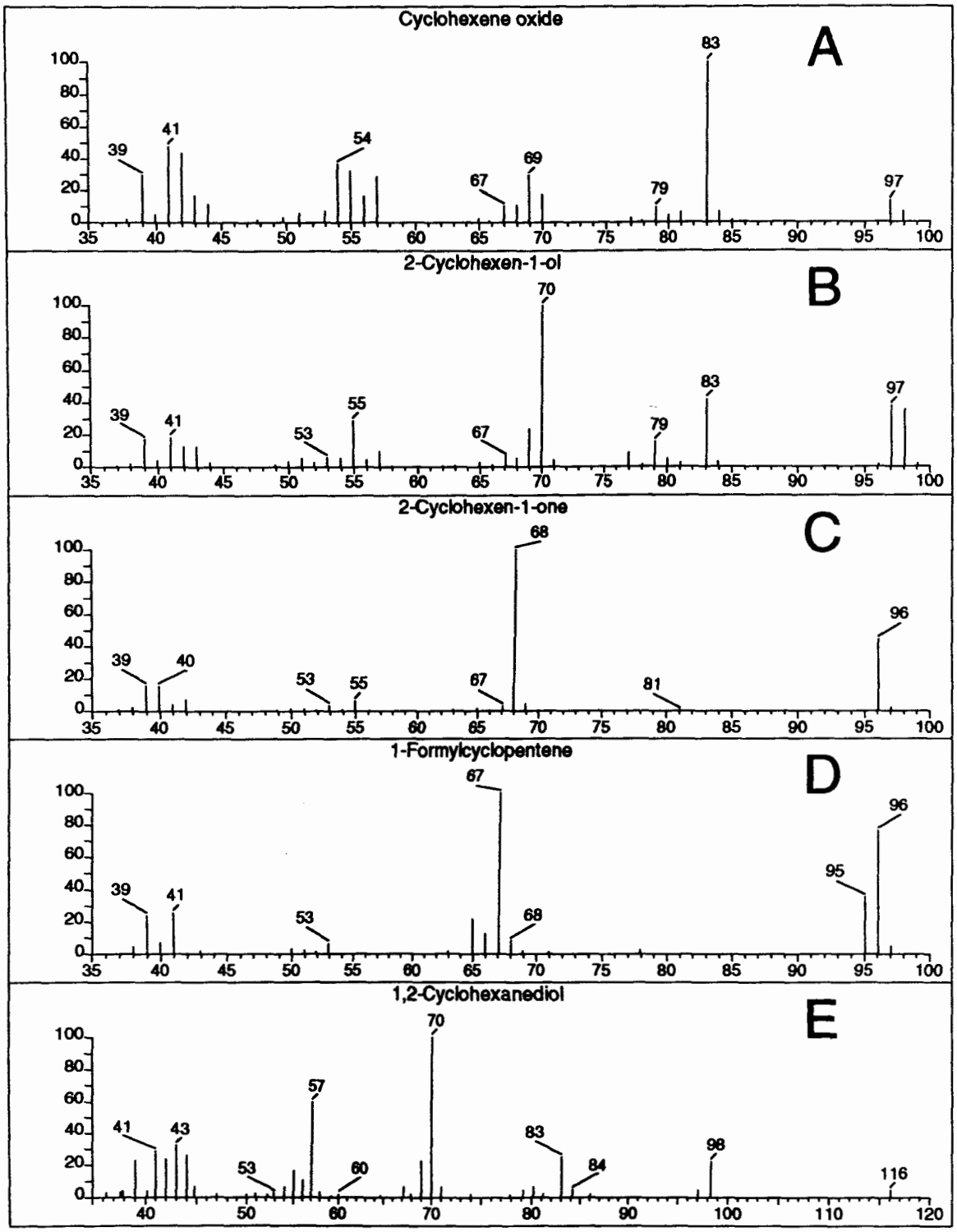


Figure 3. Mass spectra of artifacts from autoxidation of cyclohexene present in the methylene chloride used for extraction.

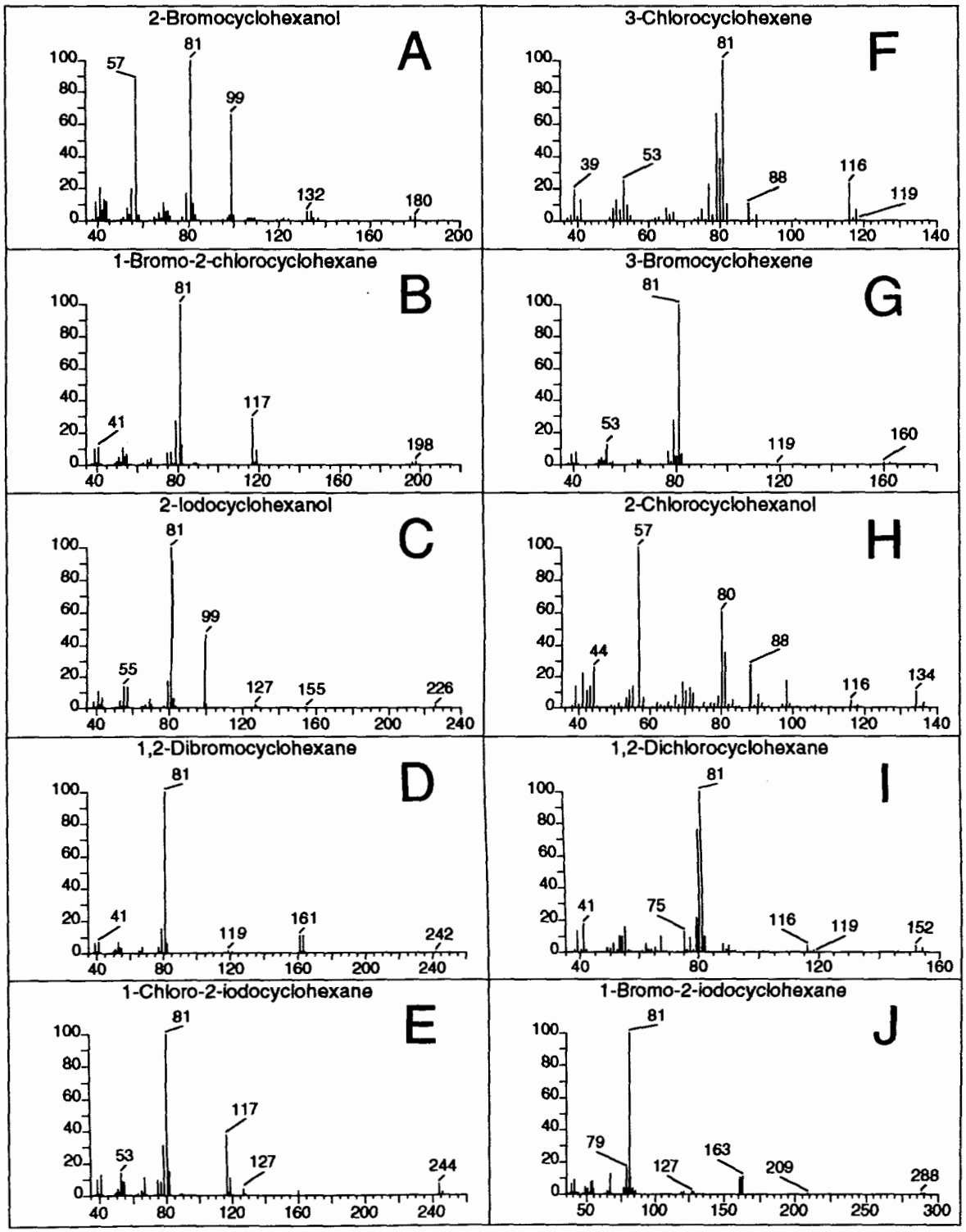


Figure 4. Mass spectra of artifacts from reaction of halogens with cyclohexene present in the methylene chloride used for extraction.

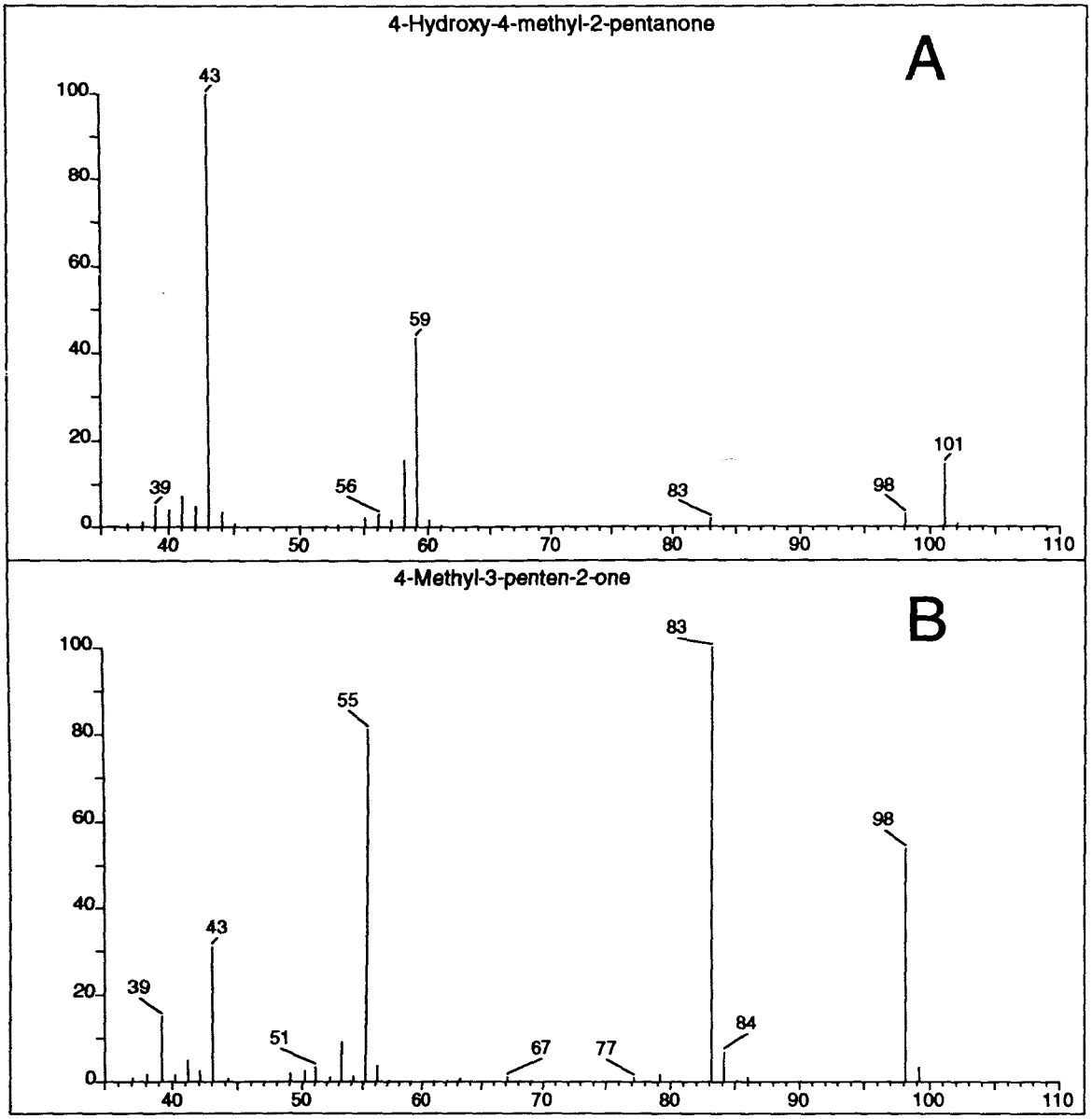


Figure 5. Mass spectra of two common aldol condensation products of acetone.

60

ANALYSES OF 2,4-D, 2,4,5-T, AND SILVEX IN HAZARDOUS WASTES AND TCLP EXTRACTS USING HPLC

Charles R. Hecht, Senior Analytical Chemist, Frank Thomas, Senior Scientist, John W. Kolopanis, Director of Analytical Programs, Chemical Waste Management, Inc., 150 West 137th Street, Riverdale, Il. 60627

ABSTRACT

Reversed phase HPLC coupled with ultraviolet detection has been used for the analysis of chloropheoxy herbicides for many years, and proven to be a sound analytical technique. Numerous applications have been researched and well documented in the technical journals.

The use of HPLC and the consequent ability to analyze these herbicides in the free acid form leads to a significant cost and time savings. Current methodology using SW-846 Method 8150 requires a series of lengthy ether extractions, followed by a K-D concentration and caustic hydrolysis, followed by further ether extractions and K-D concentration. Diazomethane esterification is then needed before gas chromatographic analysis can be done. Typically 8 samples require 2 days by a single analyst for the complete extraction, hydrolysis, derivatization and GC cycle. Additionally, there are major health and safety concerns with the use of ether and diazomethane.

A streamlined analyses was developed for 2,4-D, 2,4,5-T, and silvex using a simple two hour potassium hydroxide hydrolysis followed by acidification and a four minute reversed phase HPLC analysis. This method was evaluated on a number of hazardous waste matrices including wastewater, contaminated soils, oils, waste solvents, ash, sludges, and TCLP extracts. Typically 16 samples or TCLP extracts can be prepared and analyzed by a single analyst in 1 day.

Experimental results have been extremely good with less than 10% relative standard deviation reported during method detection limit studies for all three compounds. Sample preparation and analysis conditions, chromatography, UV spectra, precision and accuracy data, and spike recovery data will be presented.

INTRODUCTION

Liquid chromatography (LC) has been used in the pharmaceutical and food industries for many years because of the ability to analyze many different types of compounds (eg. varied compound classes that are thermally labile, high molecular weight or non-volatile.) More recently liquid chromatography has gained interest in the environmental field. In addition to an approved method for the analysis of polynuclear aromatic hydrocarbons (PNA's), the EPA has also devoted a significant amount of time and money to the evaluation of liquid chromatography/mass spectrometry because of its promising use in the environmental field.

The chlorophenoxy herbicides are of major concern to the environmental community as well as the regulatory agencies because of their toxic effects and widespread use. The monitoring of these compounds is needed to prevent adverse environmental and health effects. The analyses of these compounds is required under the RCRA program 40 CFR. Part 261.24 requires the TCLP extraction and analysis for the compounds when determining if a solid waste displays a hazardous characteristic. In addition, 40 CFR Part 268 requires the analysis of these compounds by total constituent analysis in waste extracts when determining if a hazardous waste meets the Land Disposal Restriction treatment standards. Analyses of hazardous waste and TCLP extracts for the presence of these herbicides is currently performed using SW-846 Method 8150. Method 8150 is both time consuming and potentially hazardous. The use of ethyl ether as the extraction solvent and diazomethane as the methylating agent are of major concern because of their explosive and toxic properties. The method is very labor intensive requiring multiple preparation steps before analyses can be performed. It has proven difficult to consistently achieve quality results in the complex hazardous waste matrices outlined in this paper. The HPLC method has proven to be analytically sound over a wide range of matrices, and its use, with the simplified preparation procedure can decrease analyses time four fold as well as eliminate the use of ethyl ether and diazomethane.

PURPOSE

The purpose of this work was to develop a streamlined method utilizing HPLC with ultraviolet detection that can determine herbicides in hazardous waste matrices and TCLP extracts. The simplification of the extraction and analyses will increase analyst safety, reduce hazardous chemical use (eg. ethyl ether and diazomethane) and reduce the analytical costs and sample turnaround times.

THEORY

In liquid chromatography as in most chromatographic techniques, separation of the analytes is achieved by partitioning the analytes between the mobile and stationary phases. In LC the solubility of the analytes in a solvent based mobil phase versus their solubility in a liquid stationary phase dictates the separation. The two basic types of partitioning are normal phase (eg. the stationary phase is more polar than the mobil phase), and reverse phase (eg. the mobil phase is more polar than the stationary phase). The availability of a wide range of solvent types and stationary phases in addition to being an ambient technique makes LC applicable to a wide range of compound types. The need to make volatile and thermally stabile compounds needed for gas chromatographic (GC) analysis is eliminated. Because of this the chlorophenoxy acid herbicides can be analyzed in their acid form instead of the methyl ester form needed for GC. This eliminates the diazomethane derivatization step of Method 8150.

INSTRUMENT DESCRIPTION

The HPLC instrumentation used for this study was purchased from Millipore/Waters. The instrument was configured as follows:

Model 600-MS controller and solvent delivery system

Model 991-MS Photodiode array detector

NEC 386/20 data system with PDA software

Nova Pak C18 Radial Compression Column 8x100mm, 4 micron

Nova Pak C18 Guard Pak, 4 micron

Rheodyne Model 7125 manual injection valve with 500uL external sample loop

EXPERIMENTAL PROCEDURE AND DATA REVIEW

Chromatographic Conditions

The HPLC/UV chromatograph of the herbicide acids is shown in Figure 1. The peak shapes are excellent, baseline resolved and of approximately equal intensity. The mobile phase used was 75% methanol / 25% water with 0.5% H_3PO_4 at a flowrate of 2.5mL/min. A 500uL injection volume was delivered using an external sample loop. The photodiode array detector was programmed to scan from 200 to 240 nm. 207nm was used as the primary quantitation wavelength with 227nm and 235nm used as confirmatory and secondary quantitation wavelengths. Standard spectra and contour plots are shown in Figures 2 and 3.

Instrument Calibration

Instrument calibration was done at multiple levels to define the linearity and working range of the photodiode array detector. Figure 4 shows the calibration curve plotted as the least squares fit for nanograms on column versus peak height.

Hazardous Waste
Precision and Accuracy Study

Precision and accuracy studies were done on four different hazardous waste matrix types, water/oil mix, contaminated soil, PCB oil, and waste solvents. Table 1 shows the data collected. For a 200 ppm spike of various esters <10% relative standard deviation is reported for all matrices with all but one in the 1-6% range.

Hazardous Waste Sample Preparation

Five grams of sample is accurately weighed into a 100mL volumetric flask. (NOTE: If the sample is a dense organic liquid eg. high PCB oils, chlorinated solvents etc., weigh 2.5g of sample into the 100mL volumetric then add 2.5g hexadecane, then mix well.) Fifty mL of deionized water is then added to the volumetric flask. The sample is made alkaline by adding 10mL of 37% KOH solution. Alkaline conditions are verified by checking the pH and if needed additional KOH is added. The sample is then stirred at 70-80°C for 2 hours. The extract is then brought to 100mL volume with deionized water after drawing off any oil layer or filtering off any solid material. The extract is then made acidic by adding hydrochloric acid. The acidified extract is analyzed using reversed phase HPLC.

Hazardous Waste Sample Analyses

As a method ruggedness test a variety of hazardous waste samples were analyzed both as received and after spiking to check for possible matrix effects or interferences. Samples were spiked at both 200 and 1000 ppm. Sample types included PCB oils, dielectric fluids, oil bottoms, waste oils, contaminated solvents, lab liquids, solids, sludges, incinerator ash, dry scrubber solids, and others. Table 2 shows the data collected expressed as percent recovery.

Data Discussion

Tables 1 and 2 demonstrate the precision and accuracy of the HPLC/UV method when analyzing hazardous waste. Hazardous waste matrices are extremely varied and complex and typically require extensive cleanup procedures when using current SW-846 methodologies. The HPLC/UV method is robust enough to handle a wide variety of matrices. Less than 10% RSD was seen when doing replicate analyses of spiked samples. The four matrix types in Table 1 were chosen because they represent the common and complex matrix types typically analyzed. Table 2 shows that spike recoveries of between 73 and 127% were seen during routine analyses. A variety of esters were used in the study.

TCLP Extract
Precision and Accuracy Study

Precision and accuracy studies were done on both TCLP extraction fluids #1 and #2. Table 3 shows the data collected. For a 1 ppm spike of the methyl esters, extraction fluid #1 shows <1% RSD, fluid #2 shows <2% RSD.

TCLP Extract Sample Preparation

Fifty mL of TCLP extract is added to a 100mL volumetric flask. The extract is made alkaline by adding 5mL of 37% KOH solution. Alkaline conditions are verified by checking the pH and if needed additional KOH is added. The extract is stirred at 70-80°C for 2 hours. The extract is reacidified to pH 2 using hydrochloric acid, then brought to 100mL final volume with deionized water. The acidified extract is analyzed using reversed phase HPLC.

TCLP Sample Analyses

As a method ruggedness test a variety of waste sample TCLP extracts were analyzed as received and after spiking to check for possible matrix effects or interferences. Extracts were spiked with methyl esters at approximately 1ppm. Sample types included sludges, carbon fine dust, used fuel filters, contaminated soils, sands and debris, sludges and others. Table 4 shows the data collected.

Data Discussion

The data in Tables 3 and 4 demonstrates how precise and straightforward the analysis of TCLP extracts by HPLC/UV is. Less than 2% RSD and average recoveries of between 90 and 100% at a 1ppm spike level are easily and consistently attainable. The minimal sample preparation requires approximately 2.5 hours, and the entire procedure is carried out in a single 100mL volumetric flask.

CONCLUSIONS

1. High pressure liquid chromatography with ultraviolet detection is an excellent alternative analytical tool to GC/ECD for the analysis of the chlorophenoxy herbicides.

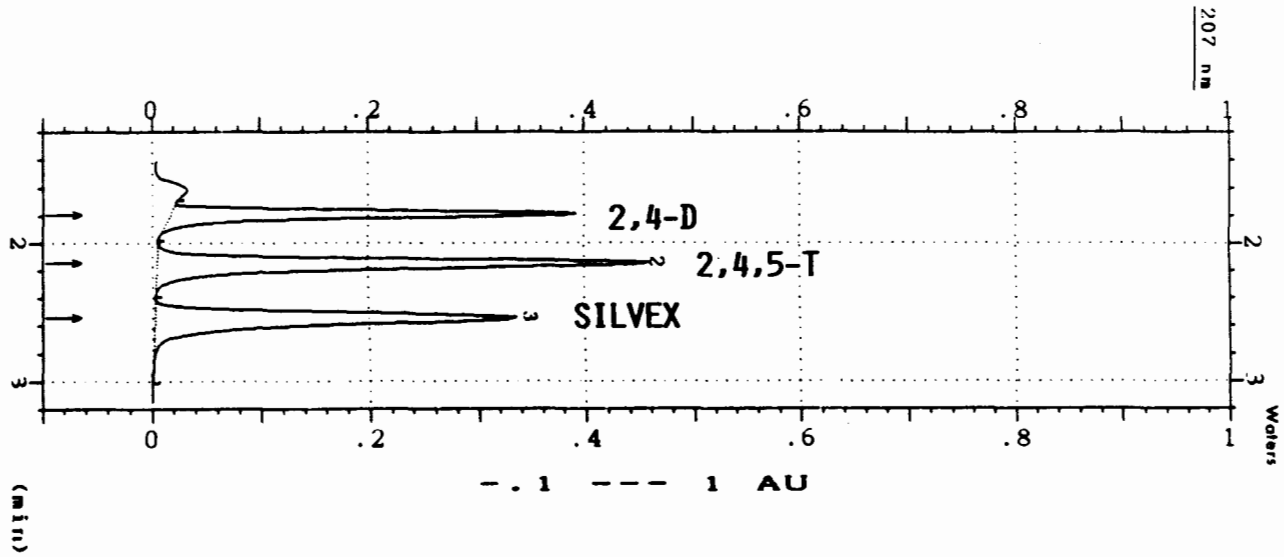
2. The use of the simplified sample preparation procedure increases analyst safety and significantly reduces analysis time. The use of ethyl ether and diazomethane are eliminated, and easily four times the number of samples can be analyzed by a single analyst as compared to Method 8150.

3. The combined use of HPLC/UV and the simplified sample preparation procedure produces a robust, analytically sound method that can be used to analyze hazardous waste and TCLP extracts.

FIGURE 1
HPLC/UV CHROMATOGRAPH

31220 0071

Waters 991 Integrator			Waters
LC724.DT3	05-06-1992 14:09:27	Sample name	1ppm std
Y-scale	1.1 AU/FS	Paper speed	20 mm/min
Sampling time	44 msec *16		
Sense	normal	Column	mm ID * mm
Resolution	1.4 nm	Packing material	
Time range	1.2 --- 3.2 min	Mobile phase	
Interval	.82 sec	Flow rate	ml/min
Baseline	OFF	Pressure	
Smoothing	7 points	Slope	.5 AU/min
Drift	.002 AU/min	Height	.001 AU
Width	.02 min	Min. area	.0001 AU*min
Time double	30 min	Minus peak	OFF



31220 0071

Waters 991 Integrator		LC724.DT3	Waters
05-06-1992	14:09:27	Sample name	1ppm std
Sampling time	44 msec *16	Baseline	OFF
Sense	normal	Resolution	1.4 nm
Y-scale	1.1 AU/FS	Paper speed	20 mm/min
Time range	1.2 --- 3.2 min	Interval	.82 sec
Smoothing	7 points	Slope	.5 AU/min
Drift	.002 AU/min	Height	.001 AU
Width	.02 min	Min. area	.0001 AU*min
Time double	30 min	Minus peak	OFF
Column	mm ID * mm	Packing material	
Mobile phase		Flow rate	ml/min
Pressure			

Report File LC724.DT3

207 nm

No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	1.79	0.3512	1.69	1.98	0.024254	24.299	I
2	2.14	0.4453	1.98	2.39	0.039654	39.728	I
3	2.54	0.3295	2.39	3.01	0.035905	35.973	I

FIGURE 2
ULTRAVIOLET SPECTRA

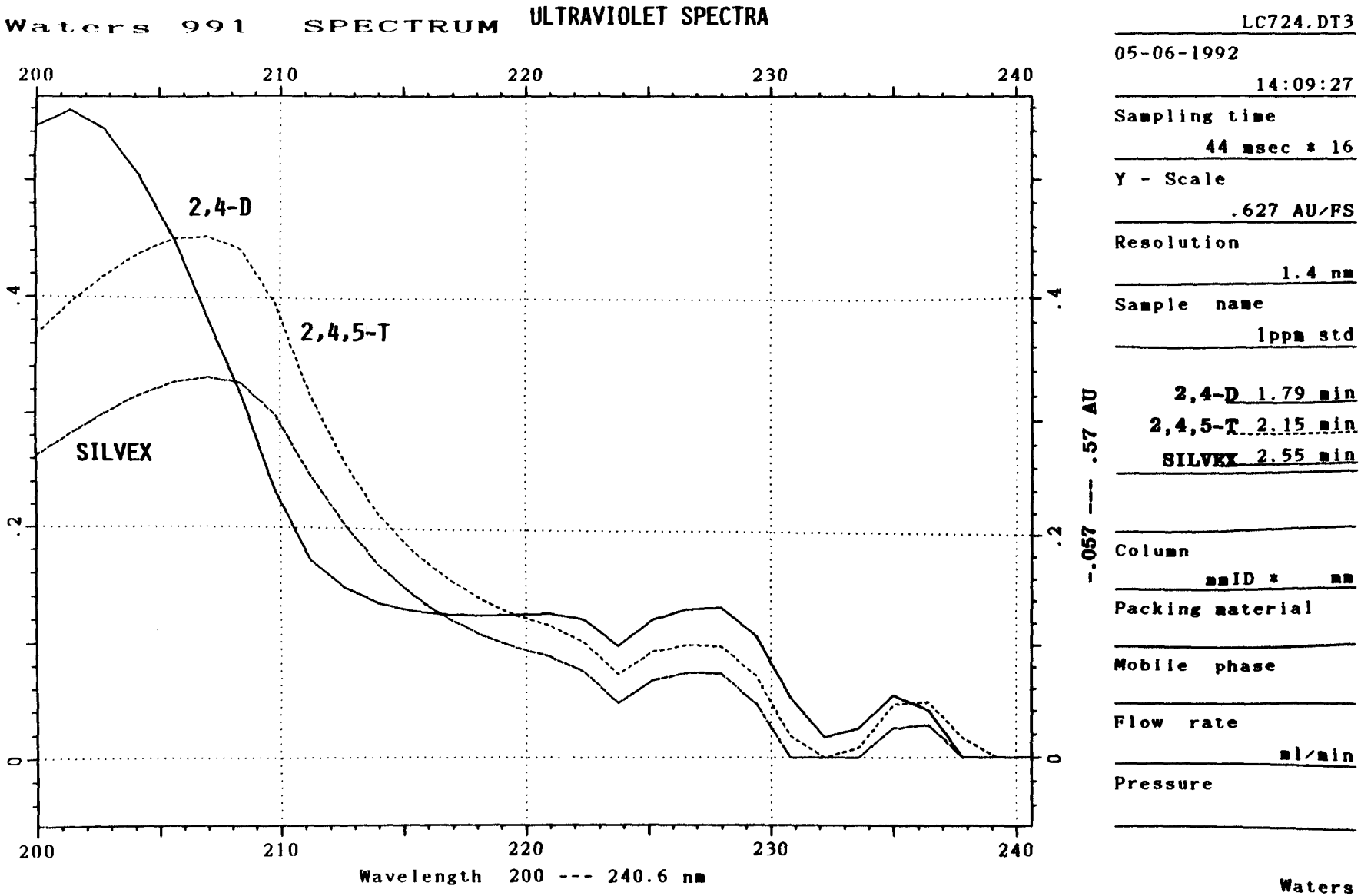


FIGURE 3
CONTOUR PLOT

Waters 991 Contour plot — Waters

LC724.DT3	05-06-1992 14:09:27	Sample name	1ppm std
Sampling time	44 msec *16	Paper speed	100 mm/min
Y-scale	.01 --- 1 AU	Baseline	OFF
step	.1 AU	Column	mm ID * mm
Wavelength	200 --- 240.6 nm	Packing material	
Resolution	1.4 nm	Mobile phase	
Time range	1.2 --- 3.2 min	Flow rate	ml/min
Interval	1 sec	Pressure	

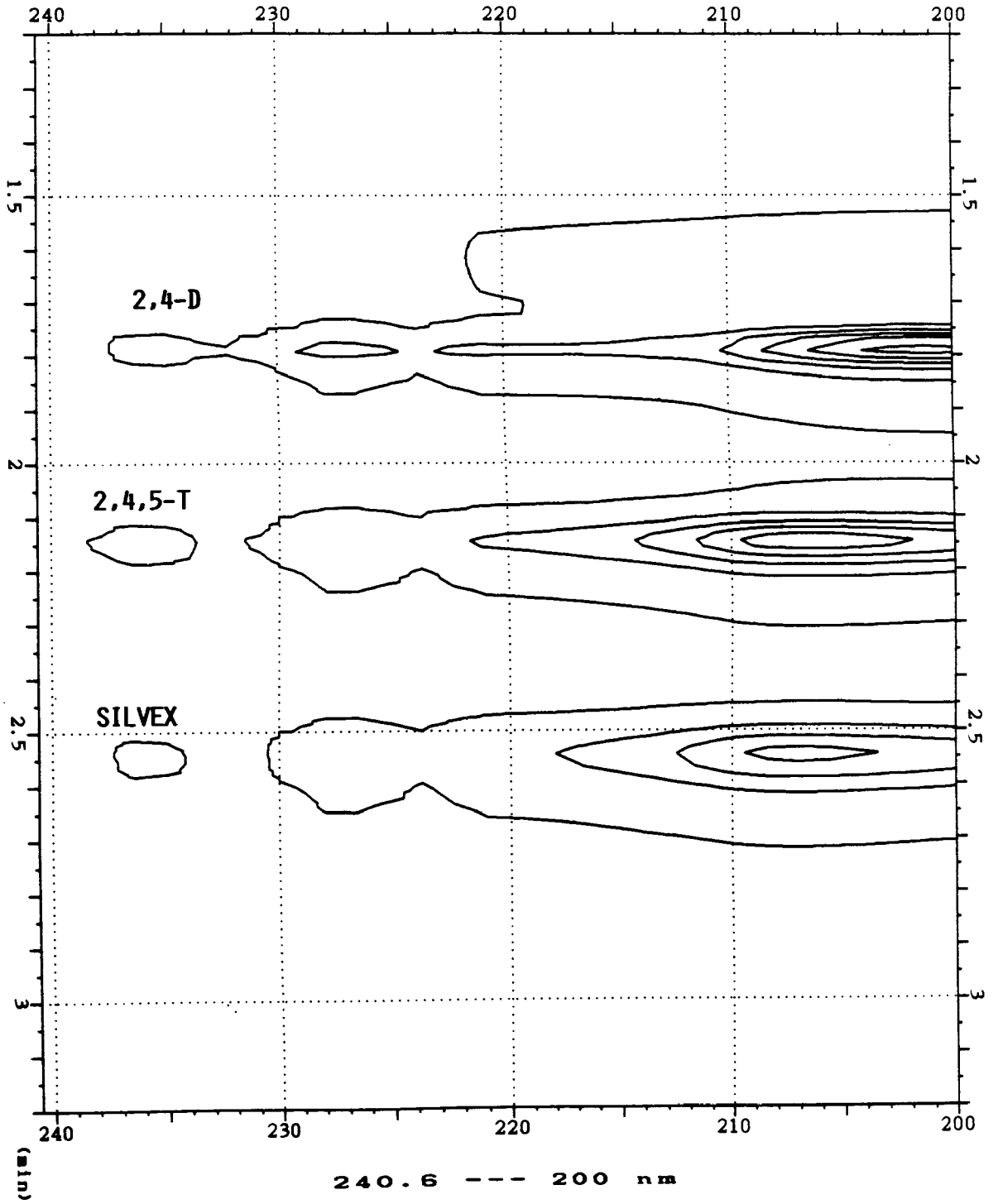


FIGURE 4

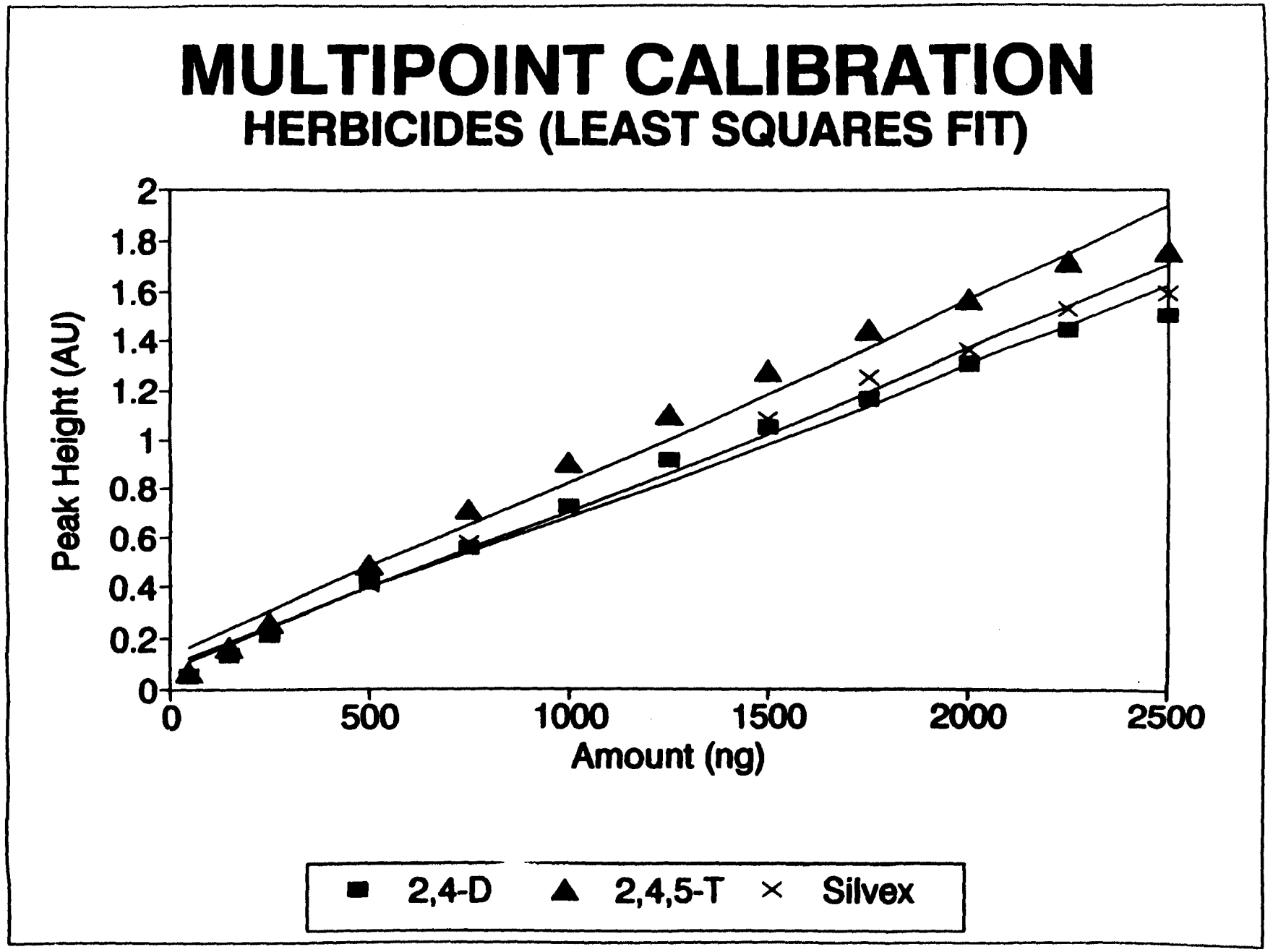

MULTIPOINT CALIBRATION
HERBICIDES (LEAST SQUARES FIT)
Peak Height (AU)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
2500
Amount (ng)
2,4-D
2,4,5-T
Silvex

Table 1

PRECISION AND ACCURACY

Waste Matrices

	Water/Oil Mix (50980) Sample Amt = 5g			Contaminated Soil (51517) Sample Amt = 5g		
	2,4-D (a) (ppm)	2,4,5-T (b) (ppm)	Silvex (ppm)	2,4-D (ppm)	2,4,5-T (ppm)	Silvex (ppm)
Spike level	186	140	195	199	185	198
Unspiked	ND	ND	ND	ND	ND	ND
Replicate 1	191	137	218	200	208	191
Replicate 2	211	136	228	212	216	205
Replicate 3	194	143	222	208	214	200
Replicate 4	198	144	221	205	212	200
Replicate 5	189	139	224	195	209	193
Replicate 6	191	142	224	205	205	193
Replicate 7	204	143	228	192	200	185
Replicate 8	203	145	228	201	209	193
Average	198	141	224	202	209	195
Av % Rec	106	101	115	102	113	98
Std. Dev	7.78	3.36	3.72	6.63	5.08	6.30
% RSD	3.94	2.38	1.66	3.28	2.43	3.23

	PCB Oil (50368) Sample Amt = 5g			Waste Solvents (50161) Sample Amt = 2.5g (c)		
	2,4-D (ppm)	2,4,5-T (ppm)	Silvex (ppm)	2,4-D (ppm)	2,4,5-T (ppm)	Silvex (ppm)
Spike level	199	185	194	953	943	969
Unspiked	ND	ND	ND	ND	139	ND
Replicate 1	182	222	173	997	1075	715
Replicate 2	199	218	165	1020	1157	827
Replicate 3	210	222	178	1012	1118	906
Replicate 4	205	228	187	1024	1129	902
Replicate 5	193	210	164	968	1099	948
Replicate 6	205	214	165	1007	1115	845
Replicate 7	192	213	156	1004	1119	931
Replicate 8	211	224	173	988	1054	974
Average	200	219	170	1003	1108	881
Av % Rec	100	118	88	105	103	91
Std. Dev	10.06	6.17	9.66	18.17	32.07	83.21
% RSD	5.04	2.82	5.68	1.81	2.89	9.45

Note: All concentrations reported as acid equivalents of esters.

(a) Isopropyl ester used.

(b) Isooctyl ester used.

Methyl esters used for all others

(c) 2.5g sample + 2.5g hexadecane

Table 2

Waste Matrices

Sample Matrix	Percent Recovery			Comments
	2,4-D	2,4,5-T	2,4,5-TP	
PCB contam. solvent	119	127	116	Isopropyl, isooctyl, methyl esters
PCB contam. lab liquids	101	108	100	Methyl esters
PCB contam. flamm liquid	105	111	103	Methyl esters
PCB contam. water & oil	101	96	104	Free acids
Ash	101	99	95	Ethyl, n-butyl, methyl esters
Ash	103	109	87	Isopropyl, n-butyl, ethyl hexyl esters
Ash composite	101	109	100	Methyl esters
Brick/slag composite	103	113	100	Isopropyl, n-butyl, ethyl hexyl esters
Dry scrubber solids	98	99	99	Ethyl, n-butyl, methyl esters
Dry scrubber solids	98	101	94	Isopropyl, n-butyl, ethyl hexyl esters
PCB oil	105	111	101	Methyl esters
PCB oil	105	111	104	Methyl esters
PCB transformer oil	113	115	89	Methyl esters
Dielectric fluid/mineral oil	90	98	82	Methyl esters
Oil bottoms/waste oil	86	84	93	Methyl esters, 23ppm 2,4,5-T in samp
Mineral oil with PCB	104	102	104	Free acids
Pheromone scrap	110	101	81	Methyl esters
Electrostatic liq developer	107	113	96	Methyl esters
Solv contam solid/sludge	95	73	89	Methyl esters,212ppm 2,4,5-T in samp
Methoxychlor	97	102	108	Free acids
Holding tank film	98	98	102	Free acids

Note: Samples were spiked at approximately 200ppm

Table 3

PRECISION AND ACCURACY
TCLP

	Extraction Fluid # 1 Sample Amt = 10mL			Extraction Fluid # 2 Sample Amt = 10mL		
	2,4-D (ppm)	2,4,5-T (ppm)	Silvex (ppm)	2,4-D (ppm)	2,4,5-T (ppm)	Silvex (ppm)
Spike level	0.95	0.94	0.98	0.95	0.94	0.98
Unspiked	ND	ND	ND	ND	ND	ND
Replicate 1	0.96	0.99	1.05	0.98	0.99	1.03
Replicate 2	0.96	0.98	1.05	1.01	1.01	1.07
Replicate 3	0.95	0.99	1.05	0.97	0.99	1.05
Replicate 4	0.95	0.98	1.04	0.97	1.00	1.03
Replicate 5	0.97	0.99	1.05	0.98	1.01	1.04
Replicate 6	0.95	0.99	1.04	0.95	0.99	1.04
Replicate 7	0.95	0.99	1.04	0.96	0.98	1.03
Average	0.96	0.98	1.04	0.97	0.99	1.04
Av % Rec	100.63	104.62	106.55	102.21	105.76	105.96
Std. Dev	0.01	0.00	0.01	0.02	0.01	0.01
% RSD	0.89	0.47	0.58	1.92	1.17	1.31

Note: All concentrations reported as acid equivalents of esters.

Table 4

TCLP Sample Matrices

Sample Type	Percent Recovery			Comments
	2,4-D	2,4,5-T	2,4,5-TP	
Drill cuttings	102	104	106	
Sand and paint chips	102	106	107	
Used fuel filters	85	108	105	
Off spec lamp component	105	104	105	
Shot gun blast	102	103	99	
Waste sludge	103	106	107	
Dock sludge	98	98	104	
WWT sludge	100	MI	106	Original sample contamination
Paint sludge	99	107	104	
Acetone contam. soil	100	106	107	
Demolition debris	98	107	104	
Contam. soil & concrete	95	114	104	
Asphalt, dirt, and sand	96	108	100	
Mercury contam. debris	91	103	104	
Activated carbon	100	103	105	
Furnace ash	92	102	103	
MSD carbon	100	105	103	
Carbon fine dust	93	96	106	
Filter cake	79	MI	100	Matrix interference

Note: samples spiked with approximately 1ppm methyl esters

61 AN INTERLABORATORY CALIBRATION STUDY OF A THERMOSPRAY-LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY METHOD FOR THE DETECTION OF CARBAMATES IN ENVIRONMENTAL MATRICES.

ORGANIC

Tammy L. Jones, Research Chemist, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119, and Lopez-Avila V., MidWest Research Institute, California Operations, Mountain View, California, 94043.

ABSTRACT

Substantial numbers of hazardous compounds are not currently regulated by the U.S. Environmental Protection Agency (U.S. EPA) simply because there are no available or reliable methods to quantitatively measure them. These compounds pose difficulty when analysis is done by conventional analytical methods (e.g., gas chromatography) because they can be non-volatile (polar or high molecular weight) or thermally labile. Carbamates are a class of such compounds, and they include some of the most widely used pesticides in agriculture. Methods for carbamate determination are necessary for support of the Environmental Defense Fund decree (EDF vs. Reilly, Civ. No. 89-0598), as supervised by the Office of Solid Waste (OSW). The EDF consent decree mandates that EPA, under the Resource Conservation and Recovery Act (RCRA), develop methods for and list the carbamates found in industrial waste streams. Therefore, it is important that reliable and rugged analytical methods be developed for the analysis of this class of compounds.

A single-laboratory evaluation of a thermospray-liquid chromatography/mass spectrometry (TS-LC/MS) method was previously developed for the U.S. EPA. The interlaboratory calibration study reported here was undertaken as part of the support for the OSW method development process and for support of the EDF consent decree.

Nine carbamate pesticides (aldicarb, CAS# 116-06-3; bendiocarb, CAS# 22781-23-3; carbaryl, CAS# 63-25-2; carbendazim, CAS# 10605-21-7; carbofuran, CAS# 1563-66-2; diuron, CAS# 330-54-1; linuron, CAS# 330-55-2; methomyl, CAS# 16752-77-5; and oxamyl, CAS# 23135-22-0) were selected for evaluation in this calibration study. Seven of the analytes (aldicarb, bendiocarb, carbofuran, oxamyl, methomyl, carbendizam, and linuron) were chosen from the target analyte list provided in the consent decree and the other two carbamates are of importance to the State of California.

The main goal of this study was to obtain a preliminary assessment of the ability of the TS-LC/MS to reliably detect and quantitate carbamate pesticides. The purpose of this work will be to collate and statistically evaluate the data collected during the interlaboratory calibration study.

62

THE DETERMINATION OF SUB PART-PER-BILLION LEVELS OF VOLATILE ORGANIC COMPOUNDS IN AIR BY PRE-CONCENTRATION FROM SMALL SAMPLE VOLUMES

Norman A. Kirshen, Environmental Program Manager and Elizabeth B. Almasi, GC/MS Chemist, Varian Chromatography Systems, 2700 Mitchell Drive, Walnut Creek, California 94598

ABSTRACT

Trace level Volatile Organic Compounds (VOCs) in ambient air are normally determined according to EPA Method TO-14. This method describes the analysis in ambient air of 41 VOCs, ranging in boiling point from -29 to 215°C. It covers a concentration range from 0.2 to 20 parts per billion, volume/volume (ppb), and specifies sample enrichment with a 400 mL air sample on glass beads at -160°C. While this sample volume provides sub-ppb levels of VOC detection for target analytes when using a quadrupole mass spectrometer detector in SIM mode or when using GC detectors, the identification of non-target analytes may only be done in full scan mode for higher concentration. Also with this sample volume a Nafion dryer is needed for water removal thereby lowering the recovery of polar VOCs.

Because of the very high senstivity of the ion-trap MS, relatively small volumes (60 mL) are adequate to obtain the required or lower detection levels. An integrated air analysis system based on a GC/Ion-trap MS has been investigated and is described. This system has a built-in cryogenic trap and necessary valving, internal standard gas sampling valve loop, and is controlled from the GC/MS workstation. The linearity, precision, and method detection levels obtainable with this system when using small volumes are reported. In addition, examples of the quantitative and qualitative analysis of ambient air samples are shown.

INTRODUCTION

The determination of basic air pollutants in ambient air is of paramount importance as legislative acts, such as the 1990 amendments to the Clean Air Act (CAA) of the United States, take effect. Federal, state and local actions will ultimately reduce emissions from industrial and mobile sources to meet the requirements of the CAA. The analytical techniques which are used to ensure that allowed emissions are not exceeded must provide sensitive and definitive measurements of volatile organic compounds (VOCs) in ambient air at the sub parts per billion volume/volume (ppb) level.

The United States was quick to initiate experimental guidelines for VOC analysis in air. The resulting EPA method TO-14,[1-5] is the most commonly used method for VOC analysis worldwide and therefore it has been used as a guideline for the following study.

Method TO-14 describes the analysis in ambient air of 41 VOCs, ranging in boiling point from -29 to 215°C (Table 1). It covers a concentration range from 0.2 to 20 ppb, specifies sample enrichment (400 mL) on glass beads at -160°C, thermal desorption, separation on a capillary column, and detection with a mass spectrometric detector. The first draft of the Contract Laboratory Program (CLP) method[6] was published in February 1991. The samples to be analyzed by the CLP method are from known or suspected hazardous waste sites, therefore the concentration range is from 2 to 100 ppb, higher than required for ambient air monitoring.

Previous work with TO-14 systems based on GC detectors[7] has confirmed that volumes of approximately 400 mL are required to obtain sensitivities of 0.2 ppb. The same requirements apply to quadrupole mass spectrometers. Because of the very high sensitivity of the ion-trap MS, relatively small air volumes (60 mL) are required to obtain these or lower detection levels. An integrated air/soil gas analysis system based on an GC/Ion-Trap MS has been investigated and is described here. This system has a built-in cryogenic trap, internal standard gas sampling valve loop, sixteen sample automation and is controlled from the GC/MS workstation. The linearity, precision, and method detection levels obtainable with this system when using small volumes are reported. In addition, examples of the quantitative and qualitative analysis of ambient air samples are shown.

Table 1 Quantitation Ions, Retention Times, %RSD and Method Detection Limits for Analytes in Method TO-14.

Compound	Quan Ion	RT* (min)	%RSD** (area)	MDL (ppb)
Dichlorodifluoromethane	85	13:05	3.8	0.01
Chloromethane	50	14:11	8.5	0.03
1,2-Dichloro-1,1,2,2-tetrafluoroethane	85	15:11	3.5	0.01
Vinyl Chloride	62	15:30	6.0	0.02
Bromomethane	94	16:56	4.7	0.01
Chloroethane	49	17:36	9.0	0.03
Trichlorofluoromethane	101	19:23	3.2	0.01
1,1-Dichloroethylene	61	20:25	5.6	0.02
Dichloromethane	49	20:42	3.9	0.01
1,1,2-Trichloro-1,2,2-trifluoroethane	101	21:07	3.8	0.01
1,1-Dichloroethane	63	22:10	4.8	0.01
c-1,2-Dichloroethene	61	23:08	4.4	0.01
Chloroform	83	23:28	3.7	0.01
1,2-Dichloroethane	62	24:14	4.1	0.01
1,1,1-Trichloroethane	97	24:30	4.6	0.01
Benzene	78	24:59	3.4	0.01
Carbon Tetrachloride	117	25:08	3.4	0.01
1,2-Dichloropropane	63	25:50	2.9	0.01
Trichloroethene	130	26:05	3.8	0.01
c-1,3-Dichloropropene	75	26:59	4.7	0.01
t-1,3-Dichloropropene	75	27:32	5.7	0.02
1,1,2-Trichloroethane	97	27:43	3.9	0.01
Toluene	91	28:03	2.4	0.01
1,2-Dibromoethane	107	28:47	2.9	0.01
Tetrachloroethene	166	29:19	3.5	0.01
Chlorobenzene	112	30:06	3.8	0.01
Ethylbenzene	91	30:33	4.6	0.01
m,p-Xylene	91	30:47	2.9	0.01
Styrene	104	31:12	5.2	0.02
1,1,2,2-Tetrachloroethane	83	31:19	4.7	0.01
o-Xylene	91	31:21	5.0	0.02
4-Ethyltoluene	105	33:02	7.0	0.02
1,3,5-Trimethylbenzene	105	33:09	8.9	0.02
Benzylchloride	91	33:15	10.1	0.03
1,2,4-Trimethylbenzene	105	33:45	10.3	0.03
m-Dichlorobenzene	146	33:58	3.2	0.01
p-Dichlorobenzene	146	34:05	4.3	0.01
o-Dichlorobenzene	146	34:37	4.8	0.01
1,2,4-Trichlorobenzene	180	37:56	9.3	0.03
Hexachlorobutadiene	225	39:11	8.0	0.03

*RT includes the concentration step also, column DB-1
**%RSD calculated from area responses of 9 replicate runs.

EXPERIMENTAL

System Description

The schematic of the GC/Ion-trap MS system is shown in Figure 1. The built-in trapping and preconcentrating device, the Variable Temperature Adsorption Trap (VTAT, Figure 2) is capable of trapping and preconcentating VOCs from air on glass beads at -160°C or on an adsorbent such as Carbosieve™/Carbotrap™ at ambient temperatures. In the present study only the subambient mode was used.

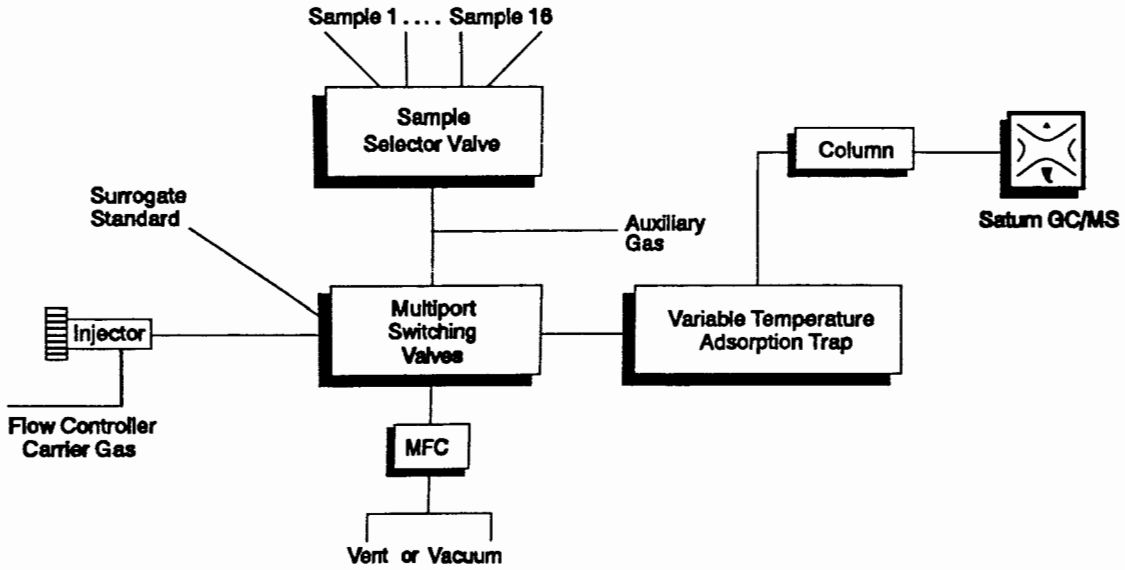


Figure 1. Schematic of a GC/Ion-trap MS System for VOCs.

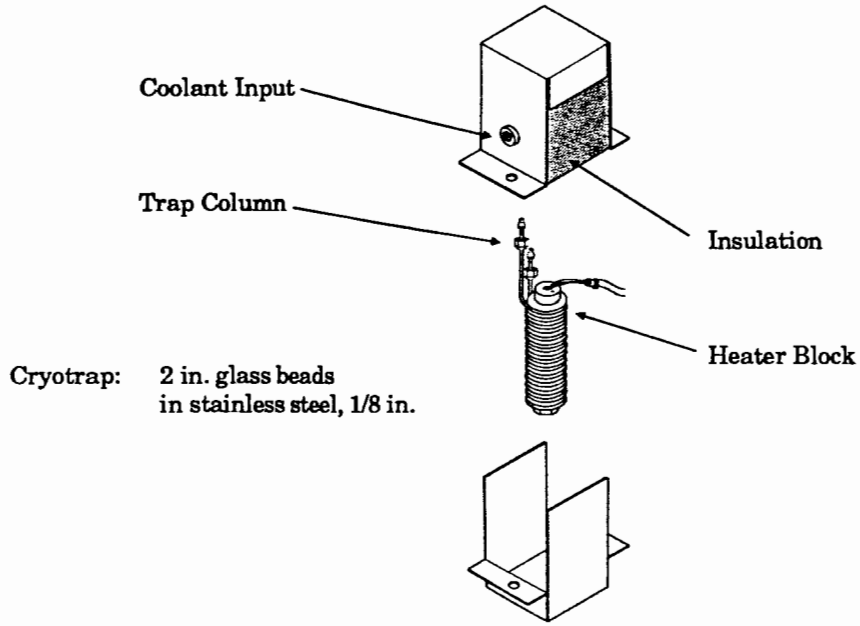


Figure 2. The variable temperature absorption trap (VTAT).

Instrumentation and Conditions

Cryogenic concentrator:

- Variable Temperature Adsorption Trap (VTAT), 5 cm of 60/80 mesh silanized glass beads
- Two automated valves, 4- and 10-port; capable of sample and internal standard (I.S.) introduction
- Electronic mass flow controller, 0-100 mL/min, with readout box
- Vacuum pump (metal diaphragm)

Pneumatics:

Air sample flow rate: 20 mL/min
Column flow rate: 1 mL/min He
Auxiliary flow rate: 20 mL/min He

Temperatures:

VTAT: -160°C for 4 min, 180°C/min to 120°C, hold
Valves: 160°C
Column: -50°C for 6 min, 8°C/min to 160°C, hold

Columns:

DB-1 (J&W), 60m x 0.32 mm I.D., 1 μm film or
DB-624 (J&W), 60m x 0.32 mm I.D., 1.8 μm film

Ion-trap MS (Varian Saturn II):

Scan Range: 47-260 u
Scan Rate: 0.8 sec/scan (3 μscan/analytical scan)
RF storage Level: 210 DAC Steps; background Mass: 45 u
Segment Breaks: 70/78/150; Tune factors: 120/70/100/70
Automatic Gain Control (AGC) Target: 20000
Emission Current: 30 μA (Optimized parameters might vary instrument to instrument)

Standard:

Alphagaz TO-14 standard, 41 component, 2 ppm

Procedure

In Method TO-14 a critical part of the analysis is the preconcentration step. In the first stage of this enrichment process the sample (generally VOCs present in low or sub ppb concentrations) is flushed through the lines with a flow set by the electronic mass flow controller, while the loop (0.25 mL) is filled by the internal standard (if required). After the initial column and VTAT temperatures are equilibrated, the air sample and internal standard are directed to the -160°C VTAT and the VOCs are deposited onto the glass beads.

The duration of this "trapping" time can be varied and the volume of the analyzed sample changed accordingly. The sample flow during this step, usually 20 mL/min is held constant by the mass flow controller. In this study the trapping time was 3 minutes resulting in a 60 mL sampled volume. After the sample VOCs are deposited, the residual air is removed from the VTAT by the auxiliary flow. Then the VTAT is heated to 120°C and the analytes are backflushed to the capillary column where they are focussed, separated, and detected. Later the VTAT is cooled down in preparation for the next analysis.

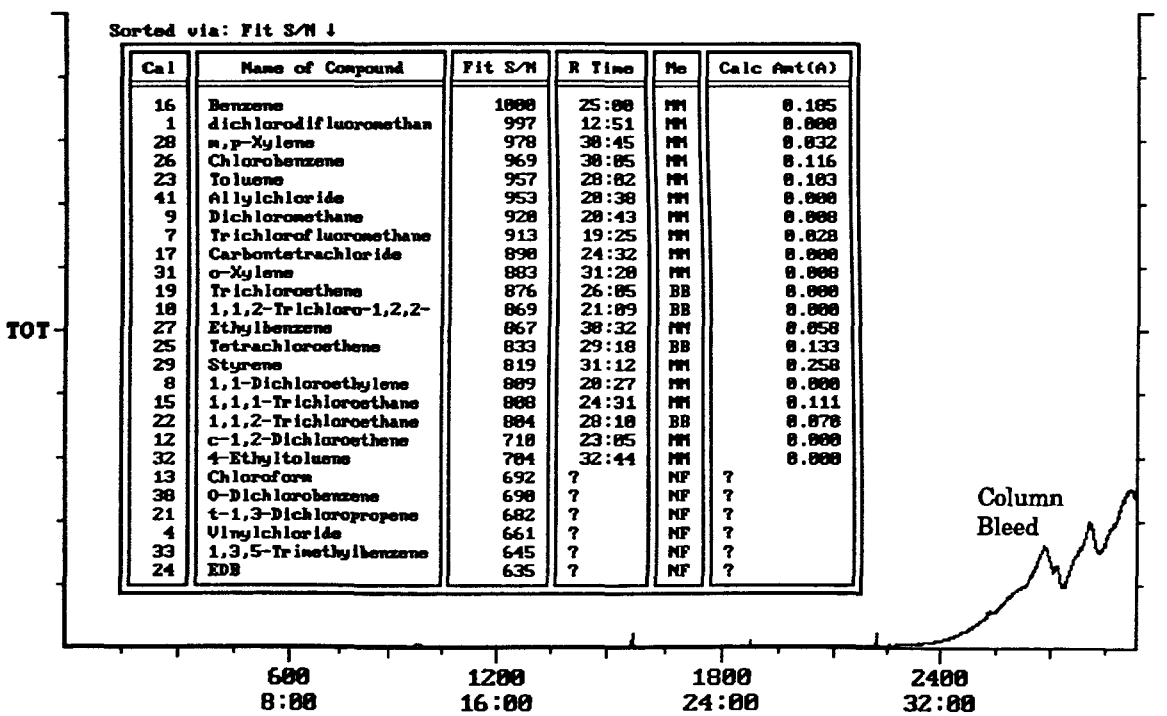
The main difference between the experimental parameters used in this work and those specified in the TO-14 method is the sample size. The method specifies a sample volume of 400 mL. This volume of air can introduce a significant amount of water that might either plug the VTAT or capillary column. Elimination of this residual water is possible with a semipermeable membrane dryer such as a Nafion™ dryer. The removal of water with this type of dryer results in the loss of any trace polar organics that might be in the sample. The sensitivity of the GC/Ion-trap MS allows trace level VOC detection by preconcentrating only 60 mL of sample. This small sample reduces the interference of water and eliminates the need for a Nafion dryer.

RESULTS

The linearity, precision, and method detection limits (MDL) were examined and real samples were analyzed. Before analysis, blank runs were performed. Very often even good quality compressed air has impurities. The Reconstructed Total Ion Current chromatogram (RTICC) of a blank and the accompanying data file is shown in Figure 3. Only trace VOCs of approximately 0.2 ppb or less were found.

The standard and samples were introduced to the system from stainless steel SUMMA® polished canisters. The standard used was a 41 component, 2 ppm VOC mixture (Alphagaz) diluted with air to the desired concentrations. RTICCs of 2 ppb and 0.25 ppb v/v standards are shown in Figures 4 and 5. Gaussian peak shapes are exhibited by all the compounds including the "gases" (the six most volatile compounds) as shown by their mass chromatograms in the Figure 4 insert. For the quantitation of the gases a peak smoothing algorithm was used, allowing precise quantitation of these components even at low concentrations.

The precision and MDL were determined by multiple injections of a 60 mL, 0.1 ppb standard. Standard deviations of the single ion areas were calculated for nine runs and were between 2-9%, the average of the 41 compounds being 5%, Table 1.



Sorted via: Fit S/N ↓

Cal	Name of Compound	Fit S/N	R Time	Me	Calc Amt(A)
16	Benzene	1000	25:00	MM	0.105
1	dichlorodifluoromethan	997	12:51	MM	0.000
28	m,p-Xylene	978	30:45	MM	0.032
26	Chlorobenzene	969	30:05	MM	0.116
23	Toluene	957	28:02	MM	0.103
41	Allylchloride	953	20:38	MM	0.000
9	Dichloromethane	920	20:43	MM	0.000
7	Trichlorofluoromethane	913	19:25	MM	0.020
17	Carbontetrachloride	890	24:32	MM	0.000
31	o-Xylene	883	31:20	MM	0.000
19	Trichloroethene	876	26:05	BB	0.000
10	1,1,2-Trichloro-1,2,2-	869	21:09	BB	0.000
27	Ethylbenzene	867	30:32	MM	0.050
25	Tetrachloroethene	833	29:10	BB	0.133
29	Styrene	819	31:12	MM	0.250
8	1,1-Dichloroethylene	809	20:27	MM	0.000
15	1,1,1-Trichloroethane	800	24:31	MM	0.111
22	1,1,2-Trichloroethane	804	20:10	BB	0.070
12	c-1,2-Dichloroethene	710	23:05	MM	0.000
32	4-Ethyltoluene	704	32:44	MM	0.000
13	Chloroform	692	?	NF	?
30	O-Dichlorobenzene	690	?	NF	?
21	t-1,3-Dichloropropene	682	?	NF	?
4	Vinylchloride	661	?	NF	?
33	1,3,5-Trimethylbenzene	645	?	NF	?
24	EDB	635	?	NF	?

Figure 3. RTICC and result file of a blank (pure air sampled) run. NF indicates target compounds not found (below minimum spectral fit value).

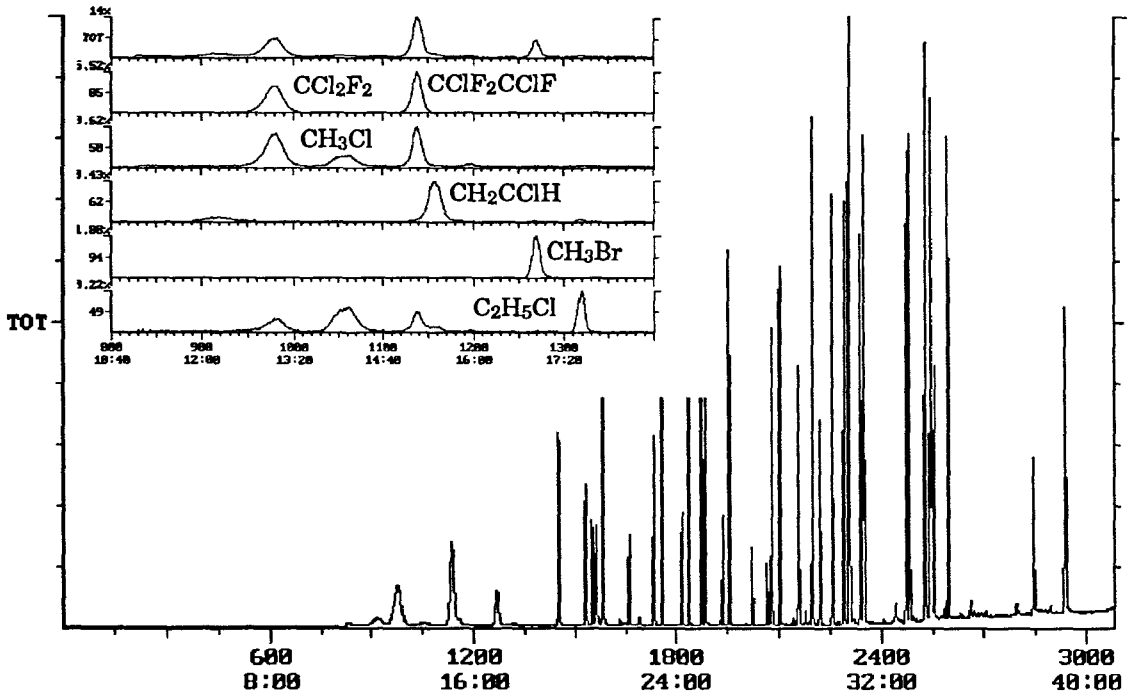


Figure 4. RTICC of 41 VOC compounds, 60 mL, 2 ppb v/v and mass chromatogram of the gases.

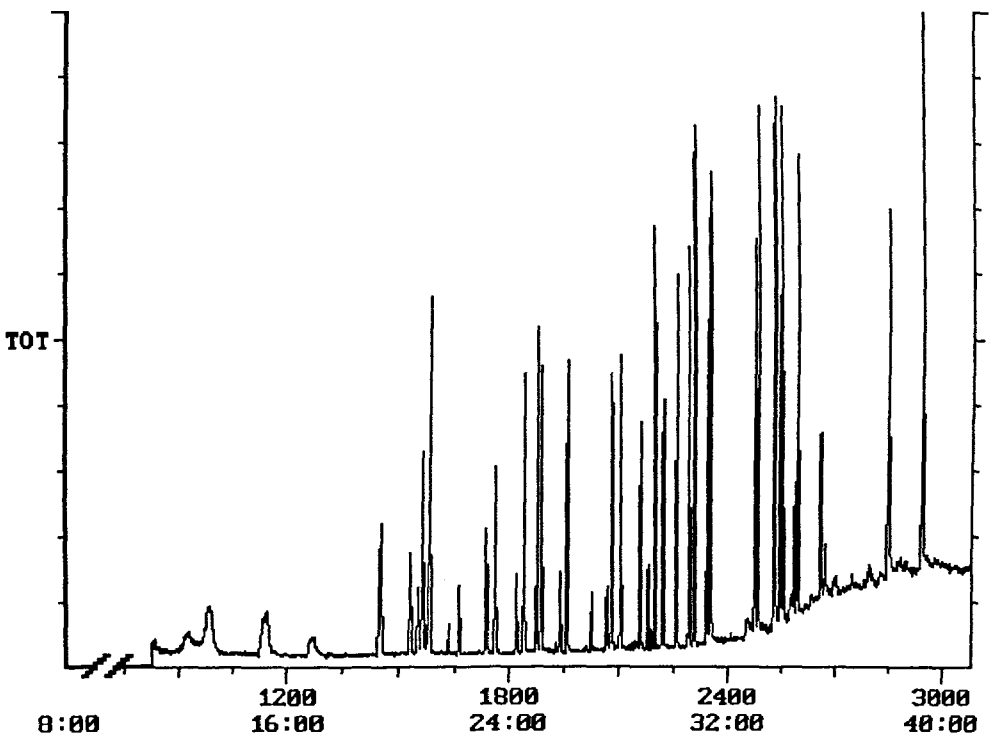


Figure 5. RTICC of 41 VOC compounds, 60 mL, 0.25 ppb v/v

The MDL was calculated from integrated areas of single quantitation ions (nine replicate runs) with the following formula:

$$MDL = s \times t$$

where s is the standard deviation of the replicate analyses and t is the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The calculated MDLs were between 0.01-0.03 ppb.

Linearities of the quantitation ion responses versus concentration for the 41 components were examined over the range required in the method, 0.1 to 20 ppb v/v, and were found to be very good. Representative linearity plots are shown in Figures 6a and 6b.

In addition to identifying and quantitating target components in a sample it is often necessary to identify and estimate the quantities of non-target analytes. For example, dibromochloromethane, a non-target analyte is identified and its concentration estimated at 2 ppb in Figure 7a.

INTERFERENCES

In ambient air some components are present at much higher concentrations than the VOCs. The two most significant components which are concentrated together with the VOCs from the air are water (mentioned above) and CO_2. The reduced sample volumes used here suppress the problems caused by these components. For example, to represent a very humid sample, an air sample was collected just above the surface of a 60°C water bath. At this temperature the vapor pressure of water is 0.2 atmospheres. The chromatogram and results shown in Figures 7a and 7b indicate that the preconcentration process was not affected by the high level of moisture.

Carbon dioxide which is also present in air at high concentrations can be eliminated as an interference by choosing the scanning range from 47 to 250 u and setting the background mass at 45 u. Then CO_2 (44 u) is not stored or detected by the Saturn mass spectrometer and the detection of the early eluting VOCs is enhanced.

APPLICATIONS

Two sample applications are shown using the same conditions. The first sample shows a chromatogram and the resulting report from ambient air collected in Walnut Creek, California on a rainy day in rush hour traffic (Figures 8a and 8b). The aromatics which are the major components of exhaust gas emissions found under these conditions are evident. The second sample was collected at an industrial site to screen for several polar organics. The RTICC and the mass chromatograms at 31 and 45, characteristic mass ions used to quantitate methanol and ethanol, respectively are shown in Figure 9.

SUMMARY

An integrated air/soil gas analysis system based on a GC/Ion-trap MS has been investigated and applied to the analysis of VOCs following EPA Method TO-14. The very high sensitivity of the ion-trap MS allows the use of relatively small air volumes (60 mL) to obtain both qualitative confirmation (full scan spectra) and quantitative determination of sub ppb levels of VOCS. MDLs of 0.01-0.03 ppb have been calculated from multiple runs at 0.1 ppb.

Since water interference is minimized using this small air volume, the use of Nafion dryers has been eliminated allowing the determination of polar as well as non polar organic compounds.

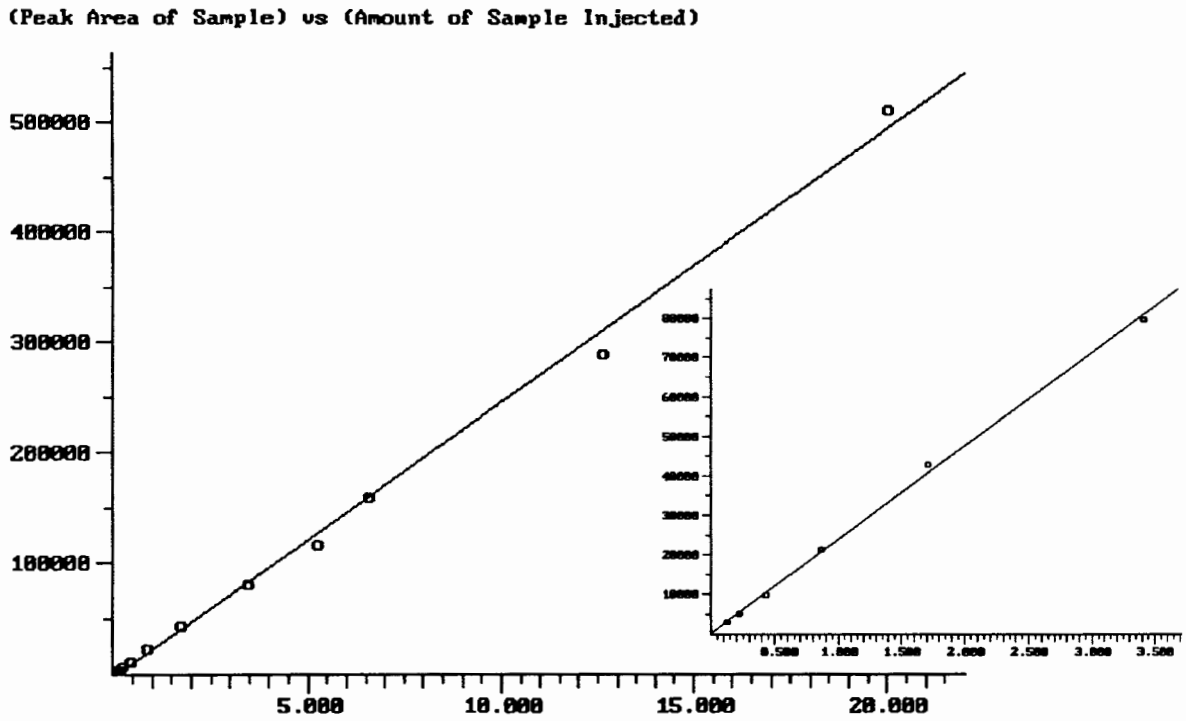


Figure 6a. Linearity of Bromomethane, 0.1-20 ppb.

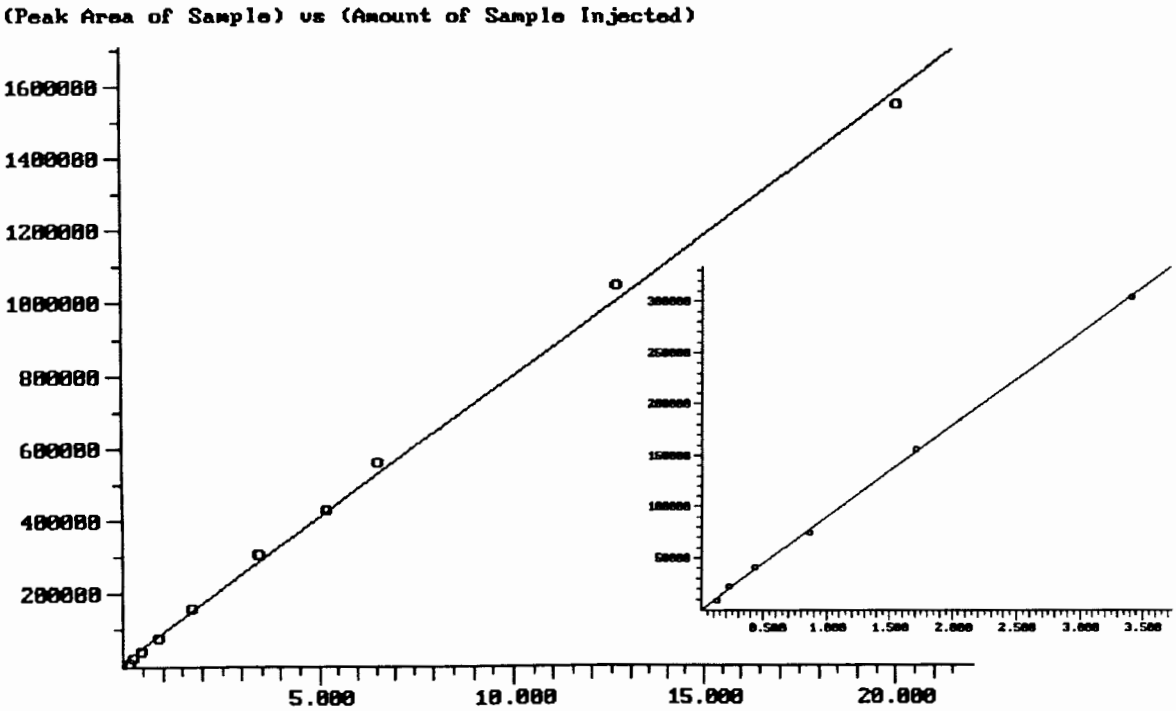


Figure 6b. Linearity of 1,2,4-Trimethylbenzene, 0.1-20 ppb.

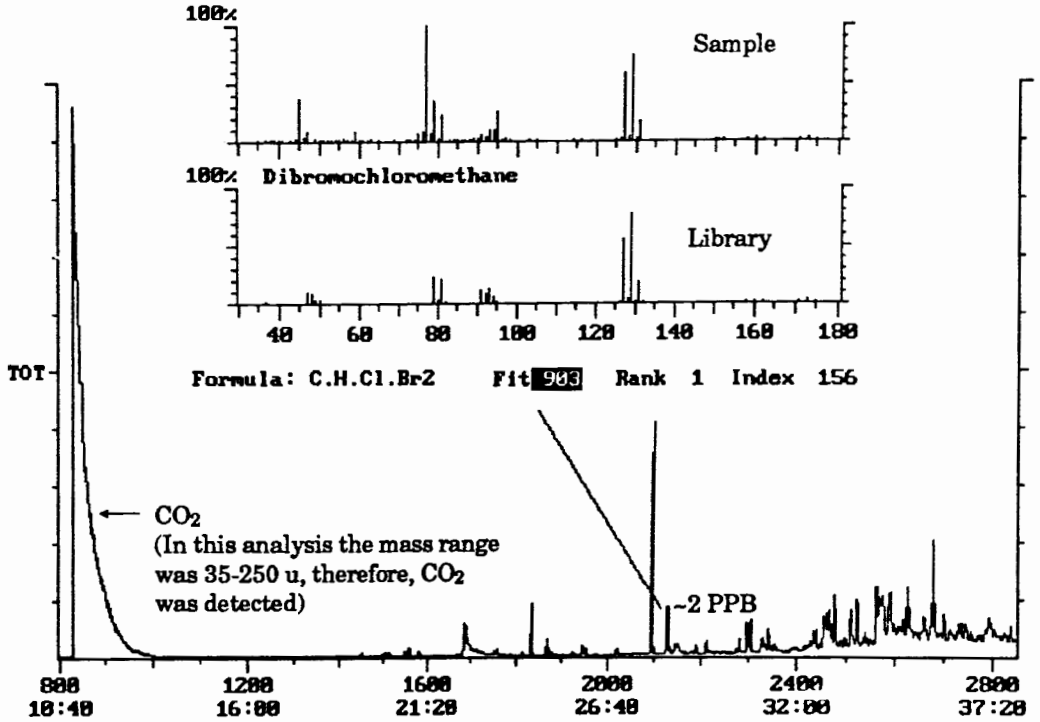


Figure 7a. RTICC of 60 mL air sample collected above the surface of a 60°C water bath dibromochloromethane, a non-target analyte is identified (fit 903/1000), estimated concentration 2 ppb.

Sorted via: Calc Amount(A) ↓

Cal	Name of Compound	Fit S/N	R Time	Me	Calc Amt(A)	Units
23	Toluene	982	27:55	VB	5.220	PPB/V
15	1,1,1-Trichloroethane	829	24:26	BV	1.061	PPB/V
36	Benzylchloride	949	33:51	VV	0.793	PPB/V
2	Chloromethane	821	13:59	BB	0.655	PPB/V
16	Benzene	983	24:54	VV	0.605	PPB/V
33	1,3,5-Trimethylbenzene	987	33:39	VV	0.593	PPB/V
34	1,2,4-Trimethylbenzene	989	33:39	VV	0.587	PPB/V
39	1,2,4-Trichlorobenzene	937	37:51	BB	0.510	PPB/V
9	Dichloromethane	941	20:40	BV	0.499	PPB/V
31	o-Xylene	985	31:15	BV	0.458	PPB/V
29	Styrene	990	31:06	BB	0.362	PPB/V
27	Ethylbenzene	983	30:27	VB	0.347	PPB/V
35	m-Dichlorobenzene	939	33:53	BV	0.304	PPB/V
28	m,p-Xylene	987	31:15	BV	0.252	PPB/V
7	Trichlorofluoromethane	994	19:21	BV	0.248	PPB/V
21	t-1,3-Dichloropropene	776	27:26	VV	0.243	PPB/V
5	Bromomethane	984	16:53	BB	0.217	PPB/V
13	Chloroform	971	23:26	BV	0.194	PPB/V
10	1,1,2-Trichloro-1,2,2-	979	21:06	BB	0.165	PPB/V
1	dichlorodifluoromethan	937	12:57	BB	0.149	PPB/V
26	Chlorobenzene	877	29:59	BB	0.143	PPB/V
32	4-Ethyltoluene	985	33:19	BV	0.143	PPB/V
25	Tetrachloroethene	764	29:27	BB	0.133	PPB/V
24	EDB	858	28:40	BV	0.079	PPB/V
22	1,1,2-Trichloroethane	784	27:19	BB	0.071	PPB/V
14	1,2-Dichloroethane	830	24:10	BV	0.043	PPB/V

Figure 7b. Quantitation Report of the Sample Shown in Figure 7a.

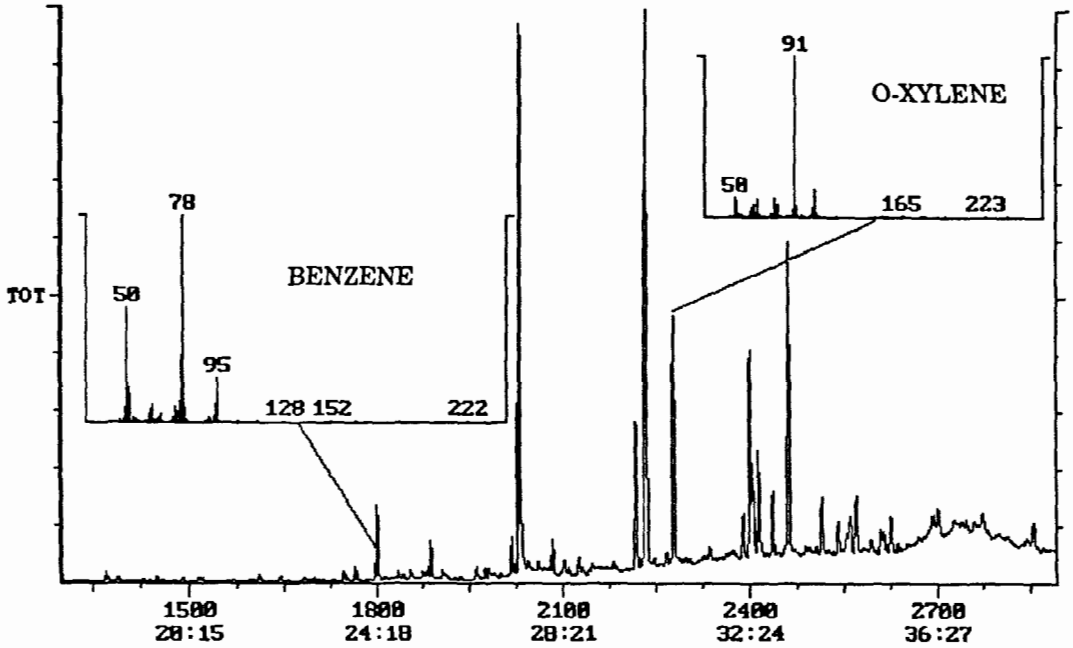


Figure 8a. RTICC of 60 mL air sample collected in Walnut Creek, California on a rainy day in heavy traffic.

Cal	Name of Compound	Fit S/N	R Time	Me	Calc Amt(A)	Units
23	Toluene	993	27:24	VB	5.927	PPB/V
28	m,p-Xylene	995	30:10	VV	3.105	PPB/V
31	o-Xylene	989	30:46	BV	2.257	PPB/V
33	1,3,5-Trimethylbenzene	994	33:14	BB	2.151	PPB/V
32	4-Ethyltoluene	995	32:26	VV	1.504	PPB/V
27	Ethylbenzene	993	29:57	VB	1.455	PPB/V
16	Benzene	978	24:20	BB	0.981	PPB/V
36	Benzylchloride	890	33:51	VV	0.689	PPB/V
29	Styrene	729	30:46	MM	0.356	PPB/V
25	Tetrachloroethene	913	28:42	MM	0.280	PPB/V
34	1,2,4-Trimethylbenzene	995	33:57	MM	0.222	PPB/V
22	1,1,2-Trichloroethane	787	28:03	MM	0.175	PPB/V
14	1,2-Dichloroethane	750	24:20	MM	0.152	PPB/V

Figure 8b. Quantitation Report of the Sample Shown in Figure 8a.

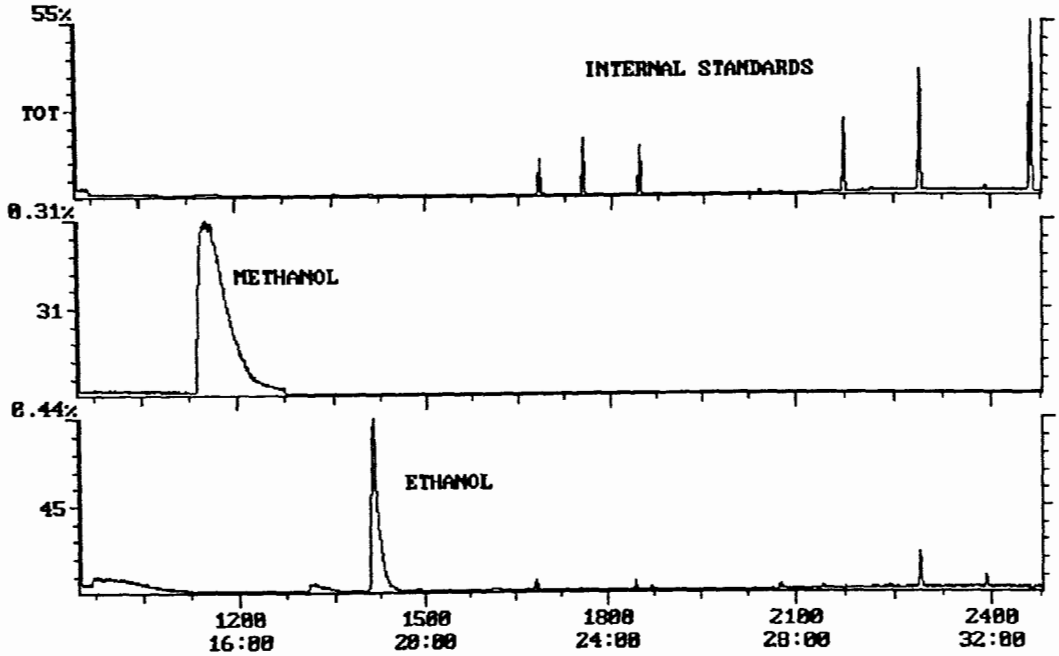


Figure 9. RTICC and characteristic ions for methanol and ethanol from a 60 mL air sample collected at an industrial site. Courtesy of Air Toxics, Ltd., Rancho Cordova, California.

REFERENCES

1. Compendium Method TO-14, The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatography Analysis, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, May 1988.

2. K.D. Oliver, J.D. Pleil, and W.A. McClenny, Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in SUMMA Polished Canisters, Atmospheric Environ. 20:1403, 1986.

3. M.W. Holdren and D.L. Smith, Stability of Volatile Organic Compounds While Stored in SUMMA Polished Steel Canisters, Final Report, EPA Contract No. 68-02-4127, Research Triangle Park, North Carolina, 1983.

4. W.A. McClenny, J.D. Pleil, J.W. Holdren, and R.N. Smith, Automated Cryogenic Preconcentration and Gas Chromatograph Determination of Volatile Organic Compounds, Anal. Chem. 56:2947, 1984.

5. W.A. McClenny, et. al., Canister-based Method for Monitoring Toxic VOCs in Ambient Air, J. Air Waste Management Association, 41, No. 10, 1308, 1991.

6. Analytical Method for the Determination of Volatile Organic Compounds (VOCs) in Air Collected in Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS), Exhibit D, Chapter 1, Part 1A, Contract Laboratory Program, February 1991.

7. Elizabeth Almasi and Norman Kirshen, The Analysis of Volatile Organic Compounds in Air, Variable Volume System, Varian GC Application Notes 19 and 32, 1989 and 1990, respectively.

63 SUPERCRITICAL FLUID EXTRACTION OF CHLOROPHENOXY ACID HERBICIDES FROM SOIL SAMPLES

Viorica Lopez-Avila, N. S. Dodhiwala, and J. Benedicto, Midwest Research Institute—California Operations, Mountain View, California 94043, and W. F. Beckert, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada 89119.

ABSTRACT

A rapid and efficient method was developed for extracting chlorophenoxy acid herbicides from soils using supercritical carbon dioxide, tetrabutylammonium hydroxide, and methyl iodide. The extraction is carried out at 400 atm/80°C/15 min static, followed by 15 min dynamic at a carbon dioxide flowrate of approximately 3 mL/min. The use of other derivatization agents (trimethylphenylammonium hydroxide, benzyltrimethylammonium chloride, and benzyltriethylammonium chloride) proved to be less effective than the tetrabutylammonium hydroxide/methyl iodide combination. Attempts made to extract other compounds currently listed in Method 8151 using supercritical carbon dioxide and tetrabutylammonium hydroxide/methyl iodide were unsuccessful, either because these compounds did not derivatize (dalapon, dinoseb, and 4-nitrophenol), or they were found to decompose (DCPA diacid, pentachlorophenol, and picloram), apparently in the injection port of the gas chromatograph, despite the fact that they were reported to be amenable to gas chromatography.

INTRODUCTION

Although supercritical fluid extraction (SFE) is becoming more and more recognized as an efficient and rapid alternative to Soxhlet extraction, the reports published so far that deal with extraction of samples by SFE are addressing mostly nonpolar organic compounds such as polynuclear aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzodioxins, etc. Recently, Hawthorne and coworkers (1) reported the extraction and methylation of 2,4-D and dicamba from stream sediment samples using supercritical fluid derivatization/extraction with trimethylphenylammonium hydroxide (TMPA) or BF_3/methanol as derivatization agents. While the derivatization with TMPA is known to require high temperatures, Hawthorne and coworkers claimed that the derivatization reaction of 2,4-D takes place during SFE with carbon dioxide at 400 atm/80°C. Their conclusion was based on the fact that increasing the concentration of TMPA yielded better recoveries of 2,4-D, while adding more TMPA to the extracts after SFE did not. The derivatization with BF_3/methanol under supercritical conditions was demonstrated in the case of 2,4-D; however, dicamba was not methylated under these conditions (1).

NOTICE: Although the research described in this paper has been supported by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

The purpose of our study was to develop an SFE method for extracting chlorophenoxy acid herbicides (Table 1) from soils using supercritical carbon dioxide. It was desirable that the extraction and the derivatization reaction be conducted simultaneously since the chlorophenoxy acid herbicides need to be converted to their corresponding methyl esters anyway in order to be analyzed by gas chromatography.

Several derivatization agents, e.g., trimethylphenylammonium hydroxide (TMPA), benzyltrimethylammonium chloride (BTMAC), benzyltriethylammonium chloride (BTEAC), and tetrabutylammonium hydroxide/methyl iodide (TBA/MI) were investigated. The extractions were carried out with supercritical carbon dioxide alone and with supercritical carbon dioxide modified with 10 percent methanol. Attempts were also made to extract other compounds currently listed in Method 8151 using supercritical carbon dioxide and tetrabutylammonium hydroxide (25 percent in methanol)/methyl iodide.

EXPERIMENTAL

The nine chlorophenoxy acid herbicides (Table 1), except dicamba, were purchased from Aldrich Chemical (Milwaukee, WI). Dicamba was purchased from Chem Service (West Chester, PA). The corresponding methyl esters were purchased from Crescent Chemical (Hauppauge, NY). All compounds were used as received without further purification (their purities were stated to be at least 98 percent, except MCPA at 95 percent and 2,4-DB at 97 percent). Stock solutions of the individual acids or esters were prepared in methanol at 10 mg/mL and kept at 4°C in the dark. A spiking solution of the chlorophenoxy acids was made by combining the individual stock solutions and diluting them to 1 mg/mL.

Derivatizing agents were purchased as solutions in methanol or as neat materials. TMPA (1.5 percent in methanol) was purchased from Eastman Kodak Company (Rochester, NY) and Fluka Chemical (Ronkonkoma, NY). To prepare TMPA in methanol, ethanol, and isopropanol, we evaporated 20 mL of 1.5-percent TMPA in methanol to dryness under a gentle stream of nitrogen, and then dissolved the residue in 3 mL methanol, ethanol, or isopropanol. BTMAC and BTEAC (purity 98 percent) were purchased as neat materials from Fluka Chemical. Forty grams of each were dissolved separately in 100 mL methanol for use in the experiments. TBA (25-percent solution in methanol) and MI (neat) were purchased from Fluka Chemical.

The extractions were performed using an Isco (Lincoln, NE) SFE System 1200 with an Isco Model 260D syringe and an Isco Model SFX 2-10 extraction module. The extraction module has shutoff valves at the inlet and outlet of the extraction vessel, allowing static and dynamic extractions to be performed. The SFE system was equipped with two fused-silica restrictors (37-cm length x 50-μm ID), which resulted in flowrates of approximately 2.5 mL/min (as liquid carbon dioxide). All extractions were carried out at 400 atm; the extraction temperature was varied (80°C, 100°C), and the static and dynamic times were also varied (from 5 to 15 min), as indicated in the tables with results. The extracted analytes were collected in 2 mL methanol. Initially, some of the extracts were concentrated to 1 mL by blowdown evaporation using a gentle stream of nitrogen. This, however, resulted in poor recoveries of the test analytes, and the blowdown evaporation was therefore not used in subsequent experiments.

All extracts were analyzed by GC/MS using the operating conditions given in Table 2. Attempts were made to analyze the extracts by GC with electron capture detection (ECD); however, the presence of excess derivatization reagent (MI) in the extracts interfered with the GC/ECD determination. Quantification of the analytes was performed using internal standard calibration. The two internal standards used were acenaphthene-d_{10} and phenanthrene-d_{10} (Table 3).

RESULTS AND DISCUSSION

Extraction without derivatizing agent

Preliminary experiments to recover the underivatized target compounds from sand samples were carried out with supercritical carbon dioxide, but the recoveries were low and difficult to reproduce. The recoveries ranged from 0 to 65 percent, when we extracted two 2-g samples, spiked with the chlorophenoxy acid herbicides at 2,500 μg/g in parallel, at 150 atm for 10 minutes, 200 atm for another 10 minutes, and 250 atm for an additional 10 minutes (the temperature of the extraction was maintained at 70°C, and the extraction was performed dynamically using a 30-cm length x 50-μm ID fused-silica restrictor heated at 100°C). In addition, the recoveries were not reproducible. For example, the recovery of 2,4-DB was 37 percent in one experiment, but only 7.1 percent in the other. In the case of 2,4,5-TP, the recovery was 54 percent in one experiment, but only 6.7 percent in the other. Other researchers (3) have reported similar results. Thus, we focused our study on finding conditions under which these chlorophenoxy acid herbicides can be extracted from a solid matrix and, at the same time, are derivatized to their corresponding methyl esters.

Extraction in the presence of selected derivatizing agents

Solutions of BTMAC and BTEAC in methanol were selected as ion-pair methylating reagents based on results by Chiang and coworkers (3,4), who reported that the chlorophenoxy acid herbicides can be extracted from soil samples and esterified in situ to their corresponding methyl esters using BTMAC. The authors further claimed that the pH of the BTMAC solution (4.8) appeared to be beneficial to the formation and stabilization of the methyl esters.

TMPA in methanol was selected as ion-pair methylating reagent based on results by Hawthorne and coworkers (1) who reported that 2,4-D and dicamba were extracted from a soil sample as methyl esters (the extraction was carried out at 400 atm/80°C/5 to 45 minutes static, followed by 5 to 15 minutes dynamic, and the amount of reagent per 2-g samples spiked at 20-ppm levels varied from 50 to 1,000 μL).

Our data (Table 4) indicate low recoveries of the derivatized chlorophenoxy acid herbicides from sand when BTMAC and BTEAC were used as derivatization reagents, regardless of the extraction temperature, and mostly good recoveries with TMPA. When we used BTMAC or BTEAC, we detected not only the methyl esters but also the benzyl esters and ethyl esters, respectively.

Additional experiments were performed with TMPA dissolved in methanol, ethanol, and isopropanol to determine whether the methylation reagent is TMPA or the alcohol in which

TMPA is dissolved. The recoveries are given in Table 5. In all cases, we found the methyl esters and only traces of ethyl or isopropyl esters.

Extraction in the presence of TBA/MI

Tetrabutylammonium hydroxide and MI were selected as derivatizing agents because they were successfully used by Hopper (5) to derivatize five chlorophenoxy acid herbicides (2,4-D; 2,4,5-T; 2,4-DB; 2,4,5-TB; and 2,3,6-TBA) and pentachlorophenol in foods. After preliminary work with the TBA/MI reagent, we concluded that TBA acts as an ion-pair reagent which assists in the transfer of the acid from the solid matrix into the stream of carbon dioxide. TBA and MI are dissolved by the carbon dioxide and transported into the collection solvent, which in our case was methanol. Upon injection of the extract into the GC/MS system, the acids are obviously converted to their corresponding methyl esters. The minimum injector temperature at which the methylation reaction occurs is 100°C. To determine the reproducibility of the methylation reaction, we prepared 10 working standards of nine chlorophenoxy acids in methanol, added TBA and MI (nominal concentrations of the test compounds were 100 ng/μL), and injected these solutions into our GC/MS system (injector temperature was held at 250°C). The derivatization yields (Table 6) were determined by comparing the instrument responses for these 10 injections with those obtained by analyzing a composite standard containing the nine methyl esters. The reproducibility of the methylation reaction was 8.6 percent or better, except for dicamba at 16.6 percent, and most compounds had percent RSDs between 7 and 8 percent. The absolute derivatization yields ranged from 46.4 to 93.6 percent, with two compounds exhibiting yields lower than 70 percent (2,4,5-T at 46.4 percent and dicamba at 57.3 percent).

After these preliminary experiments, we proceeded with the determination of the actual extraction recoveries by SFE/TBA/MI. All experiments had to be performed with spiked materials due to the lack of certified standard reference materials. Three different matrices (sand, clay soil, and topsoil) were spiked at two concentrations with the chlorophenoxy acids (only seven of them were available at the time these experiments were performed) and extracted immediately. Table 7 summarizes the individual recoveries for each of the seven compounds. Figures 3 and 4 present the average recoveries for each spike level and each matrix across the seven compounds. Overall, the recoveries were quantitative at the two spike levels.

Attempts to extract other compounds currently listed in Method 8151 using SFE combined with TBA/MI were unsuccessful, either because the compounds did not derivatize to the methyl or butyl ester (dalapon, dinoseb, and 4-nitrophenol), or the derivatization product decomposed, as in the case of DCPA diacid, pentachlorophenol, and picloram. We also found that the analysis of the extracts of some of these compounds, when injected into the GC/MS system, exhibited large peaks that did not match those of the corresponding methyl esters. These peaks were identified as the butyl esters. For two of the compounds, we found that the concentrations of the butyl esters were 4 and 16 times as high as those of the methyl esters. The experimentally determined ratios of the butyl esters to methyl esters are shown in Table 8.

A draft protocol of this method was prepared and is currently being reviewed. A round-robin study has tentatively been scheduled for later this year.

REFERENCES

1. Hawthorne, S. B., Miller, D. J., Nivens, D. E., and White, D. C., "Supercritical Fluid Extraction of Polar Analytes Using In Situ Chemical Derivatization," Anal. Chem. 64, 405-412 (1992).

2. Richards, M., Dow Chemical, personal communication (1991).

3. Chiang, L., Magee, R. J., and James, B. D., "Chromatographic Determination of Chlorinated Phenoxyacetic Acids by Simultaneous Extraction-Methylation and Application to Soil Analysis," Anal. Chim. Acta. 255, 187-196 (1991).

4. Chiang, L., Markovec, L. M., Magee, R. J., and James, B. D., "A Convenient Method Using Methanol/Benzyltrialkylammonium Reagents for Simultaneous Extraction and Methylation of 2,4-Dichlorophenoxyacetic Acid in Soil, with Subsequent Analysis via Gas Chromatography," J. Agric. Food Chem. 39, 1110-1112 (1991).

5. Hopper, M. L., "Methylation of Chlorophenoxy Acid Herbicides and Pentachlorophenol Residues in Foods Using Ion-Pair Alkylation," J. Agric. Food Chem. 35, 265-269 (1987).

TABLE 1. CHLOROPHENOXY ACID HERBICIDES INVESTIGATED IN THIS STUDY

Compound no.	Compound name	CAS no.	Chemical name
1	Dicamba	1918-00-9	3,6-Dichloro-2-methoxy benzoic acid
2	MCPP	93-65-2	2-(4-Chloro-o-tolyloxy) propionic acid
3	MCPA	94-74-6	4-Chloro-o-tolyloxy acetic acid
4	Dichlorprop	120-36-5	2-(2,4-Dichlorophenoxy) propionic acid
5	2,4-D	94-75-7	2,4-Dichlorophenoxy acetic acid
6	2,4,5-TP	93-72-1	2-(2,4,5-Trichlorophenoxy) propionic acid
7	2,4,5-T	93-76-5	2,4,5-Trichlorophenoxy acetic acid
8	MCPB	94-81-5	4-(4-Chloro-o-tolyloxy) butyric acid
9	2,4-DB	94-82-6	4-(2,4-Dichlorophenoxy) butyric acid

TABLE 2. GC/MS OPERATING CONDITIONS FOR THE ANALYSIS OF THE METHYL ESTERS OF CHLOROPHENOXY ACID HERBICIDES

Parameter	Value
GC instrument	Hewlett-Packard GC/MS Model 5971A or equivalent
Column	PTE-5 30-m length x 0.25-mm ID or equivalent, 0.25-μm film thickness
Column supplier	Supelco, Inc., Bellefonte, PA
Carrier gas flowrate	0.87 mL/min (helium)
Temperature program	80°C to 140°C at 20°C/min, 140°C to 250°C (5-min hold) at 4°C/min
Injector temperature	250°C
Detector temperature	250°C
Injection volume	1 μL
Solvent	Methanol
Type of injector	Split/splitless; splitless mode; 60 sec
Detector type	MSD or equivalent
Scanning mass range	40 to 600 amu
Scan rate	$\leq$1 sec

TABLE 3. RETENTION TIMES, INTERNAL STANDARDS, AND QUANTITATION IONS RECOMMENDED FOR GC/MS ANALYSIS

Compound no.	Compound name	RT (min)	IS used for quantitation[a]	Quantitation ion (m/z)[b]
1	Dicamba	8.38	IS-1	203
2	MCPP	9.14	IS-1	169
3	MCPA	9.54	IS-1	214
4	Dichlorprop	10.16	IS-1	162
5	2,4-D	10.97	IS-1	199
6	2,4,5-TP	13.22	IS-1	196
7	2,4,5-T	14.43	IS-2	233
8	MCPB	14.23	IS-2	101
9	2,4-DB	15.79	IS-2	101
IS-1	Acenaphthene-d_{10}	7.76	--	164
IS-2	Phenanthrene-d_{10}	13.49	--	188

[a] The concentration of the internal standard is 20 ng/μL.
[b] The quantitation ions recommended in this method are actually for the corresponding methyl esters of the chlorophenoxy acid herbicides.

TABLE 4. PERCENT RECOVERIES OF THE CHLOROPHENOXY ACID HERBICIDES (AS METHYL ESTERS) FROM SPIKED SAND BY SFE AT 80°C AND 150°C WITH CARBON DIOXIDE USING SELECTED DERIVATIZING AGENTS[a]

Compound no.	Compound name	BTMAC[b]	BTEAC[c]	TMPA[d]
Temperature—80°C				
1	Dicamba	1.8	ND[e]	89.1
2	MCPP	8.8	11.7	71.5
3	MCPA	14.8	ND	85.6
5	2,4-D	15.1	10.4	71.4
7	2,4,5-T	4.3	8.8	ND
8	MCPB	13.1	4.3	79.7
9	2,4-DB	11.0	7.8	68.9
Temperature—150°C				
1	Dicamba	6.0	ND	73.5
2	MCPP	12.2	21.8	65.7
3	MCPA	27.3	47.9	73.5
5	2,4-D	29.1	39.4	62.9
7	2,4,5-T	27.8	27.2	13.4
8	MCPB	11.5	9.1	95.7
9	2,4-DB	11.4	10.3	79.1

[a] The extractions were performed at 400 atm/80°C/15 min static, followed by 15 min dynamic, with the reagents added to the sample in the extraction vessel. Extraction vessel volume: 10 mL for BTMAC and BTEAC experiments and 2.5 mL for TMPA experiments. The sample size was 2 g and the spike level was 250 μg/g per compound. Compounds 4 and 6 were not available for spiking. The extracted material was collected in 2 mL methanol and adjusted to 5 mL for GC/MS analysis. Single determinations.

[b] The volume of reagent was 3 mL BTMAC solution (40 percent in methanol).

[c] The volume of reagent was 3 mL BTEAC solution (40 percent in methanol).

[d] The volume of reagent was 1 mL TMPA solution (10 percent in methanol).

[e] ND - not detected.

TABLE 5. PERCENT RECOVERIES OF SEVEN CHLOROPHENOXY ACID HERBICIDES (AS METHYL ESTERS) FROM SPIKED SAND BY SFE WITH CARBON DIOXIDE AND 10 PERCENT TMPA IN METHANOL, ETHANOL, OR ISOPROPANOL USING AN ISCO EXTRACTION SYSTEM

Compound no.	Compound name	TMPA in methanol	TMPA in ethanol	TMPA in isopropanol
1	Dicamba	89.1	102	73.8
2	MCPP	71.5	52.9	61.0
3	MCPA	85.6	11.1	ND[b]
5	2,4-D	71.4	56.1	39.4
7	2,4,5-T	ND	ND	ND
8	MCPB	79.7	68.3	47.9
9	2,4-DB	68.9	38.4	14.5

[a] The extractions were performed at 400 atm/80°C/15 min static, followed by 15 min dynamic, with 1 mL TMPA solution added to the sample in the extraction vessel (10 percent in methanol, ethanol, or isopropanol). Extraction vessel volume: 2.5 mL. The sample size was 2 g and the spike level was 250 μg/g. Compounds 4 and 6 were not available for spiking. The extracted material was collected in 5 mL solvent (methanol, ethanol, or isopropanol). Single determinations.

[b] Not detected. Approximate detection limit was 10 ng/μL.

TABLE 6. TYPICAL DERIVATIZATION YIELDS FOR THE CHLOROPHENOXY ACID HERBICIDES WITH TBA/MI[a]

Compound no.	Compound name	Derivatization yield	Percent RSD
1	Dicamba	57.3	16.6
2	MCPP	73.1	7.2
3	MCPA	93.6	7.5
4	Dichlorprop	93.3	7.5
5	2,4-D	87.1	7.4
6	2,4,5-TP	84.6	7.2
7	2,4,5-T	46.4	8.6
8	MCPB	87.1	3.1
9	2,4-DB	86.6	5.9

[a] The number of determinations was 10. The derivatization yield was determined at a concentration of 100 ng/μL in solution. The target analyte/TBA/MI solution was injected into the GC/MS system at an injector temperature of 250°C. The GC/MS operating conditions are given in Table 2.

TABLE 7. PERCENT RECOVERIES OF SEVEN CHLOROPHENOXY ACID HERBICIDES (AS METHYL ESTERS) BY SFE WITH SUPERCRITICAL CARBON DIOXIDE

		Sand				Clay soil				Topsoil			
Compound no.	Compound name	50-ppm spike		250-ppm spike		50-ppm spike		250-ppm spike		50-ppm spike		250-ppm spike	
1	Dicamba	87.5	103	98.4	82.6	94.0	108	90.9	85.4	91.0	111	128	
2	MCPP	79.0	76.0	83.4	57.4	92.5	99.0	72.7	70.6	80.5	75.5	85.8	
3	MCPA	100	110	102	73.5	121	122	84.5	80.5	90.5	96.5	98.7	
5	2,4-D	85.0	103	91.7	68.8	105	97.0	77.2	70.4	80.0	85.0	90.6	
7	2,4,5-T	77.0	116	86.3	67.5	106	120	75.2	69.0	83.5	97.5	94.9	
8	MCPB	107	108	114	61.8	107	104	91.6	96.4	111	106	100	
9	2,4-DB	124	124	126	70.4	128	141	102	105	123	120	109	

[a] The extractions were performed at 400 atm/80°C/15 min static, followed by 15 min dynamic, with the reagents (0.5 mL TBA 25 percent in methanol and 0.5 mL MI) added to sample in the extraction vessel. Extraction vessel volume: 10 mL. The sample size was 2 g and the spike level was 50 ppm or 250 ppm per compound. Compounds 4 and 6 were not available for spiking. The extracted material was collected in 2 mL methanol. Duplicate determinations, except for the topsoil at 250-ppm spike level.

TABLE 8. DERIVATIZATION OF METHOD 8151 COMPOUNDS WITH TBA/MI—RATIO OF BUTYL ESTER TO METHYL ESTER CONCENTRATION

Compound name	Ratio of butyl ester to methyl ester
Acifluorfen	4.03
Bentazon	0.05
Chloramben	0.75
2,4-D	0
2,4-DB	0
Dalapon	a
DCPA diacid	b
Dicamba	6.4
3,5-Dichlorobenzoic acid	16.0
Dichlorprop	0.25
Dinoseb	a
5-Hydroxydicamba	c
MCPA	0.09
MCPB	0.13
MCPP	0.14
4-Nitrophenol	a
PCP	d
Picloram	e
2,4,5-T	0.13
2,4,5-TP	0.30

[a] Not able to detect formation of esters.
[b] The derivatization product appears to decompose.
[c] This compound was not available for testing.
[d] The derivatization product was found to be tetrachlorophenol.
[e] The only compound detected in this reaction was the decarboxylated picloram.

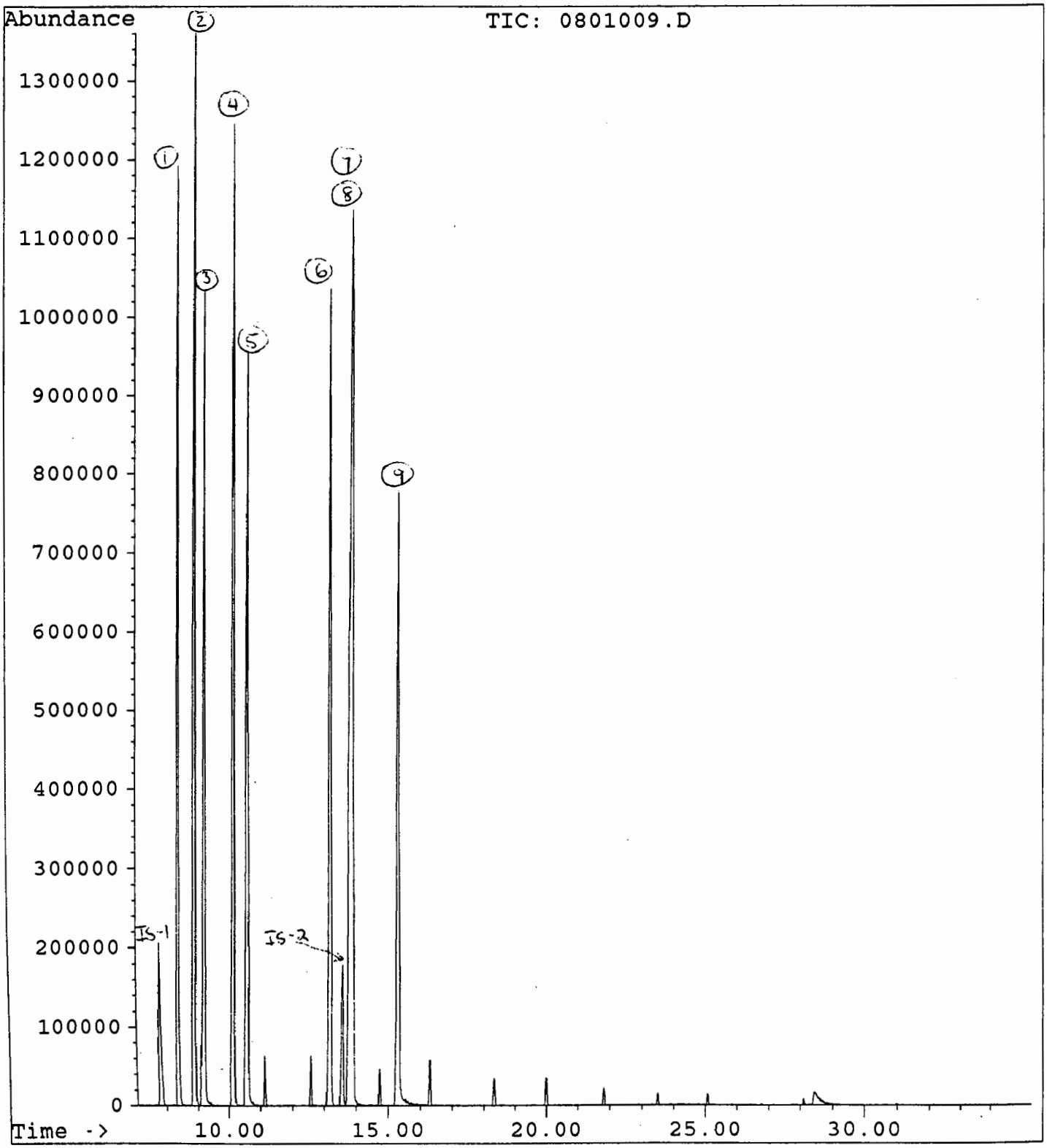


Figure 1. GC/MS chromatogram of the composite standard containing the methyl esters of the chlorophenoxy acid herbicides. The GC/MS operating conditions are given in Table 2.

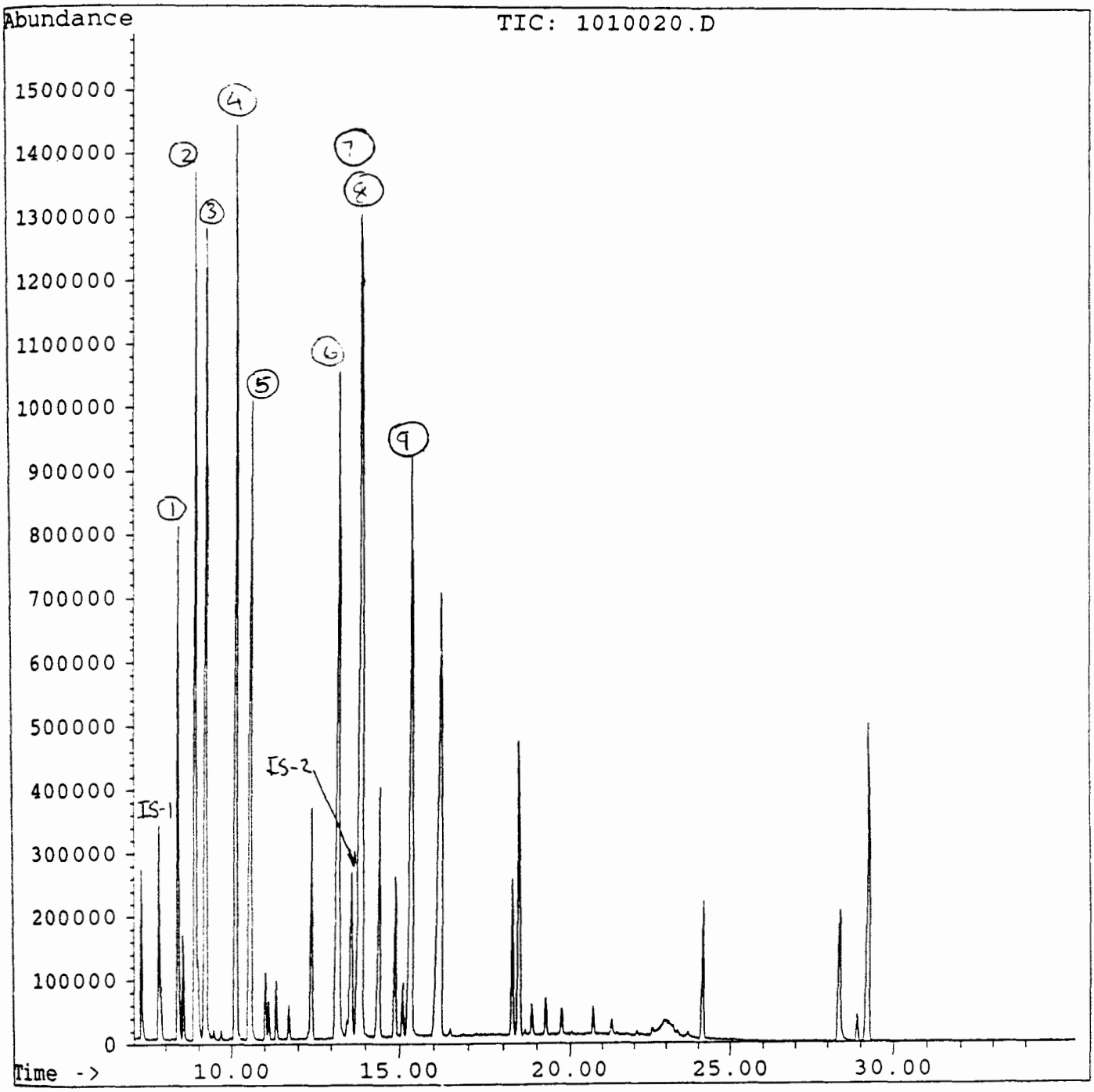


Figure 2. GC/MS chromatogram of the chlorophenoxy acid herbicides derivatized to their corresponding methyl esters upon injection into a GC/MS system (injector temperature 250°C). The GC/MS operating conditions are given in Table 2.

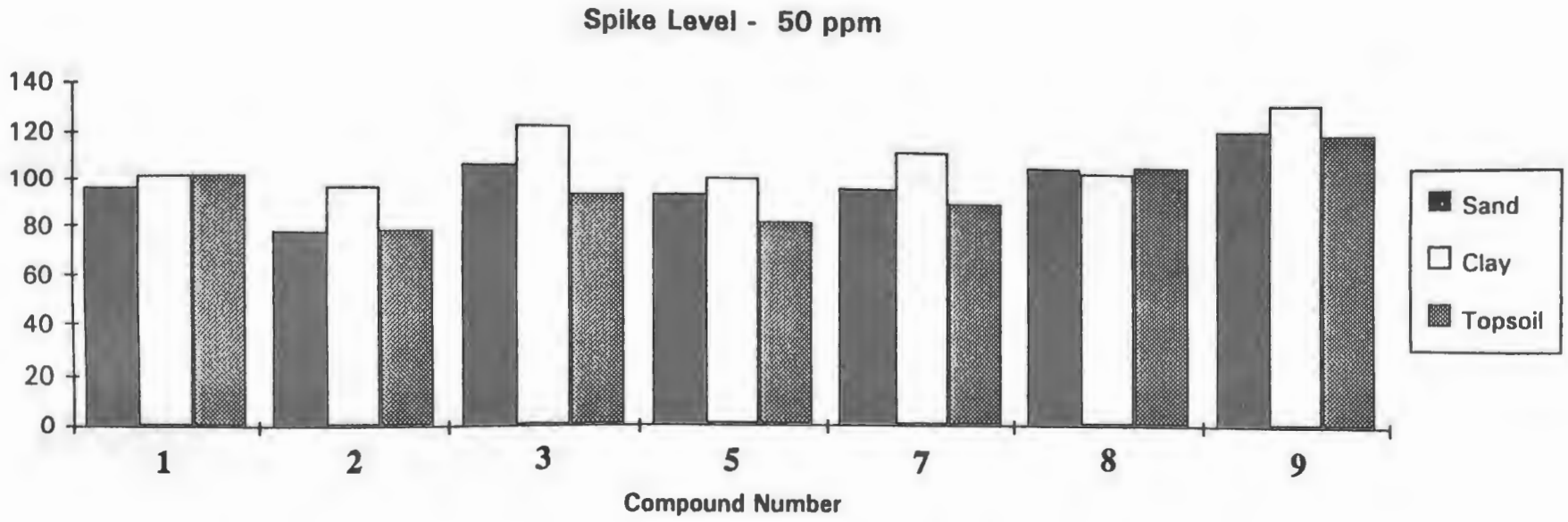


Figure 3. Average recoveries of the seven chlorophenoxy acid herbicides extracted from sand, clay soil, and topsoil samples spiked at 50 ppm. The extractions were performed at 400 atm/80°C/15 min static, followed by 15 min dynamic, with the TBA/MI reagent added to the samples in the extraction vessels.

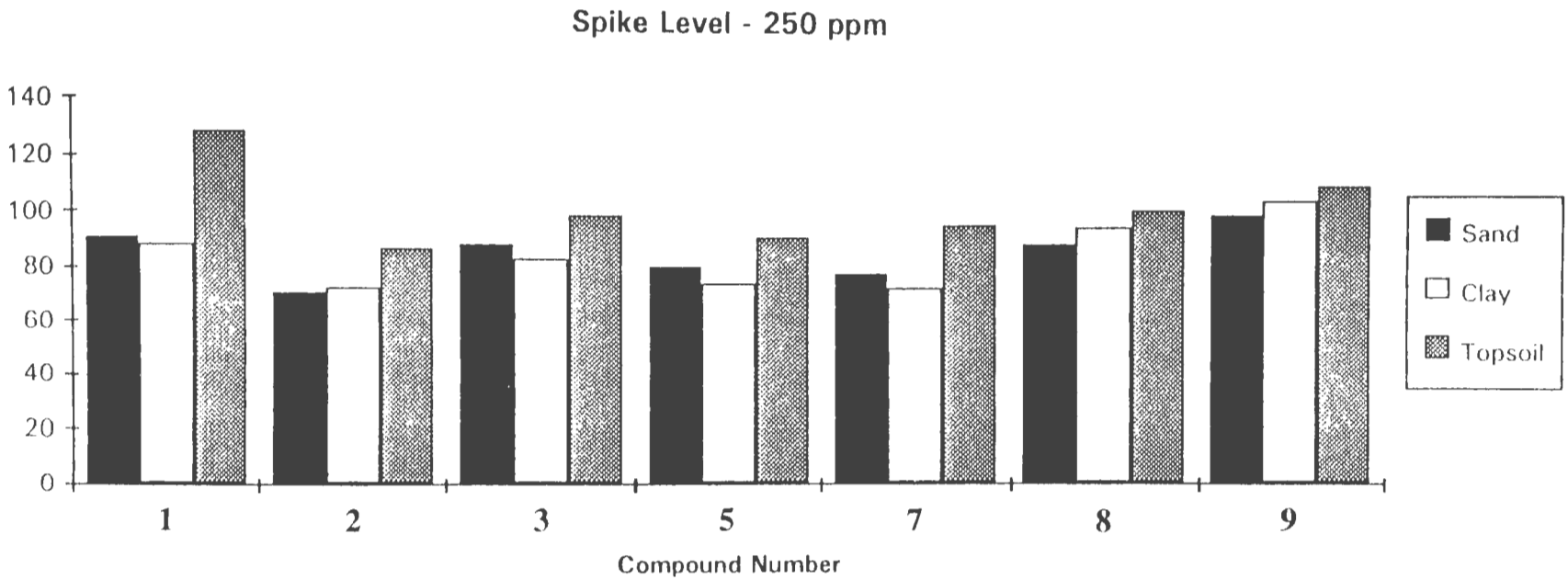


Figure 4. Average recoveries of the seven chlorophenoxy acid herbicides extracted from sand, clay soil, and topsoil samples spiked at 250 ppm. The extractions were performed at 400 atm/80°C/15 min static, followed by 15 min dynamic, with the TBA/MI reagent added to the samples in the extraction vessels.

64

METHODS OF ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

Gale G. Sutton, Laboratory Director, Galson Corporation,
6601 Kirkville Road, East Syracuse, New York 13057
(315) 432-0506

The benefits of understanding laboratory analytical methods for volatile organic compounds (VOCs) should not be underestimated. Differences of detection limits, quality control and method limitations can result in significant variations in analytical results. Knowledge of analytical methods can limit unnecessary laboratory costs and decrease laboratory turnaround without sacrificing the quality or usability of the results.

Volatile analyses of water and soil samples consists of: a sample concentration technique, the separation of analytes from the matrix (as well as from other analytes) and finally detection and quantitation. The following types of equipment serve these purposes: an injector, a purge and trap liquid sample concentrator, chromatography columns, and detectors (FID, ECD, Hall/ELCD, PID, and mass spectrometer).

Each regulatory program has designated its own methods and each method has distinct advantages. There are certain advantages some methods have over others. Drinking water methods such as 502.2, 503.1 and 524.2 are sometimes used for low level groundwater analysis. EPA methods 601, 602 and 624 are part of the NPDES/SPDES (Clean Water Act) program. RCRA (SW846) divides its methods into sample preparation and concentration methods (i.e. 5030-purge and trap) and analysis methods (i.e. 8010, 8020, 8021, 8015, and 8240). Finally, CERCLA and NYS DEC ASP have developed their own variation of RCRA volatile method 8240.

Along with the analytical differences concerning calibration, detection and quantitation, the quality control requirements are also specific to each method. Quality control checks, matrix spikes, duplicates, and deliverables may be specified or (as in the case of RCRA methods) may be loosely defined.

In conclusion, the choice of method can affect the usability of the data. The best method for a project will be the one that provides the fastest turnaround, assures the required detection limits and yields successful validation performance.

65

ISOLATION OF PCDD/PCDF FROM COMPLEX SAMPLE EXTRACTS WITH AN AUTOMATED MODULAR LIQUID CHROMATOGRAPHIC SYSTEM USING DISPOSABLE PREPACKED CHROMATOGRAPHIC COLUMNS

Hamid Shirkhan, Fluid Management Systems, 125 Walnut Street, Watertown, MA 02172, and T. O. Tiernan, D. J. Wagel, G. F. VanNess, J. G. Solch and J. H. Garrett, Department of Chemistry, Wright State University, Dayton, OH 45435.

ABSTRACT

Previous reports from our laboratory have described the development and testing of two computer-controlled low-pressure liquid chromatographic systems for isolating polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from complex sample extracts containing these. The pump and multi-port Teflon solenoid valves of the automated system were connected to glass chromatographic columns and were controlled by a microprocessor which was interfaced to a computer. The first automated system sequentially directed as many as five sample extracts through separate multi-layer silica gel and activated alumina columns and then through a common carbon column. Experiments conducted with this sequential system demonstrated that the silica and alumina column eluates did not need to be concentrated prior to adding each eluate to the next column, and that the sequentially processed samples were not cross-contaminated, even when samples containing high and low concentrations of PCDD/PCDF were processed in series. The concentrations of PCDD/PCDF which were measured in incinerator flyash, paper sludge and wastewater extracts, which were fractionated with the automated system, were in excellent agreement with the concentrations measured in identical extracts which were cleaned up by using the normal manual procedures. In addition, the extracts processed with the automated system contained lower levels of background interferences than the manually prepared samples. Approximately 16 hours are required for the sequential system to process five sample extracts. To reduce the time required to prepare a set of samples, a modular system was constructed in which each module contained all of the hardware components which are required to prepare a single sample extract. A computer was interfaced to eight of these modules and instructions were downloaded to the concurrently operating modules. Each module of this parallel-processing liquid chromatographic system processed an extract for GC-MS analysis in two hours and these chromatographic separations were highly reproducible. The glass columns used with the automated system in these previous studies required careful manual cleaning and repacking between each set of samples. In order to further reduce the effort required to process a set of samples with the automated system, prepacked silica, alumina and carbon columns were obtained from a supplier and their use was evaluated in the present study. Use of these new disposable Teflon columns can result in saving approximately three hours of labor between each set of samples processed, and the prepacked columns are easily attached to the automated system. The chromatographic properties of the prepacked columns were found to be quite similar to those of the previously used columns. Results of experiments evaluating the reproducibility and stability of the prepacked columns will be presented. The concentrations of PCDD/PCDF and the levels of background interferences in samples prepared with the prepacked columns will also be compared to results obtained with laboratory-prepared columns during the earlier studies.

INORGANICS

66

THE EFFICACY OF MICROWAVE HOT ACID LEACHING FOR DETERMINATION OF METALS.

Lois Jassie, Elaine Hasty, Robert Revesz, CEM Corporation, 3100 Smith Farm Road, Matthews, North Carolina 28105; H. M. Kingston, Department of Chemistry, Mellon Hall, Duquesne University, Pittsburgh, Pennsylvania 15282

INTRODUCTION

The primary environmental concerns regarding hazardous wastes in the geosphere are the possible contamination of groundwater aquifers by waste leachates and leakage from the wastes. Through complex interactions of a combination of landfills, streams, wells and aquifers, these hazardous wastes, in particular those containing toxic metals that find their way into the geosphere, have the potential to effect biota and human health. Processes that influence the availability of toxic, heavy metal mobility include sorption by the soil, ion exchange and interaction with soil bacteria, etc. These activities are highly dependent on a number of chemical parameters that include pH, temperature, and soil type.

Properties of metals dissolved in water depend largely on the metal species, thus speciation of metals in aqueous systems plays a crucial role in characterization of ground water and wastewaters. Hydrated metal complexes, organometallics, metals incorporated into crystalline minerals and adsorbed forms can have vastly different solubilities and transport properties. It is difficult to know the amount of these potentially harmful pollutants that make their way into potemtially potable water sources. Through a complex interplay of natural and man-made phenomena many of these materials become available to the dynamic and ever-changing environment. Leaching, especially by acids, tends to mobilize otherwise precipitated hydrated metal oxides and at reduced pH retains many metal ions in solution. Biologically available pollutants are also available to man through incorporation into the food chain. Shellfish tend to concentrate a number of pollutants, including heavy metals and finding them at elevated levels in this tissue is generally considered an indicator of contamination. Analysis of solid wastes, soils, contaminated sludges, biological tissue or waste water for action levels of regulated toxic metals is in essence a sample preparation exercise that must parallel, to some extent, the bioavailability of these toxic metals. This paper will examine the application of microwave-assisted leaching schemes to the analysis of heavy metals in samples of environmental interest, in particular, sediments, soils, biological tissues, and water matrices.

History of the Development of EPA Microwave Methods-A number of individuals and groups have interacted with various Environmrntal Protection Agency (EPA) programs over the last five years to produce the three principal microwave test methods for trace elements currently pending approval. A microwave method for preparation of industrial furnace feedstreams for trace metals is also in the system.

Nation-wide approval was sought by CEM Corporation for the closed vessel microwave digestion of wastewater samples for metals determination. Under the Clean Water Act, we have applied for a variance to use an alternate test procedure based on microwave heating for the analysis of (metal) pollutants. A proposed rule to amend 40 CFR part 136 appeared in the October 25, 1991 Federal Register approves this method as an alternate (additional) procedure for the determination of thirteen metals in domestic and industrial wastewater at specified concentrations by inductively coupled plasma optical emission spectrometry (ICP-OES). These metals and their limits of quantitation are shown in Table I. The

method is also approved for the determination of 11 metals by direct aspiration AAS, and for 10 metals by DCP/AES analysis.

Table I. Elements and their Limits of Quantitation Established by the EPA for Domestic and Industrial Wastewater Samples Prepared by Microwave Digestion for ICP/AES Analysis

Element	Maximum Concentration, µg/mL
Al	50
Sn	50
As	50
Ba	0.5
Cd	0.5
Cr	10.0
Cu	6.0
Fe	50.0
Pb	0.4
Mn	5.0
Ni	40.0
Se	80
Zn	10.0

Concurrently, efforts were undertaken in conjunction with the Office of Solid Waste (OSW) for the RCRA program and the Office of Emergency and Remedial Response for the CERCLA (Superfund) program to produce microwave dissolution methods for the analysis of metals in solids and aqueous samples, respectively. These methods seek to bridge the gap between older prescription based methods and performance based methods. For example, Method 3015 for aqueous samples other than drinking water contains the prescription for conducting the test in a "follow me " type procedure. However, it is dependent on calibration of the microwave unit for correct transference of the critical parameters of the test in order to accurately reproduce the requisite conditions under which decomposition occurs. Both methods also contain the performance criteria for correct implementation of the procedure. That is, they stipulate the important temperatures at which dissolution must be conducted in order to achieve conditions for reproducibly leaching metals.

Chemistry and Methodology-The empirical basis of the tests is derived from studies on the decomposition temperatures for the principal components of biological and botanical matrices (Kingston & Jassie, 1988). Specific procedures were developed to prepare a variety of standard reference materials (SRMs) for elemental analysis. Tailoring the decomposition of a specific matrix means that samples like wheat flour, which are largely carbohydrate with small amounts of protein and no fatty component, are easily digested in nitric acid at 145-150 °C. Decomposition at the appropriate target temperature does not however insure total recovery of any given analyte from solution; the chemistry is also important. Organic and inorganic matrices as well, require HF to release elements that may be bound up in the siliceous phase.

Comparison of Methods 3015 and 3051-This target temperature concept has been developed into the performance based criteria that are features of the two new proposed U. S. EPA SW-846 (microwave) Methods 3051 and 3015 for the sample

preparation of solid wastes and waters. Shown below is a table comparing the empirically derived parameters for both tests. The performance criteria for Method 3015 include 160 ± 4 °C for 10 minutes followed by 160-170 °C for 10 minutes. Similarly for Method 3051, samples must reach 175 °C in < 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute heating period.

Table II. Comparison of Parameters in EPA Methods 3015 and 3051

	Vessel type	# of vessels	Sample size	HNO_3 mL	Time min	Temp. °C	Program Power, W
Method3015 (aqueous) RCRA	PFA	5	45 mL	5	10	1) 160 ± 4	545
					10	2) 160-170	344
	LDV	5	45mL	5	10	1) 160 ± 4	473
					10	2) 160-170	237
Method3051 (solids) CERCLA	PFA	6	0.5 g	10	5.5	1) 175	574
					4.5	2) 170-180	
	LDV	6	0.5 g	10	5.5	1) 175	445
					4.5	2) 170-180	256

note: PFA-All PFA Teflon Vessel
LDV-Lined Digestion Vessel

Current Status and Activities of EPA vis a vis Microwave Methods- Final approvals of the NPDES method await adjudication of comments from the field. Both SW-846 Methods 3015 and 3051 were released prematurely. The long-awaited 2nd revision of the third update of the Statement of Work is complete. Its appearance in the Federal Register however, has been delayed pending some internal conflict resolution.

Role of Standards in Method Validation- Reference Materials (RMs) are widely used in the the analytical community to evaluate analytical methods and laboratory performance. Proper use of such materials is imperative to insure that information derived from them is scientifically accurate and defensible. Criteria for their use include a reasonable match with the client matrix and elemental concentrations of roughly the same order of magnitude (Becker et al, 1991). It is also helpful to select an element with small uncertainties, the more easily to detect bias. Herein lies a dilemma. How well can these RMs be used to validate something for which they were not certified?

Among the most widely used reference materials are those from the National Institute of Standards and Technology (NIST), the National Research Council (NRC) of Canada, and the International Atomic Energy Agency (IAEA). The U. S. Geologic Survey has several water standards, and U. S. EPA labs use consensus standards. EPA consensus materials generally have been extensively analyzed and, for certain elements, there are concentrations, occasionally, with confidence intervals. According to the laws of statistics, large numbers of analyses of the same elements will tend to cluster around a certain value. However, problems of method bias, systematic, or random errors that may be present, can skew these expected normal distributions. Even if all laboratories performed the same analysis the same way, all of the results could be similarly biased. Some of these problems have been addressed in the validation study of the proposed

microwave solids method and in the bias study for the proposed microwave method for aqueous samples.

In 1989, the deputy administrator of EPA established the Environmental Monitoring Management Council (EMMC) whose charge was to develop a solution to monitoring problems within the Agency. The first issue addressed by EMMC was the integration of the Agency's environmental monitoring methods and quality control techniques. A multi-part program consisted of simultaneous efforts to integrate five existing methodologies, devise a system of coordinating the future development of methods across the Agency, and develop a system for the speedy approval and publication of new methods (Freidman, D.,1992). Among the five laboratory techniques selected for their broad utility and suitability for demonstrating the feasibility of methods integration are 1) conventional and 2) microwave-assisted strong acid extraction of elemental species from liquids and solids. In the preparation of draft methods, efforts have been made to develop a single acid mixture composed of nitric and hydrochloric acids and the accompanying experimental conditions that can be used in both conventional and microwave extractions to give comparable results. Such conditions for the mixed acids have been derived empirically for the microwave technique as one of the research goals of an interagency agreement between NIST and EPA Region III Laboratory. Temperature profiles of these conditions will be discussed.

RESULTS AND DISCUSSION

In this section examples of extraction and leaching in various environmental applications will be presented. In most cases, information was derived from the analyses of samples prepared by microwave dissolution in hot nitric acid. Examples of microwave assisted leaching of soil samples using aquaregia also will be discussed, and one sequential fractionation will be cited.

Sequential Leaching-To mimic environmental conditions that might be encountered in nature, Mahan sequentially extracted Ca, Fe, Cr, Mn, Pb, and Zn from sediments using microwave leaching techniques (Mahan et al, 1986). They felt sequential fractionation was particularly useful since anthropogenically produced metals normally show up in the labile fractions rather than in the residual sediment. Nitric and hydrochloric acid (4:1) leaching played a prominent role in assessing the residual metals and, when HF was added, total metals could also be determined. Selected metal recoveries for SRM 1645 River Sediment in the fractionation scheme are shown below. Because water waste and leachates inhabit various environments that are dynamic and continuously changing, perhaps we should be trying to compare one-step acid leaching procedures to such fractionation schemes.

Table III. Metal Recovery by Bonding Fraction in Microwave Extraction of NBS SRM1645 River Sediment Determined by FLAAS

Metal	Exch+Carb	Anoxic	Organic	Residual	Total	Certificate
Fe,%	0.17	2.5	0.85	3.5	7.0	11.3± 0.6
Cr,%	0.08	2.6	0.76	0.11	3.6	2.96± 0.14
Mn,µg/g	103	279	55	124	561	785 ± 48
Pb,µg/g	160	434	163	nd	757	714± 14
Zn,µg/g	358	1215	280	168	2021	1720± 85

Iron was tied up in the silica fraction because subsequent decompositions with HF recovered the remaining iron from the residual fractions and in a total digest of starting material as well. For both SRM1645 and SRM1646 Estaurine Sediment, summing the fractions for the other metals gave consistently high results when compared to the certificate value. This led them to suspect a systematic error either in the extraction procedure or in the determination of the metals.

One-step Leach Procedures-Under contract from OSW, Research Triangle Institute (RTI) conducted a collaborative study validating the microwave-based acid dissolution SW-846 Method 3051 for soils, sediments, sludges, and oily wastes (Binstock et al, 1989). Using reference materials, and a simulated oily waste composite of two reference materials, the analysis of precision showed an order of magnitude variation in repeatability of elemental determinations, e.g. 8.5% for Mn to 85% for Mo in the sediment. The study also showed that 1) if an extra limit of error, ± 20%, of the total value is acceptable, then the microwave method may be satisfactory to estimate the concentration of Zn, Pb, Ni, Mn, Cu, and Cd in sediment, 2) estimates of concentration can be done with about the same precision as open beaker digestions for the same metals, and 3) for all of the soil, sediment and oily matrices, with somewhat better precision than classical open vessel techniques. When the uncertainty bounds of the SRM are statistically enlarged, the extra limit of error often allows a larger number of experimentally determined mean values to be acceptable. It would be of interest to establish which sample preparation parameters (temperature, time, sample size, etc.) are most critical to reducing the large relative standard deviations that were cited for analysis of the sediment? What affect have these parameters on the recovery of metals from the SRMs or from the synthetic mixture?

Because the wear metals in oil (SRM1085) is a relatively uncomplicated matrix, dissolution in hot nitric acid should have achieved essentially complete digestion. Thus it is the only material in which it was conceivable to examine bias for the microwave method. If the criteria of "no method bias" means recovery of 90-110% of the certified value, then the following table suggests that 7 of the nine metals can be reliably estimated.

Table IV. Recovery and Bias Data for SRM 1085 Wear Metals in Oil Using Method 3051

Element	Mean ± SD	%RSD	Certificate	%Bias
Ag	234 ± 35.9	15	(296)	-20
Al	295 ± 31 .1	10	296 ± 4	0
Cr	293 ± 26.6	9	298 ± 5	-2
Cu	289 ± 23.8	8	295 ± 10	-2
Fe	311 ± 34.7	11	300 ± 4	+4
Mg	270 ± 29.1	11	297 ± 3	-9
Mo	238 ± 30.3	13	292 ± 11	-18
Ni	293 ± 25.0	8	303 ± 7	-3
Pb	279 ± 22.1	8	305 ± 8	-8

note: Elements determined by ICP-AES; Silver value for information only; Concentration in μg/g; SRM obtained from NIST.

Except for iron, all values are below their certificate values. Simple estimates of bias, the difference in means divided by the certificate value, were provided at the time of the study's completion. Recalculation of the absolute value of the bias estimate at the 0.05 significance level, suggests that 27 μg/g for Mo is larger than the critical value of

18.7μg/g. This is almost certainly the case for Mg and Pb as well. Even the confidence interval for bias in these three cases does not span zero (Becker, et al, 1988).

Fortunately, the absence of an **approved** microwave method for the preparation of soils and sediments has not kept analysts from using the method for routine screening. Laboratories often use reference materials as benchmarks to gage the laboratory performance of methods. What is the validity of using materials with certified levels of specific elements that have been analyzed for total metal concentrations? Have they become inter alia quality control standards, or performance standards for a chemical extraction process which by its very nature is incomplete? To improve the quality of analytical data coming from testing labs, reference materials are now routinely included in a batch of samples. Wide spread adoption of such practises brings with it problems of misuse and misunderstandings about the information associated with the RM certificate. In the context of quality assurance, the proper role for standard reference materials may well be as a primary reference standard against which one or more secondary laboratory reference standards are "calibrated". These secondary standards may be suitable QC samples in the batch concept; the SRM is only called upon infrequently for recalibration of the laboratory standards. Suppliers of certified reference materials may be hard pressed to fill the demand of all the busy laboratories requesting RMs, not to mention the high cost associated with such indiscriminate use. Does the analytical method shut down when no more of the RM is available? In collaboration with Jean Kane from the materials certification program in the Office of Standard Reference Materials at NIST we have begun to collect and assess data from members of the analytical community using such materials with microwave methods.

During the process of developing the microwave dissolution procedure for water samples, a number of reference materials were identified in an effort to construct a valid analysis of the bias that might be present in such a leaching technique. Members of EPA Regional Lab III (Annapolis, MD) examined a suite of water standards that were used to assess the bias of SW-846 Method 3015. Elements of interest were leached in the presence of hot nitric acid at temperatures where the organic components present in the matrix are completely oxidized. Preliminary data from the Method 3015 bias study showed that certain metals could be estimated without bias.

In her study comparing different decomposition procedures, Kruschevska showed that zinc can be determined in milk matrices that were simply digested in nitric acid. Recovery approaches 100% in nearly all cases, despite the presence of relatively large amounts of residual carbon (Kruschevska, et al, 1992). Measurable carbon residues chronicle the incompleteness of the digestion process, especially in protein-rich, cholesteric, or high-fat matrices. Additions of peroxide or sulfuric acid in the microwave preparation and temperatures of 300 °C in a high pressure asher were effective in reducing the residual carbon content of the milk samples, however, the recovery of zinc was not substantially improved. It is clear that nitric acid has been able to release the analyte of interest despite the presence of undigested material.

As the addition of peroxide to biological matrices improves the recoveries of many elements, complete mineralization using appropriate reagents such as hydrofluoric acid is needed to determine total metal content in silica-based soils and sediments. Certain metals, like cadmium and aluminum, can be fully recovered when digested in aquaregia. For example, in citrus juices, microwave digestion was comparable to a muffle furnace method for the determination of certain elements. Because the authors suspected that the products

were contaminated with tin from the metal storage container aquaregia was used for the digestions (Rezaaiyan et al,1990). The improved recoveries over nitric acid alone provide a cogent argument for the inclusion of aquaregia into both microwave Methods 3015 and 3051.

One of the most often used reference materials in environmental laboratories is NIST's SRM2704 Buffalo River Sediment. Data from selected analyses performed by microwave hot acid leaching are shown in the following table along with other reference materials that have been used routinely for quality control.

Table V. Determination of Selected Toxic Metals in Inorganic Reference Materials Prepared by Microwave Leaching in Nitric Acid

	concentration, µg/g						
	As		Cu		Pb		
Reference Mat'l	Cert.	Found	Cert	Found	Cert	Found	Ref
Buffalo River	23.4±0.8	23.5±0.32	98.6±5.0	96.3±2.14	161±17	168±4	Army
Sediment		25.2±2.1		102±1		178±1	CEM
SRM2704		31.7±6.3		93.5±4.3		125.4±11.8	ManLab
Marine Sediment PACS-1	211±11	180±1	452±1	452±8	404±20	399±9	CEM
Peruvian Soil	(90)	95±9	(80)	78±9	(100)	143±2	CEM
SRM 4355				53±6		120±8	RTI

note: numbers in parentheses are information values only

Table VI. Determination of Selected Toxic Metals in Biological Reference Materials Prepared by Microwave Leaching in Nitric Acid

	concentration, µg/g						
	As		Cu		Pb		
Reference Mat'l	Cert.	Found	Cert	Found	Cert	Found	Ref
Oyster Tissue SRM1566	13.4±1.9	–	63.0±3.5	61.0	0.48±0.04	3.5	EPA-5
						Cd	
		11.8±2.5		60.5±4.2	3.5±0.4	3.1±0.2	EPA-7
SRM1566a	14.0±1.2	13.1±0.8	–	–	–	–	Ybanez
Bovine Liver	0.047±.006	–	158±7	149±15	0.44±0.06	0.40±0.03	Lyon
SRM1577a				169±1			Sah

It is apparent from these tables that a judicious selection of elements can give good answers to the correct questions. Data from a large number of replicates may give insight into decomposition problems (matrix). Or, as in the case of high arsenic values, they may suggest a measurement problem, such as spectral interference. Measurement errors must be separated from leaching errors. Leaching efficiency for all elements is not the same, as

was shown in the RTI study and not all 26 elements for the soils or 23 elements for the waters, can be expected to behave as well as these few.

There are many ways to assess the performance of an analytical method. In GFAAS for instance, spike recoveries, standard additions, and matrix matching of blanks and standards all can provide important information on the validity of data acquired. If reference materials are required, then they should be as similar as possible to the sample and have the same concentration range for the elements under scrutiny. They must be prepared by the same sample preparation method and the chemical measurement process must be under control. A window of 20% of a certificate value for an analysis may be problematic if the acid leaching efficiency is unknown. The limit of error must be defined, otherwise such windows are arbitrary and may be meaningless in light of low efficiency extractions. For example, even in aquaregia, gold-bearing ores have low levels of extractability. Thus, accepting or mandating leach values that are 80-120% of total values may be unscientific. How do we know which partial leach comes closest to that which occurs in nature?

CONCLUSION

The importance of submitting data on method performance during the comment period cannot be overstated. It is in fact critical to assessing the robustness and durability of the methods. When the SW-846 methods finally appear, there will be a golden opportunity to participate in the method validation process. Analysts with studies on comparability of 3051 and 3050 are urged to speak up. And, in the absence of a collaborative study, performance data for Method 3015 will be essential.

For those analysts and laboratories with time on their hands, a microwave leachability study of reference materials under various simulated environmental conditions is guaranteed publication. RMs must be well characterized when used as performance standards so it is important to know what parameters affect recovery when microwave assisted leaching is performed. For example, acid combinations like aquaregia produce nitrosyl chloride and can elevated the pressures in the digestion vessels. Such a system will almost certainly behave differently from just HNO_3. Aluminum and cadmium recovery will be improved but does aquaregia increase the extraction of other metals? If the temperature of nitric acid is kept at 175 ± 5 °C, as suggested in Method3051, does the recovery improve with longer extraction times? How are metal recoveries affected by temperature? What influence does the presence of organic material have on the extraction recovery of the elements of interest from inorganic or aqueous matrices? Answers to these questions will help the analytical community to properly assess the environmental impact of hazardous wastes.

References

Becker, D., Christiansen, R., Currie, L., Diamondstone, B., Eberhardt, K., Gills, T., Hertz, H., Klouda, G., Moody, J., Steel, E., Taylor, J., Watters, R., Zeisler, R. NIST Special Publication 829, U.S. Department of Commerce, January, 1992.
Binstock, D. A., Grohse, P. M., Gaskill, A., Sellers, C., Kingston, H. M., Jassie, L. B. *J. Assoc. Off. Anal. Chem.* 74(2), **1991**, 360-366.
Friedman, D., *Environmental Lab*, April/May, 1992, 18-23.
Hewitt, A. D., Reynolds, C. M. *Atomic Spectroscopy*, 11(5), **1990**, 187-192.
Kammin, W., Manchester Laboratories, private communication, **1992.**

Kingston, H. M.; Jassie, L. B., *J. Res. Nat'l. Bur. Stds*, 93(3), **1988**, 269-274.
Kruschevska, A, Barnes, R. M., Amarasiriwaradena, C., Foner, H., Martines, L., *J. Anal. Atomic Spectrometry*, 1992 (in press).
Lyon, T. D. B., Fell, G. S., MacKay, K., Scott, R. D., *J. Anal. Atomic Spectrometry*, 6, **1991**, 559-564.
Mahan, K. I., Foderaro, T. A., Garza, T. L., Martinez, R. M., Maroney, G. A., Trivisonno, M. R., Willging, E. M. *Anal. Chem.* 59, **1987**, 938-945.
Paus, R., USEPA Region VII, private communication, **1992**.
Rezaaiyan, R.; Nikdel, S. *J. Food Sci.* 55 (5), **1990**, 1359-1360.
Sah, R. N., Miller, R. O. *Anal. Chem.* 62, **1992**, 230-233.
Ybanez, N., Cervera, M. L., Montoro, R., de la Guardia, M. *J. Anal Atomic Spectrometry* 6, **1991**, 379-384.

67 A new Device for High Pressure Microwave Digestion

Dr. R. Krämer
Berghof Maassen Laborgeräte GmbH
Harretstr. 1
W-7412 Eningen
Germany

Microwave heated digestion today is a widely known method of sample preparation in analytical chemistry.

The main advantage of this method compared with traditional ones is a very quick heating of the sample, even in the range of high temperatures (T > 200°C, since the "temperature gradient" between the sample and the microwave field is extremely large.
The possibility of quick heating reduces the total time of digestion considerably, especially at higher digestion temperatures (T > 250°C).

The pressures to be handled at such high temperatures can be 1400 psi or more. Therefore we constructed a pressure vessel made of steel (p_{max} = 2845 psi) which can be used as a microwave oven. The microwave energy is directly coupled into the steel vessel. In the same way as with traditional digestion bombs PTFE or PFA liners and, of course, quartz glass can be used in combination with the steel vessel.

The microwave heating is controlled by a pressure sensor, which allows to measure the pressure inside the bomb during the digestion procedure.

As an additional safety precaution, rupture discs are used which will burst at a well defined pressure of 2100 psi without any damage at the microwave digester.

To obtain reproduceable results it seems necessary to measure the digestion temperature. This problem was solved by installing a infrared emission thermometer, which allows to measure the temperature inside the Teflon® liner (or the quartz glasses).
The microwave heated high pressure digestion system MDA II can be used for the same applications as with traditional digestion bombs.

MICROWAVE DIGESTION OF INCINERATOR SAMPLES

Zhaoguang Yang, Ph.D., Group Leader, and G. Lynn Schwendiman, Laboratory Manager, Aptus Environmental Service-Westinghouse Electrical Corporation, P.O. Box 27448, Salt Lake City, UT 84127

ABSTRACT

The microwave assisted acid digestion method is intended to provide a rapid multielement acid leach digestion prior to analysis by ICP and AA. Recently, closed teflon vessel microwave digestion is receiving much attention as the new "high tech" metals digestion (1-5). The primary objective of this study is to investigate the relation of element recoveries between the digestion time and pressure control. Various digestion techniques are used in this comparative study: open vessel hot plate digestion and closed vessel teflon microwave digestion.

The USEPA SW-846 method 3050, 3051 and CEM digestion methods were used to prepare samples. CEM Microwave Digestion System-205 with pressure controller and ARL 3410+ICP have been used in the experiments. The results of this study indicate that element recoveries are the functions of microwave temperature, digestion time, and pressure. Microwave digestion can be done much faster than the comparable hot plate digestion.

Microwave digestion of incinerator ash offers a good alternative to conventional hot plate digestion for use in the determination of metals. The results of this study were precise and compared favorable with certified reference materials. A comparison between microwave and conventional hot plate digestion showed that the two methods give close results.

INTRODUCTION

Microwave-assisted environmental sample digestion has received considerable attention and has become well accepted in the analytical laboratory. Sample preparation is important. It is also a much neglected area in the determination of metals by atomic absorption and inductively coupled plasma atomic emission spectrometry. The problems with the conventional digestion procedures include elemental loss by volatilization, atmospheric contamination and longer digestion time requirement.

The purpose of this study was to use this technique to determine the required digestion time and pressure setting to obtain acceptable results for incinerator samples.

EXPERIMENTAL

The regent grade HNO_3, HCl and solid waste laboratory control sample were purchased from Fisher Scientific Co., Chemical Division, Fair Lawn, N.J. Standards were prepared by diluting 1000 mg/l certified ICP stock solutions (SPEX Industries, Inc., Edison, N.J.). The stock solutions were also used for spikes. Milli-Q deionized water (Millipore Corporation, Bedford, MA) was used for sample digestion and all analysis works.

A CEM microwave digestion system, Model MDS-205, was used for all microwave digestion procedures. It consisted of an operator selectable output of 0-900 w $\pm$ 90 w in 1% increments, a fluorocarbon coated microwave cavity, a three-speed cavity exhaust fan, a digital computer programmable in nine separate stages, an alternating turntable device system to rotate samples within the microwave field and a pressure control system. The closed vessel system used consists of a vessel body, safety pressure relief valve, vessel cap, venting nut and tubing, all of which were made of teflon.

CEM digestion method (6): transfer 1 g of sample into a vessel and add 20 ml of 1:1 HNO_3:H_2O solution. Program the Pressure Controller at 100 psi and set the time 30 minutes.

RESULTS AND DISCUSSION

The effectiveness of the microwave digestion technique is dependent on three primary variables: temperature, pressure and digestion time. Figure 1 and Figure 2 illustrate the affect of pressure on the recovery of various metals. According to SW846 Method 3051, 0.5g sample in 10 ml concentrated nitric acid and programed 10 minutes. It is demonstrated that the internal pressure in the digestion vessel should be above 70 psi (except Ba) for maximum recovery. In Figure 2, Barium shows a significant dependance on the pressure. Maximum recovery for Ba is only achieved at a pressure over 80-100 psi.

Digestion methods require time. The microwave digestion technique requires significantly less time then the conventional methods. CEM digestion method (1.0 g sample in 20 ml HNO_3:H_2O) was used in this group experiment except extention the time. The results illustrate that there is a variation in metal recoveries as a function of time. Figure 3 illustrates that time is significant in the recovery of Barium. Barium requires twice as much digestion time as Mn and Cd. At high concentrations, the concentration of the alkali metals and zinc gradually increases in solution, as illustrated in Figure 4. Figure 5 illustrates that Cu, As, and Cr are less dependant on time for efficient recovery in incinerator ash. The recovery of Sb and Tl vary as much as 25 percent for a digestion time between 15 and 25 minutes of digestion time as demonstrated in Figure 6. Figure 7 shows that many metals require at least 15

minutes for best recovery efficiencies.

For many years the hot plate digestion methods (SW846 3005, 3010, 3050 etc.) have been the standard techniques. Table 1 (SW846 Method 3051) is a comparison of metal recoveries in an certified incinerator ash using both the hot plate and the microwave digestion techniques. The results show comparable recoveries for each method. Table 2 (CEM Method) is a comparison of two analyses for Aptus incinerator ash. The results are within a standard deviation of each other.

There is no temperature measurement equipment in CEM MDS-205 system. According to CEM information (2,4,5,7), once the pressure achieves approximately 60-100 psi, the temperature will reached 175^{0}C. Based on the experimental results, 85-110 psi is preferred.

CONCLUSIONS

Microwave digestion offers a good alternative to conventional hot plate digestion in incinerator samples. The results obtained after microwave digestion in reference materials showed close agreement with the stated values. Also a comparison between microwave and conventional hot plate digestion showed that the two methods give close results. These results also indicate that longer digestion times may be required for some elements.

Advantages of Closed Vessel Microwave Digestion

1. Digestion work can be done much faster than other methods.

2. Sample contamination can be minimized because the teflon vessel is one of the best materials to use in trace element analysis.

3. Microwave staged program can often be left unattended to complete the digestion.

Disadvantages of Microwave Digestion

1. Reduced sample size, allows for less representativeness.

2. Expensive digestion system and parts.

3. Additional time required to assemble and clean the digestion containers and pressure controller.

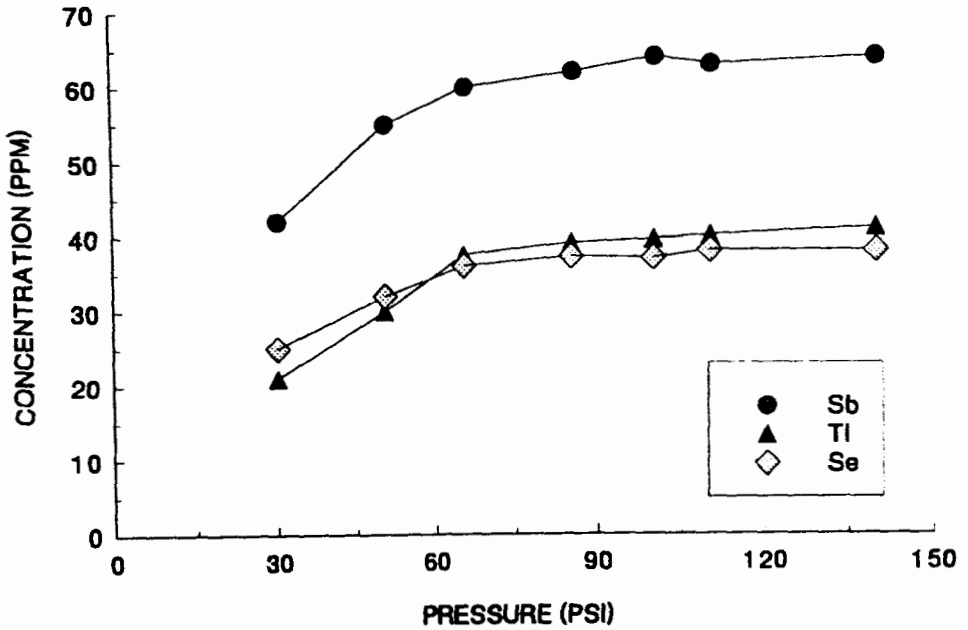


Figure 1. Concentration of Sb, Tl and Se as a function of digestion pressure.

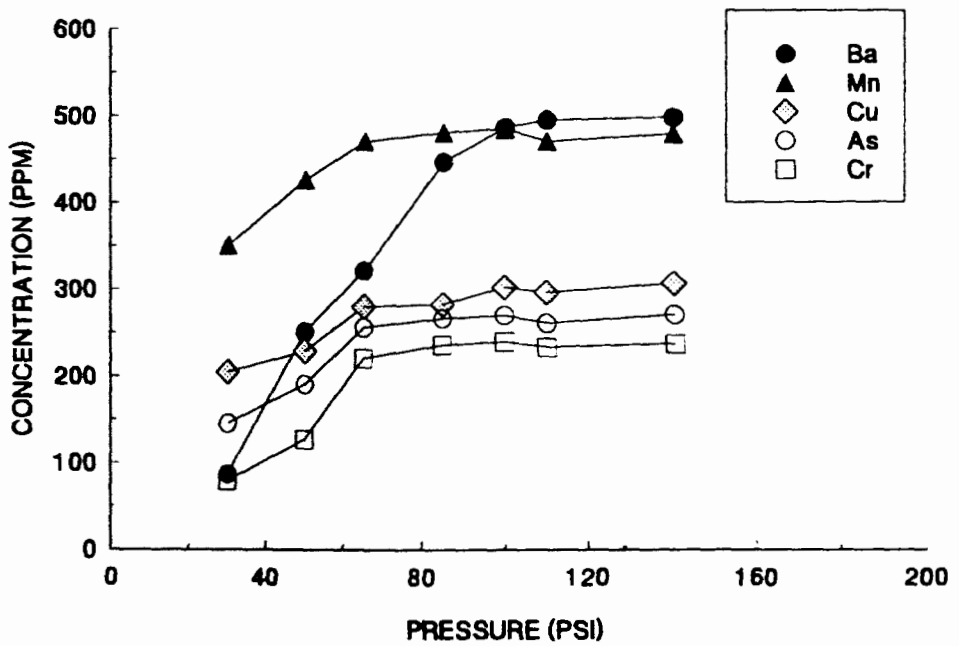


Figure 2. Concentration of Ba, Mn, Cu, As and Cr as a function of digestion pressure.

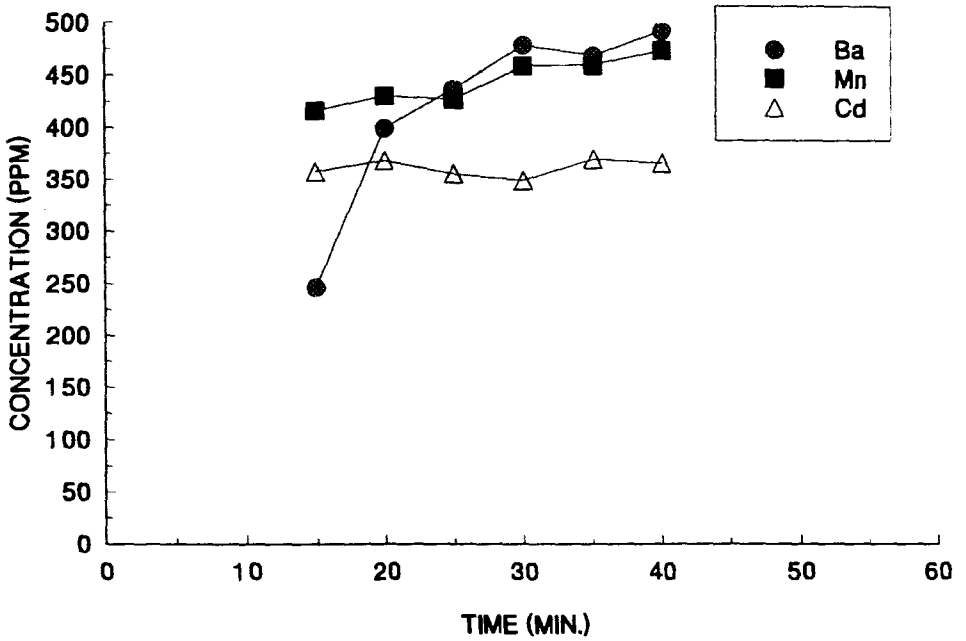


Figure 3. Concentration of Ba, Mn and Cd as a function of digestion time.

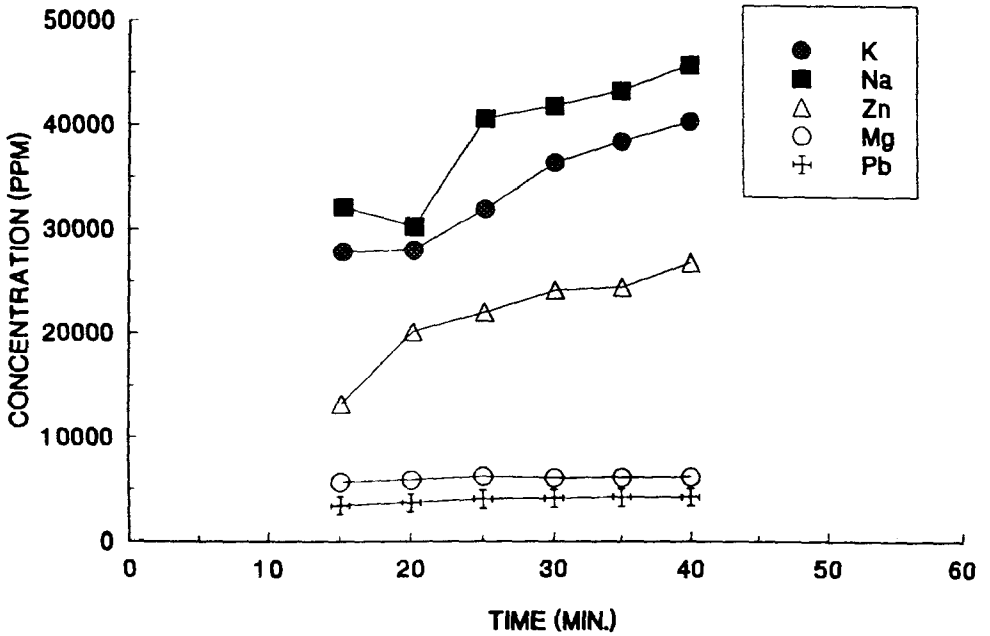


Figure 4. Concentration of K, Na, Zn, Mg and Pb as a function of digestion time.

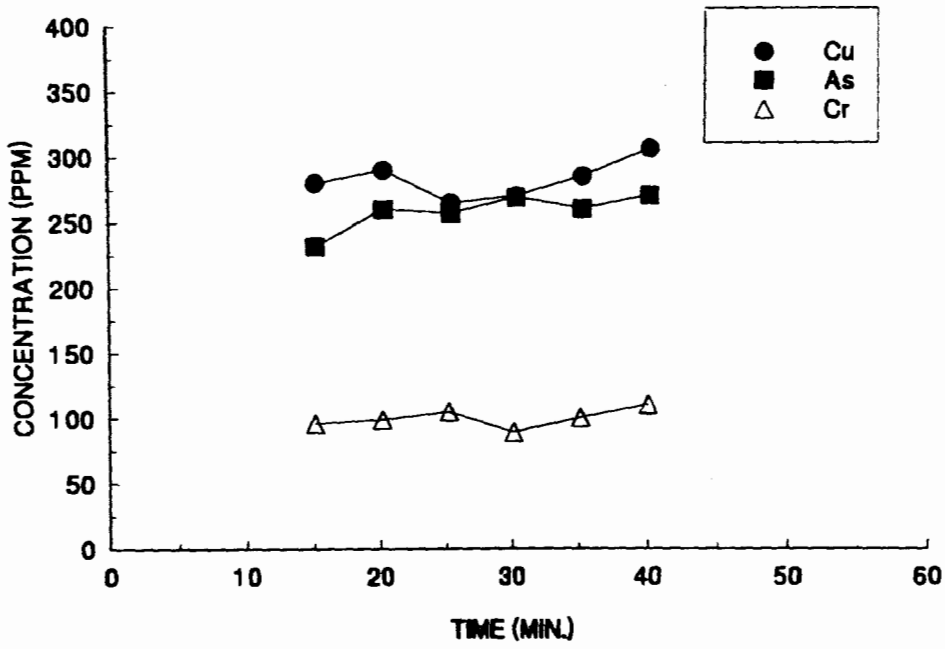


Figure 5. Concentration of Cu, As, and Cr as a function of digestion time.

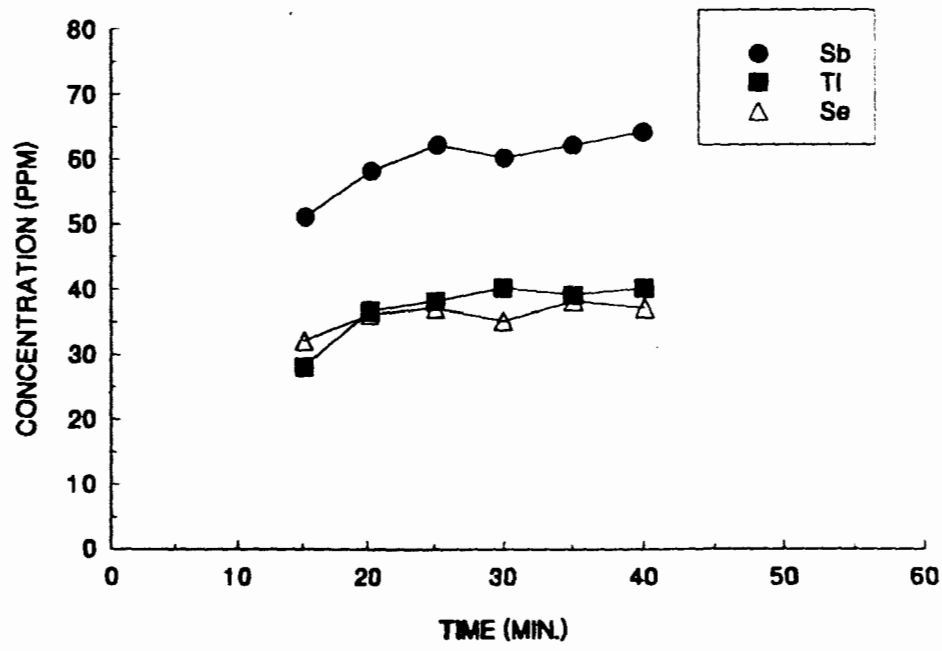


Figure 6. Concentration of Sb, Tl and Se as a function of digestion time.

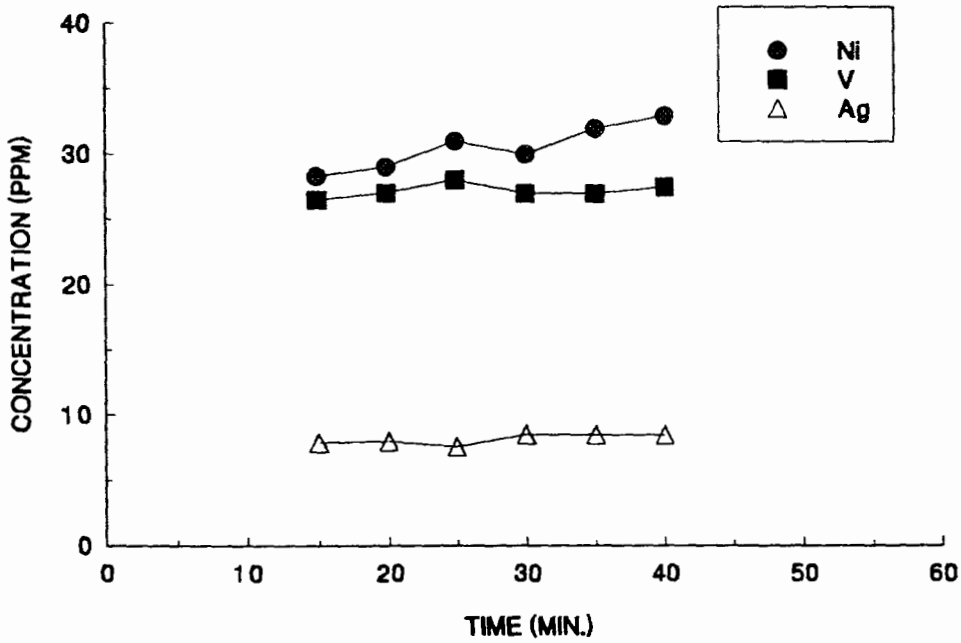


Figure 7. Concentration of Ni, V and Ag as a function of digestion time.

Table 1 Analysis Results for Incinerator Ash by ICP

Element	Hot Plat ppm	Microwave ppm	Certified Value ppm
Cd	426	425	422 ± 37
Cu	302	301	276 ± 26
Mg	6420	6151	6318 ± 750
Ni	19.8	25.0	22.4 ± 3.2
Pb	4538	4206	4531 ± 325
Zn	20659	20123	21421 ±2094

Table 2 ICP Analysis Results for Incinerator Ash

Element	Microwave ppm	Hot Plate ppm
Ag	2.75	2.28
As	268	266
Ba	493	515
K	40541	43709
Mn	472	470
Na	46019	43709
Se	36.6	32.6
Tl	38.2	40.4

REFERENCES

1. J. Nieuwenhuize and etc., "Comparison of Microwave and Conventional Extraction Techniques for the Determination of Metals in Soil, Sediment and Sludge Samples by Atomic Spectrometry," ANALYST.Vol. 116, (1991), 347.

2. E.T. Hasty and S. Littau, "Microwave Sample Preparation with Temperature Feedback Control," Presented at the 1991 Eastern Analytical Symposium, Somerset, N.J.

3. V.L. Verma and T.M. McKee, "Comparison of Procedures for TCLP Extract Digestion; Conventional vs Microwave," Present at the USEPA Seventh Annual Waste Testing and Quality Assurance Symposium, 1991, Washington, D.C.

4. E.T. Hasty, S.E. Littau and R. Revesz, "Optimization of Microwave sample Preparation Methods Using Pressure Feedback Control," Presented at the 1991 Pittsburgh Conference and Exhibition, New Orleans, LA.

5. R. Revesz and E.T. Hasty "Microwave Digestion of Soils, Sediments, and Waste Water for Analysis of Environmentally Significant Elements," Presented at the 1990 International Conference on Metals in Soils, Waters, Plants, and Animals, Orlando, FL.

6. "Microwave Application Note for Acid Extraction," Application Note EW-9 Revision, CEM Corporation, 1989.

7. Letter from G.N. LeBlanc, CEM Corp. to Z. Yang, Aptus, Inc., March 30, 1992.

69 CAPILLARY ION ANALYSIS: A NEW METHOD FOR DETERMINING IONS IN WATER AND SOLID WASTE LEACHATES

INORGANIC

Joseph P. Romano, applications chemist, Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, Massachusetts 01757

ABSTRACT

Capillary Ion Analysis (CIA) has recently been introduced as a new separations technique for the analysis of inorganic and organic ions. CIA is a branch of capillary electrophoresis (CE) which is optimized for the rapid analysis of low molecular weight anions and cations. It separates ions according to their mobility in electrolytic solutions. This paper will review the characteristics of CIA that are especially significant for the analysis of anions in ground water.

Among the many attributes of CIA are rapid, highly efficient separations with different selectivities (compared to ion chromatography), simplicity, and economy. The instrumentation has few moving parts and uses a low cost, easily replaceable hollow capillary instead of a packed chromatography column. Sample preparation is minimal because there is no chromatography column to be protected from extraneous materials in the sample. Analyses are completed in less than four minutes.

The scale of CIA electrolyte consumption is at least an order of magnitude smaller than liquid or ion chromatography eluent consumption. High sensitivity is achieved while analyzing only nanoliters of sample, using only a few microliters of electrolyte in the capillary. This ability to analyze complex samples without producing any significant volume of additional waste has caught the attention of analysts who are becoming involved in the mixed waste program.

70

USE OF CAPILLARY ELECTROPHORESIS FOR THE DETERMINATION OF ORGANIC AND INORGANIC ANIONS IN GROUNDWATER AT A SUPERFUND SITE

Laurence W. Strattan, Ph. D., and Marcela Saio, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Box 25227, Denver, Colorado 80225.

ABSTRACT

Instrument manufacturers tout capillary electrophoresis (CE) as a versatile, fast, and sensitive alternative to ion chromatography techniques for the analysis of anions. We recently used CE for the determination of inorganic acid anions and C_2-C_4 aliphatic carboxylates in groundwater at a municipal landfill that is now a Superfund site. This paper discusses the results of that project, and presents suggestions for the use of CE for environmental samples. The objective of the project was to track highly water soluble parameters which would migrate via groundwater, but not through interstitial vapor spaces in the soil.

We found that with the use of an internal standard as a retention time reference, and with the dilution of samples to an appropriate concentration range, bromide, chloride, sulfate, nitrite, and nitrate were straightforward to determine using CE. Determination of the carboxylates was also straightforward, except when much higher concentrations of inorganic anions were present, and could be performed without changing instrumental conditions. The dirtier samples required rinsing the column with KOH between samples to provide reproducible conditions. Fluoride and phosphate proved more difficult to determine due to the closeness in their retention times in chromate electrolyte, to a sensitivity to pH, and to the presence of bicarbonate in the samples.

In order to maintain narrow peaks, and thus confidence in qualitative identification, the optimum concentration for analysis was in the range of 0.5 to 10 ug/mL (ppm) for carboxylates, and 0.5 to 15 ppm for the "straightforward" strong acid anions. Precision, as relative standard deviation, and bias and were both approximately 10% or less for bromide, chloride, sulfate, and C_2-C_4 carboxylates.

INTRODUCTION

The Operating Industries Superfund site in the Los Angeles area operated from the 1940s until 1984, accepting both

industrial and municipal wastes at various times. The 190-acre site is nearly a mile long and over two hundred feet high, having filled in the saddle point between two low hills. Temperatures within the landfill can exceed 150 ^{o}F. At one time a commercial operation recovered over one million cubic feet of methane per day from the landfill. The site is currently the subject of cleanup settlements totaling over $200 million.

Because of the temperatures and the considerable volume of gas emitted from the landfill, there is the potential that volatile organic pollutants observed in groundwater off-site may have moved in part through the gas phase rather than by direct movement of groundwater. The mechanism of migration is significant to selecting appropriate remediation techniques.

We undertook this investigation, which included water miscible solvents as well as ionic species, in hopes of being able to trace the movement of hydrophilic species in groundwater. Previous analyses had identified these components at concentrations of thousands of ppm in on-site samples, and it was hoped that even with dilution the components would be detectable for some distance.

Our laboratory had recently purchased a CE instrument because the technique appeared to be both versatile and simple to use, and would provide an alternative method to ion chromatography. It seemed ideal for this project since we could determine both organic acid anions and other common anions such as chloride and sulfate without changing analytical conditions.

EXPERIMENTAL

The CE instrument used was a Waters Quanta 4000. The basic components of the system are a 30-kV power supply, two electrolyte reservoirs containing electrodes connected to the power supply, a UV detector, and the column. The column is uncoated fused silica capillary, typically of 50 to 75 micrometers inside diameter and 60 cm length.

A simplistic description of the instrument's operation is that an applied voltage separates ions in solution according to their mobility in an electrolyte. Ionic mobilities are related to basic physical properties such as charge and size. The migration of ions is the sum of two components, first the bulk or osmotic flow of liquid caused by the applied voltage, and second the migration of ions toward the electrode of opposite charge. In most CE applications such as the separation of biological molecules, these components

are in opposite directions. Waters has developed a system in which an osmotic flow modifier is added to the electrolyte. This modifier changes the sign of the effective charge on the column wall from negative to positive, reversing the direction of osmotic flow so that the two components are in the same direction. The pertinent point about the osmotic flow modifier for this discussion is that sample matrix can change the reproducibility of its effects, as will be discussed later.

The order in which species would reach the detector for these analyses is negative ions, neutrals, and positive ions. In routine operation, the analysis was terminated after detection of the negative ions of interest, and the column flushed with electrolyte to remove the remainder of the sample and to reequilibrate wall conditions.

We used the generic conditions suggested by Waters for the separation of inorganic anions, namely 5 mM chromate electrolyte containing the osmotic flow modifier. Most analyses employed a 60 cm, 75 um I.D. column and a voltage of 20 KV. A few analyses used a 60 cm, 50 um I.D. column at 30 KV. Anions were detected indirectly by UV absorbance at 254 nm. Chromate absorbs at this wavelength, but the targeted anions do not. The anion packets dilute the chromate concentration causing changes in UV intensity as they pass the detector.

Parameters which need to be controlled to achieve stable migration times are ionic strength of the electrolyte, gas content of the electrolyte, particulates, and organic content of samples. Ionic strength of the electrolyte can be affected by absorption of carbonate from the atmosphere; preparation of fresh electrolyte is the best practical way to maintain stability from day to day. Gas in the electrolyte typically causes an unstable baseline, and in extreme cases bubbles may break the electrical connection. Particulate in the column obstructs migration causing instability. The lifetime of a column is usually determined by how long it remains free of particulate. The organic content of samples is not controllable, but it must be considered, and may require modification of instrumental conditions.

The procedure for analyzing samples, starting with the installation of a new column, was to clean the inside wall by rinsing for several minutes with 0.5 N potassium hydroxide, followed by distilled water, and then electrolyte for approximately ten minutes. One or two blank runs at the beginning of each series of analyses helped to stabilize conditions. Electrolyte was prepared fresh daily, degassed

in a vacuum desiccator for 30 minutes, and filtered through a 0.45 um filter before use. The only sample preparation was filtration, possibly dilution, and the addition of internal standards at 10 to 40 ppm.

As a check of the CE results, we also determined the organic acids by gas chromatography/mass spectrometry (GC/MS) using direct aqueous injection on a polar phase fused silica capillary column. This analysis used perdeuterated analogs of acetic, butanoic, and heptanoic acids as internal standards to correct for injection port discrimination effects. Figure 1 lists instrumental conditions for the GC/MS analyses.

RESULTS

Figure 2 shows the electropherogram of a standard containing the one- to four-carbon carboxylates and seven common inorganic anions. Except for formate, the carboxylates are well separated from the common inorganic anions. This allowed the determination of carboxylates in samples containing much higher concentrations of chloride or carbonate, which elutes just after phosphate. (At the pH of these analyses these species are both in their monohydrogen forms, bicarbonate and monohydrogen phosphate.) The migration time of tungstate is midway between two groups of commonly-occuring inorganic anions.

Figure 3 shows an electropherogram for the same inorganic anions without the carboxylates. The poor separation of sulfate and nitrite is due to the relatively high concentration of sulfate, 15 ppm for sulfate vs. 2.5 ppm for nitrite. In order to maintain narrower peaks, and thus greater confidence in identification, the maximum concentration of individual anions should be limited to 10 to 15 ppm. Note also the time separation between peaks is as low as 0.03 minutes. This is of the same magnitude as the variation in migration times we observed for single components from run to run. We found that a migration time reference and the use of relative migration times was necessary to make qualitative identifications. We chose tungstate as the primary reference peak because it is relatively uncommon and it appears at a convenient migration time. We also used valerate in addition to tungstate as a reference peak for the carboxylates.

Finally, note the separation of fluoride and phosphate in Figure 3. These two parameters and formate were not determined in our analyses for a variety of reasons, including lack of interest for the immediate project. Quantitation of these parameters was not straightforward due

to inconsistent separation of fluoride and phosphate, and to the presence of relatively large amounts of carbonate in samples. The determination of these parameters could very well be possible for more experienced users of CE, and/or in samples containing less carbonate. Figure 4 shows the electropherogram of a sample containing a relatively large carbonate peak which might mask the presence of fluoride and phosphate even in the absence of other difficulties.

We also did not determine nitrate and nitrite in our analyses, solely due to the fact that holding times had long since expired by the time of our analysis. We saw no reason why they could not be determined by CE.

Figure 5 contains the electropherogram of a different sample analyzed at a marginally useful dilution. It is marginally useful because the sample matrix is so affecting peak shapes and migration times that analysis of a more concentrated sample would be useless. Even though the tungstate peak is distorted, the peak area is consistent with previous analyses.

We found it necessary to change the usual instrument cycle by adding a potassium hydroxide rinse after each sample when analyzing samples such as those shown in Figures 3 and 4. The KOH rinse removes the wall coating and any remaining sample matrix organics from the column, ensuring reproducible conditions at the start of each analysis.

For samples such as those in Figures 4 and 5, GC/MS gave lower limits of detection than CE. GC/MS would always give greater certainty of identification. However, the GC/MS method was tedious to perform because of carryover of the acids from run to run. The acids appeared to partition between salt and acid forms upon each injection, with the salt form remaining in the injection port to be partitioned again at the next injection. The use of perdeuterated acids as internal standards for quantitation helped to offset these effects, but frequent recalibration and analysis of blanks were necessary to obtain accurate results.

We found that the need to maintain narrow peaks in order to be confident of identifications based on relative migration times limited the calibration range on CE for these analyses. The useful calibration range extended from 0.5 ppm up to about 10 ppm for the carboxylates and up to 10-15 ppm for the strong acid anions.

Figure 6 contains precision and bias data for CE analysis of groundwater. Precision as indicated by the relative standard deviation of analytical triplicates is less than

10%. Bias as indicated by the percent recovery of matrix spikes was usually within the range of 90-110%. Limits of detection reported with the sample results corresponded to 0.5 ppm injected for the strong acid anions, and 1 ppm for the carboxylates. The higher figure for carboxylates is due more to sample matrix than to instrument sensitivity. The low point of calibration curves was routinely 0.5 ppm, and was sometimes 0.25 ppm.

SUMMARY

The usefulness of our results for the Operating Industries site is uncertain. The carboxylates were detected in too few samples to be useful to trace groundwater migration. However, chloride and sulfate may ultimately prove to be helpful.

CE appears to be a useful tool for environmental analyses if precautions are observed to maintain confidence in identifications. The use of a migration time reference peak seems mandatory to us. Keeping peaks narrow by avoiding concentrations above 10 or 15 ppm may be slightly less important, but is recommended. In a monitoring situation where the sample matrix is known and consistent, a calibration range up to 50 ppm or higher may be possible.

CE is certainly a nice complimentary technique to ion chromatography. The separations are based on different mechanisms, and the two could be used as alternate techniques to approach the identification of unknowns.

ACKNOWLEDGEMENTS

We wish to thank Jon Beihoffer of our laboratory and Lynn Lutz of ICF Technology Inc. for performing GC/MS analyses of carboxylic acids.

Figure 1. Gas Chromatograpic Conditions for GC/MS Analysis of Carboxylates.

Instrument:	Hewlett Packard 5890 gas chromatograph/Finnigan MAT 8200 mass spectrometer
Column:	30 m x 0.32 mm I. D. fused silica
Liquid phase:	0.25 um DB-FFAP
Carrier gas:	Helium at 25 cm/sec
Temperature program:	80°C for 2 min., 7°C/min. to 220°C, hold 2 min.
Injector temperature:	220°C
Injection volume:	1 uL
Injection mode:	splitless for 0.4 min.
Transfer line temperature:	220°C
Mass range:	35-270 daltons
Cycle time:	0. sec
Ionization mode:	electron impact at 70 eV

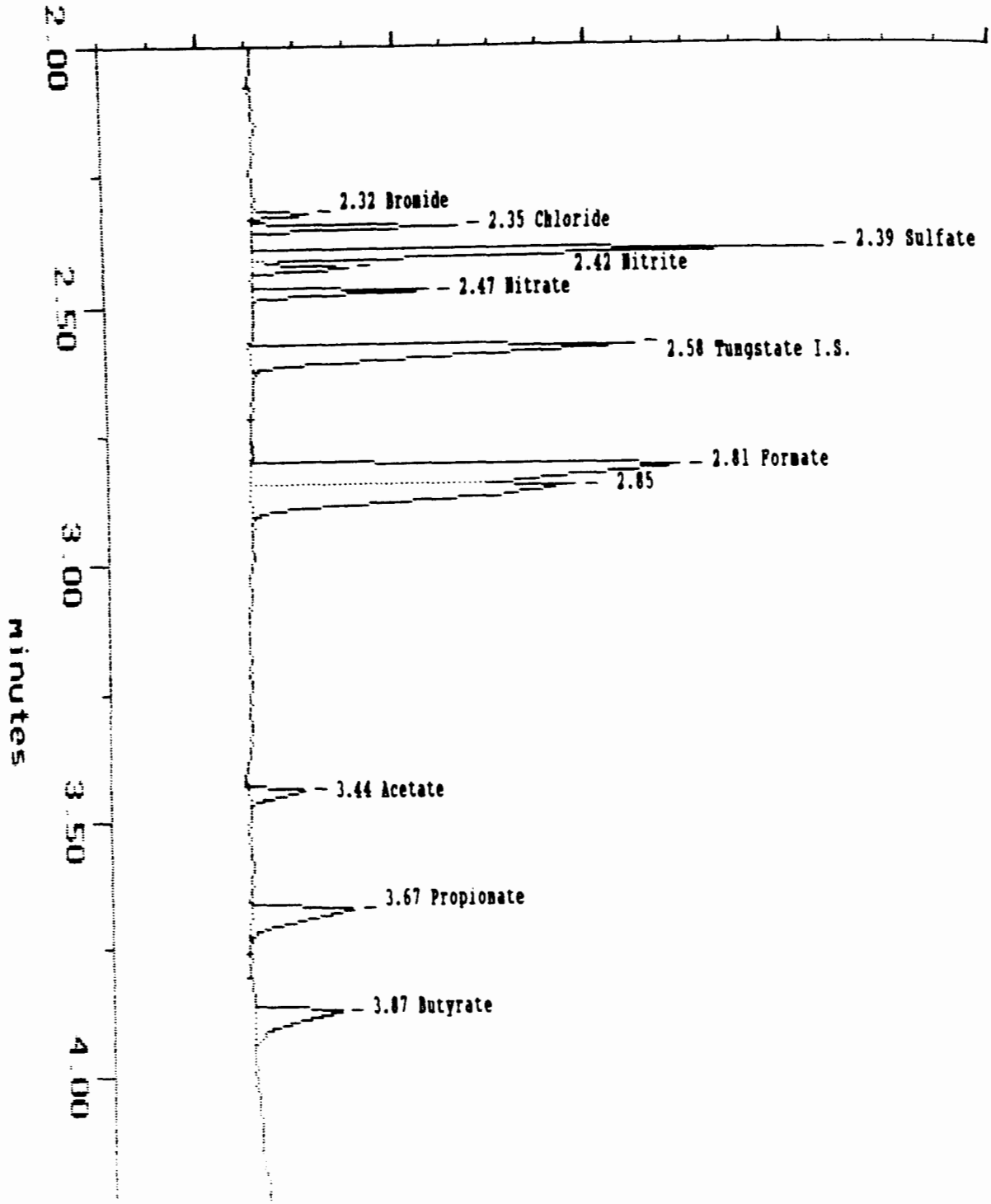


Figure 2. Electropherogram of a standard containing 40 ppm tungstate as a migration time marker, 1-15 ppm each stong acid anions, and 5 ppm of the carboxylates. The peak in the 2.8 minute region contains fluoride, formate, and phosphate.

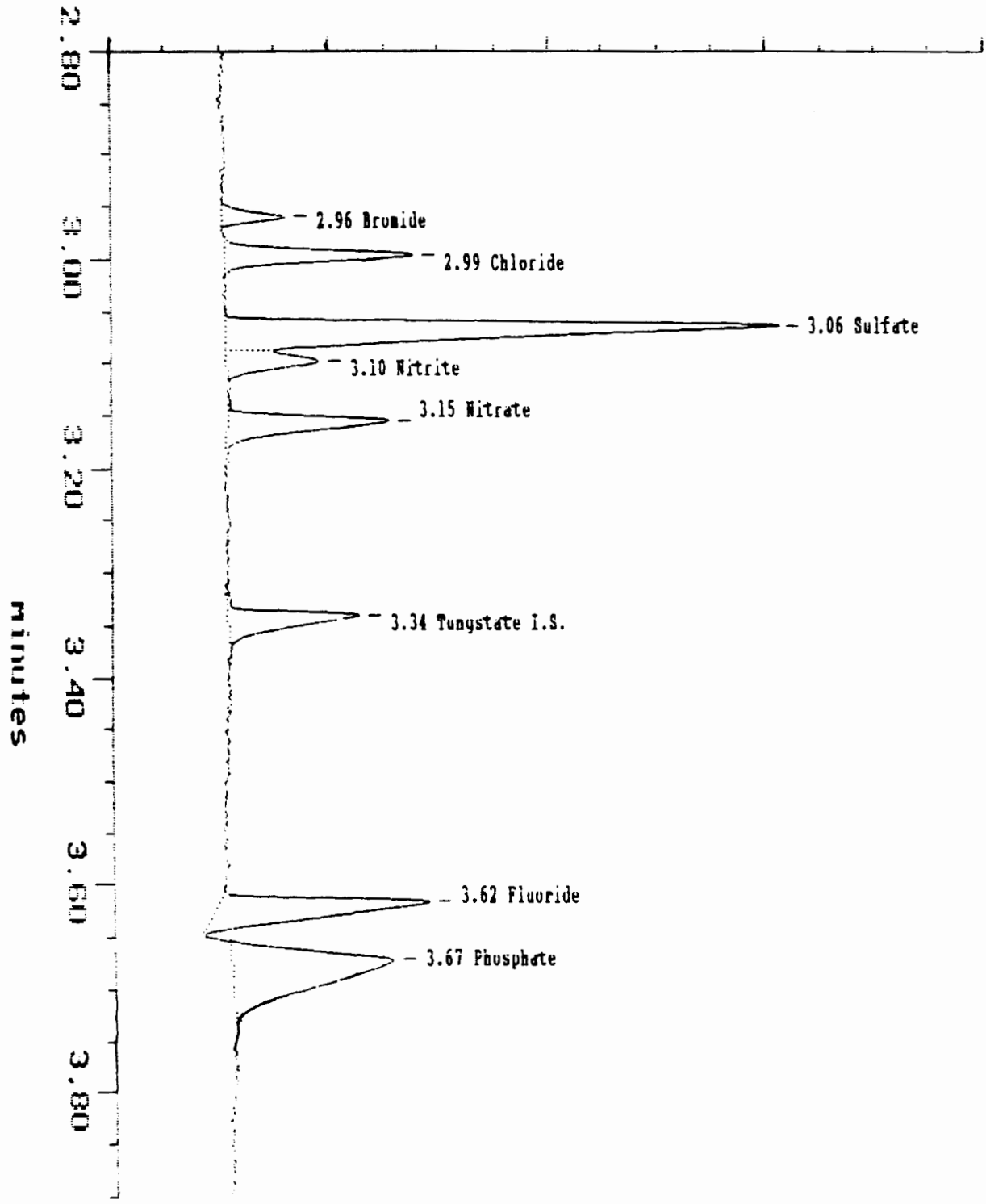


Figure 3. An expanded electropherogram of a strong acid anion standard showing peak separatons.

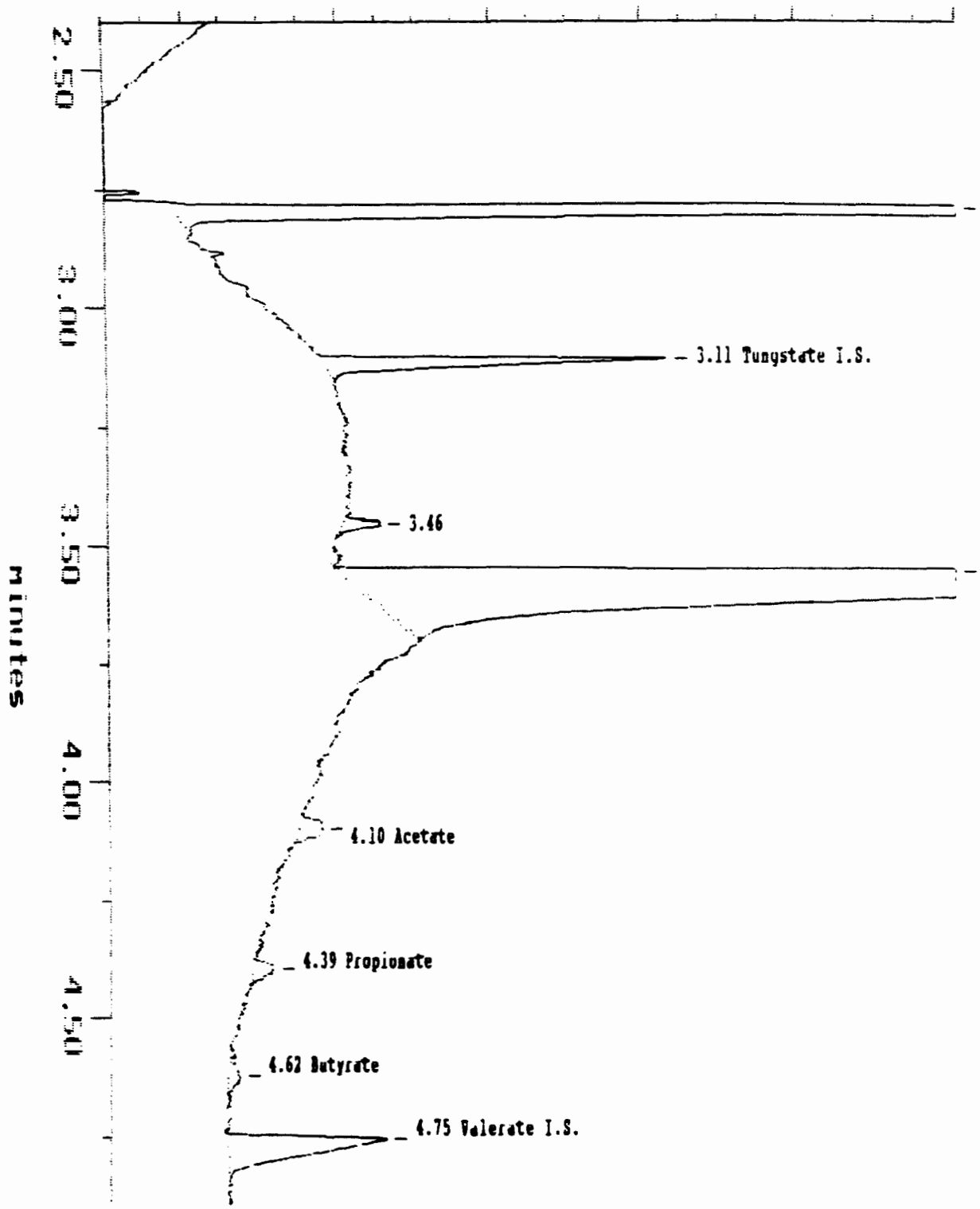


Figure 4. Electropherogram of an actual sample at a dilution appropriate for determination of carboxylates. Both tungstate and valerate have been added to the sample as migration time markers. The large peak at 3.55 minutes is bicarbonate.

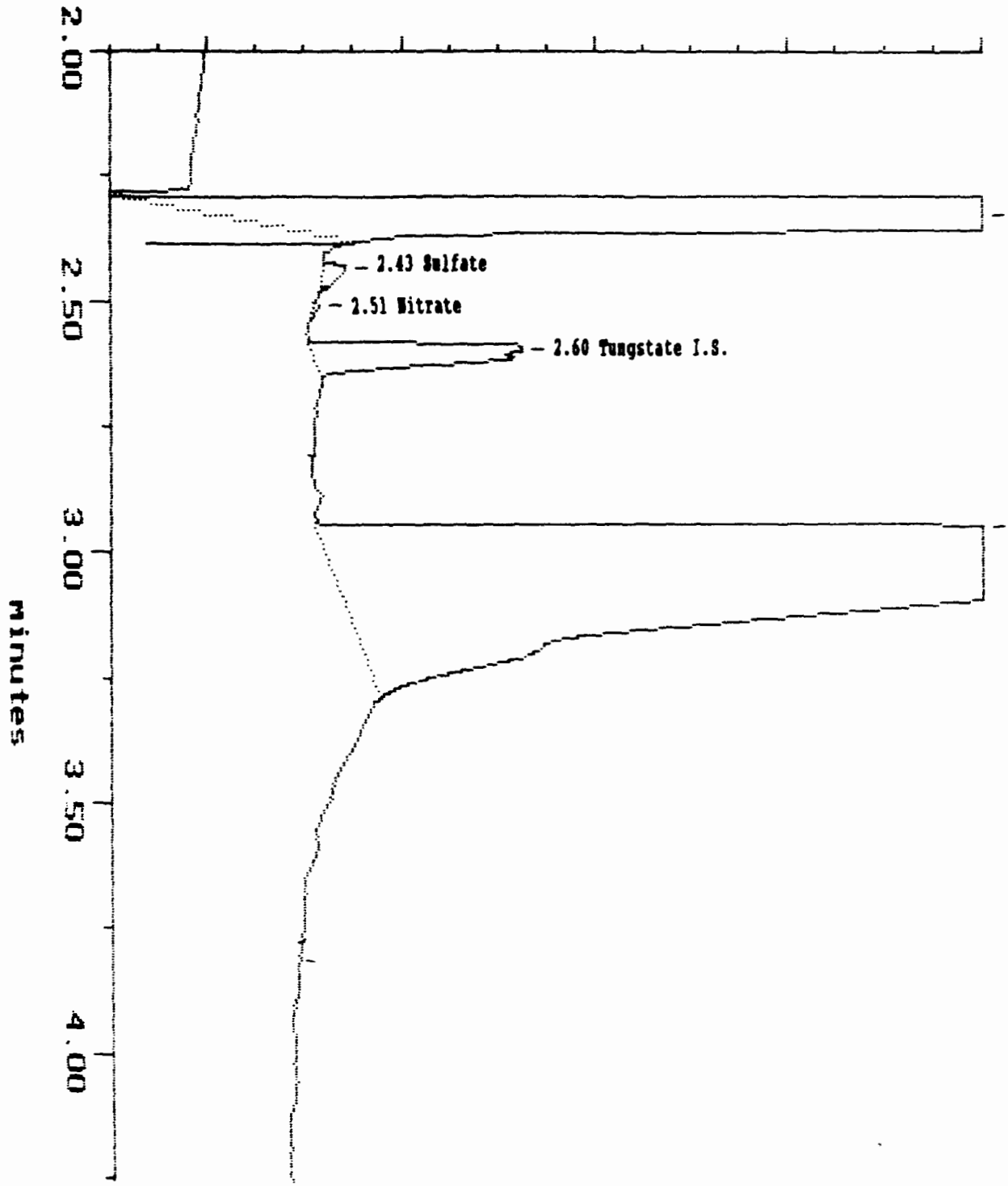


Figure 5. Electropherogram of a sample at a dilution marginally useful to show the absence of carboxylates. The sample matrix causes the peak broadening observable for tungstate.

Figure 6. Precision and Bias Results for Capillary Electrophoresis Determination of Carboxylates and Strong Acid Anions. All units are mg/L or percent.

	Acetate	Propionate	Butyrate
Sample 1			
Average Concentration:	697	254	324
Percent RSD[a]:	3.10	3.61	7.93
Matrix Spike Added:	500	500	500
Percent Recovery:	93.7	96.2	93.0
Sample 2			
Average Concentration:	49	36	ND[b]
Percent RSD:	4.45	3.53	-
Matrix Spike Added:	250	250	250
Percent Recovery:	94.4	103	96.8

	Bromide	Chloride	Sulfate
Sample 3			
Average Concentration:	ND	4073	ND
Percent RSD:	-	3.92	-
Matrix Spike Added:	15000	15000	15000
Percent Recovery:	104.7	105.0	102.9
Sample 4			
Average Concentration:	ND	95.9	227.9
Percent RSD:	-	3.60	2.53
Matrix Spike Added:	250	375	375
Percent Recovery:	104.2	105.5	104.6
Sample 5			
Average Concentration:	ND	251.8	94.8
Percent RSD:	-	0.89	1.00
Matrix Spike Added:	250	375	375
Percent Recovery:	111.4	113.1	110.4

[a] RSD = Relative Standard Deviation
[b] ND = Not Detected

71 The Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis

L. Robinson[1], F. F. Dyer[1], D. W. Combs[2], J. W. Wade[1], N. A. Teasley[1], J. E. Carlton[3], A. L. Ondracek[4] and J. R. Stokely[1]

Abstract

In the early 1950's, a U.S. government facility in Oak Ridge, Tennessee, used a process that required large quantities of Hg. It was disclosed to the public in 1983 that about 2.4 million pounds of Hg had been released into the ecosystem. The primary route of mercury into the areas outside of the plant was a stream, East Fork Poplar Creek, whose headwaters are in the vicinity of the plant. As part of a study to determine the distribution of Hg as well as As, Cr, Sb, Se, U, and Zn along the flood plains of East Fork Poplar Creek, a procedure using neutron activation analysis was developed. In this talk, the procedure will be described, typical sample analysis results presented, and quality assurance and control data will be examined in detail.

[1] Oak Ridge National Laboratory
[2] Science Applications International Corporation
[3] Oak Ridge Research Institute
[4] Great Lakes Colleges Association Participant, Albion College

Research sponsored by the Office of Energy Research, U. S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

72 USE OF TRANSPORTABLE X-RAY FLUORESCENCE FOR DETERMINATION OF SELECTED AQUEOUS TRACE CONTAMINANTS

Richard E. Phillips[2], Raymond J. Bath, Ph.D. [2], Pamela D. Greenlaw [2],
Joseph Hudek [1], Richard D. Spear, Ph.D. [1]

ABSTRACT:

The field analytical service (FAS) program of the Region II U.S. Environmental Protection Agency (EPA), Environmental Services Division, is used to support various Superfund field programs. The FAS program provides high quality transportable analytical instrumentation for on site project management. A thermal chromatograph/mass spectrograph (TC/MS) is used for organic analysis in soils; an open path Fourier-transform infrared/ultraviolet (FTIR/UV) spectrograph system is used for air monitoring; and until recently, energy dispersive x-ray fluorescence spectrometry (EDXRF) was used exclusively for metals analysis in soils. This presentation outlines a procedure whereby selected metals at the sub-ppm level can be determined in ground water, surface water and soil leachates using EDXRF.

A transportable EDXRF spectrometer equipped with secondary target excitation was employed to provide optimum sensitivity for trace metal analysis. A pre-concentration step involving the utilization of selective chelating ion exchange resins was investigated. The resin was presented in bulk using both column and batch techniques. The use of ion exchange resin impregnated paper was also investigated. Variations caused by resin packing densities were corrected for by ratioing to the appropriate target backscatter intensities.

The presentation contrasts the analytical results obtained through these various methods and compares them to those obtained by fixed-base laboratory atomic absorption instrumentation.

[1] United States Environmental Protection Agency, Region II, Edison, NJ
[2] Lockheed Engineering & Sciences, 2890 Woodbridge Ave., Building 209, Edison, NJ

73 COMPARATIVE EVALUATION OF SAMPLE PREPARATION METHODS FOR THE DETERMINATION OF METAL ANALYTES IN HIGH CONCENTRATION ENVIRONMENTAL SAMPLES

INORGANIC

Clifton Jones, Senior Inorganic Chemist, ICF Technology, Quality Assurance Technical Support Laboratory, Las Vegas, Nevada 89120 William R. Newberry III, EPA-EMSL; Xavier Suarez, ICF Technology; Dave Dobb, LESC.

ABSTRACT

The U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) protocol specifies direct nebulization inductively coupled plasma optical emission spectroscopy (ICP-OES), hydride inductively coupled plasma (HYICP), graphite furnace atomic absorption (GFAA), and cold vapor atomic absorption (CVAA) analytical techniques be used for the determination of metal analytes in high concentration environmental samples. The High Concentration Inorganic Statement of Work 9/90 (HCIN 9/90 SOW) sample preparation procedure is a potassium hydroxide (KOH) fusion method (Method 200.62-A-CLP). Solid samples (soil, sediments, and sludge), non-aqueous liquids and aqueous samples must undergo the KOH fusion sample preparation procedure.

Several problems have been observed and reported with the use of the KOH fusion method.

- Analytes that are typically determined using GFAA (Se, Sb, Pb, Cd, As, and Tl) are difficult to determine using the GFAA procedures recommended in the HCIN 6/90 SOW, because of high background effects. High background effects result from high solids content (2.0 to 2.25%) which is inherent in the KOH fusion method. Consequently, HYICP has been employed for the analyses of Se, Sb, and As.
- Pb and Tl are not easily determined using HYICP. Direct nebulization ICP-OES has been used for the analysis of Pb and Tl with decreased sensitivity. The contract-required quantitation limits (CRQL) for Pb and Tl are 100 µg/L. Estimated detection limits for Pb range from 200 to 500 µg/L for samples prepared using the KOH fusion method and analyzed by direct nebulization ICP-OES; a range 2 to 5 times greater than the CRQLs that are specified in the HCIN 6/90 SOW. Estimated detection limits for Tl by direct nebulization ICP-OES range from 1000 to 3000 µg/L; a range 10 to 30 times greater than the SOW-specified CRQL.
- Alternate sample preparation methods that reduce the high background effects so that the more sensitive GFAA may be employed for the determination of Pb or Tl are not specified in the HCIN 6/90 SOW.

Alternate procedures were proposed for preparation of samples analyzed under the HCIN 6/90 SOW. The alternate preparation methods selected for Phase I of the evaluation include:

- EPA SW-846 methods 3051 and 3015 microwave digestion for water, soils, oils, and sediments
- EPA ILM01. open beaker digestion methods for water, soils and sediments
- EPA ILM01. proposed block digester method for waters, soils, and sediments
- Proposed microwave digestion method for total metals using hydrofluoric acid (HF)
- Proposed lithium metaborate flux fusion method

The ICF-Quality Assurance Technical Support (QATS) Laboratory undertook the evaluation of the HCIN 6/90 KOH fusion method, EPA methods 3051 and 3015, and ILM01. open beaker digestion methods. The other three methods were evaluated by the EMSL-LV/LESC group and the results of the combined effort will be discussed. report. A comparison of the proposed sample preparation methods for possible inclusion in the HCIN SOW as alternate methods of sample preparation are presented with preliminary conclusions. Criteria used in conducting these evaluations include a statistical comparison of precision and accuracy, labor effort, and equipment cost.

74

ION EXCHANGE SOLID PHASE EXTRACTION: FACTORS INFLUENCING RETENTION AND ELUTION AND THEIR APPLICATION IN METHOD DEVELOPMENT

Alan J. Spilkin, Dean Rood. J&W Scientific, 91 Blue Ravine Rd., Folsom, California 95630 (916)985-7888

Abstract: Sample cleanup by solid phase extraction (SPE) usually involves the retention of desired solutes followed by their elution from the phase. Ion-exchange sorbents are dependent on four major variables. These four variables are the pKA difference between the sorbent and solute, solvent pH, ionic strength and the presence of counterions. This paper will explore the relationship of these four variables on solute retention and elution for organic anions (primarily phenoxyacid herbicides) on a strong anion exchange (SAX) phase. The impact and influence of ionic strength and counterion identity will be determined for a series of anions with different pKa's relative to the sorbent. These factors will be applied to make method development more efficient and reliable for ion exchange solid phase extraction.

INTRODUCTION

The purpose of this paper is to demonstrate a general approach to method development for ion exchange SPE applications. A strong anion exchange cartridge (SAX) and phenoxyacid herbicides were used as an example.

Experiment: Three parameters, sample pH, counterion identity and ionic strength all can play important roles in sample retention and elution. These parameters must be taken into consideration when developing a method for ion exchange. Although these parameters are often interdependent of one another, their affect on sample retention and elution were considered separately.

The structure of J&W SAX phase is a silica based trimethyl amino propyl substituent without endcapped silanols. In addition to the primary ion exchange mechanism, hydrogen bonding with surface silanols and reverse phase interactions with bonded alkyl groups can occur.

Sample pH adjustment is often employed to ionize the sample and phase. For ion exchange to occur both the analytes and the sorbent must have opposite charges. Ion exchange occurs when the pKa values for the analytes differ by at least 4 pKa units from the phase. Theoretically, 99% of a species is ionized at 2 pH above its pKa value if it is anionic or 2 pH units below its pKa value if it is cationic.

For simplicity, ion exchange can be expressed by the equations:

$R^- + PX^+ = PR^+ + X^-$ Anion Exchange
$R^+ + PX^- = PR^- + X^+$ Cation Exchange

where R is the analyte, P is the phase, and X is the associated ion that is exchanged for R.

Counterions are those ionic species in solution that can compete with the analytes for binding sites on the phase. Some counterions have stronger interactions than others.

The third parameter, ionic strength, is simply the concentration of counterions in solution. One would expect as ionic strength increases, the competition between the analytes and counterions increases.

Results: Sample pH was the first parameter investigated. To examine the effects of pH on the retention of phenoxyacid herbicides, 1.6 µg of four phenoxyacids (2,4-D, 2,4 DB, Dichlorprop and 2,4,5 TP) were loaded onto the cartridge in water at a pH range from 3 to 9. Since the phenoxyacids have pKa values between 2.6 and 4.8, one would expect that at the lower pH, most of the acid would remain neutral. Since the pKa of the phase is about 10-11, one would expect that the phase would become uncharged at the higher pH range. It is important to adjust the pH of the solution with weak counterion acids and bases to minimize the counterion effects on retention. In this case, HCl and NaOH were used to pH adjust the water. Surprisingly, all phenoxyacids retained under the varied pH conditions. The high retention indicates that the phenoxyacids are not solely bound by ion exchange but also by hydrogen bonding and/or reverse phase interaction.

The other parameters affecting analyte retention are the counterions and ionic strength. Three counterions were examined in increasing attraction towards the phase, acetate, chloride and citrate, at ionic strengths of 0.001M, 0.01M, 0.1M and 1.0M concentrations. The total concentration of phenoxyacids in solution was 0.001M. Four mLs of the phenoxyacids in the above solutions were loaded into the cartridge and collected. The phenoxyacids with the weak counterions, acetate and chloride, showed breakthrough occurring above ionic strengths of 0.01M. As expected, breakthrough in the citrate solution occurs at lower ionic strengths of nearly 0.001M. Interestingly enough, the phenoxyacids that showed highest retention, have the lowest pKa values.

The next step in the experiment was to determine at what point breakthrough occurs on the rinse step. Ideally, the strongest possible solvent should be used without incurring any breakthrough of the analytes. NaOH, a weak counterion, in water was chosen for the rinse step. At 2 mL volumes of NaOH exceeding 0.01 M, breakthrough of the acids was observed. Thus, a 2 mL solution of 0.01 M NaOH was chosen.

The elution solvent for ion exchange should contain a strong counterion to elute the analytes from the phase. In this experiment, 2 mL citrate solutions in increments of 1% from 1-5% (w/w) citric acid in water were chosen to elute the acids. At concentrations greater than 2%, there was not an appreciable difference in recovery. Surprisingly, the recovery of the 2,4D was very low, only 40% at 5% citrate. The low recovery suggests that the 60% of the 2,4D left on the phase is bound by silanol and/or reverse phase interactions.

Next, 100% methanol was tried as an elution solvent. Only the 2,4DB eluted with methanol. The next step to take was to combine the 5% citrate solution with methanol 50/50. This combination eluted nearly 100% of all the phenoxyacids. These results suggest that the phenoxyacids are bound by both ionic attraction and reverse phase and/or hydrogen bonding.

The real test was whether or not this experimental method worked on a real sample. A lake water sample was spiked with the same amount of phenoxyacids used in the method development procedure. The final method was as follows:

1. Condition: 3 mL of MeOH followed by 3 mL of water.
2. Load: Adjust sample to pH7 with HCl or NaOH.
3. Rinse: 3 mL of 0.01 M NaOH.
4. ELUTE: 1 mL of 50/50 5% citric acid (aq)/ MeOH.

The results of the deionized water compared to the lake water sample are as follows:

RECOVERIES

Phenoxyacid	water	std	sample	std
2,4 D	86	4.8	68	4.2
Dichloroprop	74	6.5	69	3.1
2,4,5 TP	85	3.3	79	4.6
2,4 DB	69	3.6	64	4.1

n=3 all recoveries in %

These results are as good or better than can be expected by liquid/liquid extraction techniques.

SUMMARY

The systematic adjustment and examination of three variables, pH, counterions, and ionic strength, resulted in high and repeatable analyte recovery for ion exchange solid phase extraction. By following this logical approach, method development for any ion exchange SPE application may be achieved. It is important to understand that other factors such as reverse phase and hydrogen bonding can influence retention and elution but may not always play a role.

75

APPLICATIONS OF X-RAY FLUORESCENCE SPECTROSCOPY TO HAZARDOUS WASTE ANALYSES

INORGANIC

Douglas Kendall, National Enforcement Investigations Center, U.S. Environmental Protection Agency, Denver Federal Center, Denver, Colorado 80225.

ABSTRACT

X-Ray fluorescence (XRF) spectrometry offers many advantages for the analysis of hazardous materials, both for field work and for laboratory work. Two of the principal advantages are ease of sample preparation and new, universal calibration methods. Three examples which illustrate areas of application of XRF spectrometry to laboratory analyses will be presented.

Often the advantage of easy sample preparation for XRF measurements is offset by the difficulty of calibrating the instrument for a specific matrix. Even if the preparation of matrix matched standards is attempted, it is impossible to guarantee that some of the actual samples will not have concentrations outside the range of the calibration standards or high concentrations of elements not in the standards. Constant progress has been made in the calibration of spectrometers using universal standards, and compensating for matrix effects using mathematical corrections (fundamental parameters methods). Results from a particular program (UNIQUANT, Philips Electronic Instruments) will be used to show the utility of this method for the quantitative and semiquantitative analysis of complete unknowns.

The determination of toxic metals in soils, slags and similar materials is a common laboratory analysis. XRF determinations are superior in terms of sample preparation and speed of analysis. Data will be presented to show the comparability of XRF to ICP and AA determinations. XRF determinations can be used to show whether acid digestions are partial or total extractions, and to confirm ICP results by an independent, alternate method.

The determination of sulfur and chlorine in waste oil is important when the oil is to be burned. The XRF determinations of sulfur and chlorine compare well with the results from oxygen bomb combustion with an ion chromatography or ICP finish. Sediment and other problems with XRF determinations can be largely overcome with a thin layer method.

AIR AND GROUNDWATER

76

HANDBOOK AND DATABASE OF RCRA GROUND-WATER MONITORING CONSTITUENTS: CHEMICAL AND PHYSICAL PROPERTIES

Ann E. Johnson, Hydrogeologist, Richard Carlston, Programmer/Analyst, Science Applications International Corporation, 7600-A Leesburg Pike, Falls Church, Virginia 22043; James R. Brown, Environmental Scientist, Vernon B. Myers, Chief, Monitoring and Technology Section, Office of Solid Waste (OS-341), U.S. Environmental Protection Agency, Washington, D.C. 20460.

Appendix IX is the list of ground-water monitoring constituents for permitted hazardous waste treatment, storage, and disposal facilities that are implementing the ground-water monitoring requirements of 40 CFR Part 264 Subpart F. The Appendix IX Handbook and Database provide specific chemical and physical properties and SW-846 analytical methods for each of the 222 constituents listed in Appendix IX, and 19 constituents that are being proposed or considered for addition to Appendix IX. For each constituent listed in Appendix IX, the Handbook and Database provide the following information, as available: Appendix IX Name; CAS Name; CAS Number; empirical formula; maximum contaminant level (MCL); molecular weight; boiling point; melting point; specific gravity; solubility; vapor pressure; Henry's Law Constant; log K_{ow}; possible SW-846 methods and their Estimated Quantitation Limits (EQLs); and chemical structure. The Appendix IX Handbook is a pocket-size manual that contains physical and chemical data for each of the Appendix IX constituents on a separate page. The Appendix IX Database is a Clipper-based data management system for PCs that is function-key driven and requires no additional software or programming ability to operate. EPA believes the Appendix IX Handbook and Database will be useful to both regulators and the regulated community in designing and evaluating ground-water monitoring programs, hydrogeologic characterizations, and corrective measures, including: determining the fate and transport of contaminants in ground water; choosing an analytical method for ground-water analysis; evaluating corrective actions; selecting treatment methods; reviewing RCRA Corrective Measures Studies; evaluating the potential for LNAPLs or DNAPLs in ground water; and contaminant transport modeling.

Introduction

The Handbook and Database of RCRA Ground-Water Monitoring Constituents contain physical and chemical properties of constituents listed in 40 CFR Part 264, Appendix IX. Appendix IX is the list of ground-water monitoring constituents for permitted hazardous

waste treatment, storage, and disposal facilities that are subject to the ground-water monitoring requirements of 40 CFR Part 264 Subpart F.

Appendix IX was intended to be a "living" list -- to be updated and revised as analytical methods are developed and standardized, and as research on the subsurface fate and transport of specific contaminants advances. The constituents contained in the Handbook and Database are those currently listed in Appendix IX, however the Handbook and Database also contain and denote constituents that are being considered for addition to or deletion from Appendix IX. The Appendix IX Handbook and Database provide specific chemical and physical properties and SW-846 analytical methods for each of the 222 constituents listed in Appendix IX, and 19 constituents that are being proposed or considered for addition to Appendix IX.

Purpose of the Handbook and Database

The Appendix IX Handbook and Database are designed to provide a concise and readily accessible resource for ground-water professionals who are designing and evaluating ground-water monitoring programs, hydrogeologic characterizations, and corrective measures, including:

- Evaluating the fate and transport of contaminants in ground water;
- Choosing an analytical method for ground-water analysis;
- Evaluating corrective actions, selecting treatment methods, or reviewing Corrective Measures Studies;
- Evaluating the potential for LNAPLs or DNAPLs in ground water;
- Contaminant transport modeling.

Computer and Software Requirements for the Database

The Appendix IX Database is a Clipper-based data management system for PCs that requires no additional software or programming ability to operate. Hardware requirements for operating the system are as follows:

- 4 Megabytes of hard drive space;
- 640 Kb of RAM;

- DOS 3.X or higher;
- Optional color monitor.

Contents of the Handbook and Database

Figures 1 presents an example of the format of the Appendix IX Handbook. Figure 2 is an example of a display screen from the Appendix IX Database. For each constituent listed in Appendix IX, the Handbook and Database provide the following information, as available:

1. Appendix IX Name: The name of the constituent as it appears on the list of ground-water monitoring constituents listed in 40 CFR Part 264 Appendix IX. The Handbook is organized alphabetically by Appendix IX name.

2. CAS Name: The name of the constituent as it appears in the Chemical Abstracts Service (CAS) Registry.

3. CAS Number: The CAS registry number.

4. Empirical Formula: The chemical formula that provides the number of each type of atom in the molecule. For metals, the Handbook and Database provide the chemical symbol.

5. Maximum Contaminant Level: The maximum permissible level of the constituent in water which is delivered to the free flowing outlet of the ultimate user of a public water system. If there does not exist a maximum contaminant level for the constituent, the notation "NA" is presented.

6. Molecular Weight: The molecular or formula weight of the constituent in grams/mole.

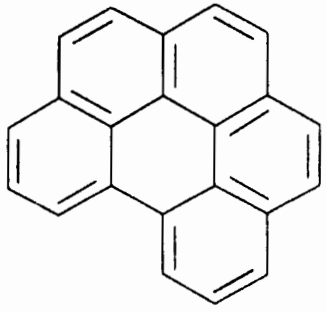
7. Boiling Point: The temperature in degrees celsius at which the vapor pressure of the constituent in aqueous form is equal to atmospheric pressure.

Benzo[g,h,i]perylene

		REF
CAS Name:	Benzo[g,h,i]perylene	
CAS Number:	191-24-2	
Empirical Formula:	$C_{22}H_{12}$	
MCL:	NA	
Molecular Weight:	276.34 g/mol	04
Melting Point:	222 °C	04
Boiling Point:	> 500 °C	04
Vapor Pressure:	1×10^{-10} mm Hg at 20°C	03
Specific Gravity:	NA	
Solubility:	2.6×10^{-04} mg/L at 25°C	03
Henry's Law Constant:	1.4×10^{-07} atm • m^3/mol at 25°C	04
Log K_{ow}	7.23	03

Possible SW-846 Analytical Methods

Method	EQL(µg/L)
8270	10
8250	41
8100	NA
8310	0.76



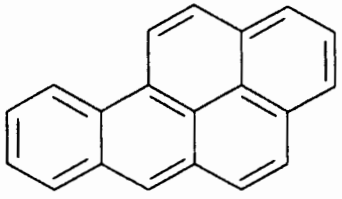
22

Benzo(a)pyrene

		REF
CAS Name:	Benzo(a)pyrene	
CAS Number:	50-32-8	
Empirical Formula:	$C_{20}H_{12}$	
MCL:	0.0002 mg/L	11
Molecular Weight:	252.32 g/mol	01
Melting Point:	179-179.3°C	01
Boiling Point:	310-312°C	01
Vapor Pressure:	5×10^{-09} mm Hg at 20°C	03
Specific Gravity:	1.351 [UT]	04
Solubility:	3.8×10^{-03} mg/L at 25°C	03
Henry's Law Constant:	4.9×10^{-07} atm • m^3/mol at 25°C	03
Log K_{ow}	5.98	03

Possible SW-846 Analytical Methods

Method	EQL(µg/L)
8310	0.23
8250	25
8270	10
8100	NA
8275	NA



23

FIGURE 1.
FORMAT OF THE APPENDIX IX HANDBOOK

Appendix IX Name	2,4,5-Trichlorophenol		
CAS Name	Phenol, 2,4,5-trichloro-		
CAS Number	95-95-4		
Empirical Formula	C6-H3-Cl3-O		
Molecular Weight	197.45 g/mol		--
Boiling Point	252 °C		--
Melting Point	68-70 °C		--
Specific Gravity	1.678 @ 25C		--
Solubility	1.19 E 03 mg/L	25 °C	01
Vapor Pressure	2.9 E-05 atm	25 °C	04
Henry's Law Constant	1.76 E-07 atm·m^3/mol		04
Log Kow	3.72		05
MCL		NA mg/L	--
Possible SW-846 Methods	Method: 8250 EQL:	NA ug/L	--

F1: Help | F2: Reference List | F3: View Structure | PgUp/PgDn | ↑/↓ | Esc

FIGURE 2.
EXAMPLE OF A DATA SCREEN FROM THE APPENDIX IX DATABASE

8. **Melting Point:** The temperature in degrees celsius at which the constituent in solid phase is in equilibrium with the liquid phase at atmospheric pressure.

9. **Specific Gravity:** The ratio of the density of the constituent at a specified temperature relative to the density of water at a specified temperature.

10. **Solubility:** The concentration of the constituent in milligrams per Liter that is required to form a saturated solution in water at a given reference temperature.

11. **Vapor Pressure:** The pressure in millimeters of mercury of the vapor phase of the constituent that is in equilibrium with its liquid or solid phase.

12. **Henry's Law Constant:** The ratio of the equilibrium concentration in atmospheres of the constituent in air relative to its concentration in moles/cubic meter in water.

13. **Log K_{ow}:** The log of the ratio of the equilibrium concentration of the constituent in octanol relative to its concentration in water.

14. **Possible SW-846 Methods:** The analytical methods presented in the USEPA publication "Test Methods for Evaluating Solid Waste" (SW-846), Third Edition (as amended by Updates I and II), that may be used to determine the concentration of the constituent in ground water. For each method, an Estimated Quantitation Limit (EQL) is given if an EQL is available. When different EQLs exist for 5 and 25 mL sample sizes, the EQL for the 5 mL sample size is provided in the Handbook and Database. When the Handbook and Database present two EQLs for one analytical method, the two EQLs represent the EQLs obtained using two different detector types.

15. **Chemical Structure:** The chemical formula written to show the relative arrangements of the atoms. For metals, the Handbook and Database provide the chemical symbol.

The information contained in the Handbook and Database is from a wide variety of recently available and standard references, including the following:

- USEPA. 1992. RREL Treatability Data Base, Version 4.0. USEPA, Glenn Shaul.

- Weast, Robert C., ed. 1986. CRC Handbook of Chemistry and Physics, 67th Edition. CRC Press, Inc., Boca Raton, Florida, 2406 pp.

- Budavari, Susan, ed. 1989. The Merck Index, Eleventh Edition. Merck & Co., Inc., Rahway, New Jersey, 1606 pp.

- Verschueren, Karel. 1983. Handbook of Environmental Data on Organic Chemicals, Second Edition. Van Nostrand Reinhold Company Inc., New York, New York, 1310 pp.

- Aldrich Chemical Company. 1990. Aldrich Catalog Handbook of Fine Chemicals. Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, 2150 pp.

- Montgomery, John H. and Linda M. Welkom. 1990. Groundwater Chemicals Desk Reference. Lewis Publishers, Chelsea, Michigan, 640 pp.

- Howard, Philip H., ed. 1991. Handbook of Environmental Fate and Exposure Data, Volumes I and III. Lewis Publishers, Chelsea, Michigan.

- Yaws, Carl, Haur-Chung Yang, and Xiang Pan. November 1991. Henry's Law Constants for 362 Organic Compounds in Water. Chemical Engineering, vol. 98, no. 11, pp. 179-185.

Operating the Database

The Appendix IX Database is completely function-key driven, and requires no programming ability to operate. When the Database is accessed by typing "APX9" at the DOS prompt, the first screen that appears is a brief description of the Database. The user can read the introductory screen using the cursor or by paging down, or access the main menu by pressing the escape key <Esc>. The main menu of the Appendix IX Database is the list of 241 constituents in the Database, listed alphabetically by Appendix IX name. With the <F3> key, the user can sort the constituents alphabetically/ numerically by toggling between Appendix IX name, CAS number, or CAS name (see

Figures 3 a, b, and c). To view data for a particular constituent, the user highlights the constituent either by using the cursor or the <Page Down> and <Page Up> keys to move through the list of constituents, or by completely or partially typing the Appendix IX name, CAS name or CAS number of a constituent. Data for the highlighted constituent is retrieved by hitting <Enter>.

Figure 2 shows a typical data screen for an Appendix IX constituent. The Database is capable of displaying multiple values for specific gravity, solubility, Henry's law constant, log K_{ow}, and possible SW-846 analytical methods and EQLs. Multiple values are accessed by highlighting the displayed value using <Page Up> or <Page Down> and moving the cursor up or down for additional values, as indicated by an arrow (see Figure 4). The <Esc> key takes the user back to the main list of Appendix IX constituents.

The Database has several other functions that may be accessed from the data screen. To view the constituent's chemical structure, the user presses the <F3> key while in the data screen (Figure 5). References for chemical and physical properties are indicated in the Database by number. The user may view specific citations by pressing the <F2> key for the Reference list (Figure 6a) while in the data display screen for a specific constituent. When a specific reference is highlighted, the user presses <Enter> for the full citation (see Figure 6b). The user may obtain help in using the database (e.g., explanations of movement keys, descriptions of function keys, and abbreviations) by hitting <F1> while in the data screen or main menu.

Summary

The Appendix IX Handbook and Database were developed to provide ground-water professionals easy access to commonly used physical and chemical properties of the RCRA ground-water monitoring constituents. The Appendix IX Database provides chemical and physical properties of the Appendix IX constituents in a user-friendly system designed to operate on minimally equipped PC systems.

Acknowledgements

This paper was written, in part, by members of U.S. EPA's Office of Solid Waste, Washington, D.C. It has not been reviewed by the Agency and the contents do not necessarily reflect the views and policies of EPA. Mention of trade names, commercial products, or publications does not constitute endorsement or recommendation for use.

05/29/92 Appendix IX Chemical Constituents Database System 09:06:09

Version 1.0

Appendix IX Name	CAS Number
2,3,4,6-Tetrachlorophenol	58-90-2
2,3,7,8-TCDD	1746-01-6
2,4,5-T; 2,4,5-Trichlorophenoxyacetic acid	93-76-5
2,4,5-Trichlorophenol	**95-95-4**
2,4,6-Trichlorophenol	88-06-2
2,4-D; 2,4-Dichlorophenoxyacetic acid	94-75-7
2,4-Dichlorophenol	120-83-2
2,4-Dimethylphenol; m-Xylenol	105-67-9
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2

F1: Help | F2: Reindex | F3: Toggle Sort | Enter: Select Item | Esc: Quit

FIGURE 3a.
2,4,5-TRICHLOROPHENOL SORTED BY APPENDIX IX NAME

05/29/92 Appendix IX Chemical Constituents Database System 09:06:16

Version 1.0

CAS Registry Name	CAS Number
Phenol	108-95-2
Phenol, 2,2'-methylenebis[3,4,6-trichloro-	70-30-4
Phenol, 2,3,4,6-Tetrachloro-	58-90-2
Phenol, 2,4,5-trichloro-	**95-95-4**
Phenol, 2,4,6-trichloro-	88-06-2
Phenol, 2,4-dichloro-	120-83-2
Phenol, 2,4-dimethyl-	105-67-9
Phenol, 2,4-dinitro-	51-28-5
Phenol, 2,6-dichloro-	87-65-0
Phenol, 2-(1-methylpropyl)-4,6-dinitro-	88-85-7

F1: Help | F2: Reindex | F3: Toggle Sort | Enter: Select Item | Esc: Quit

FIGURE 3b.
2,4,5-TRICHLOROPHENOL SORTED BY CAS NAME

05/29/92 Appendix IX Chemical Constituents Database System 09:06:21

Version 1.0

CAS Number	Appendix IX Name
95-57-8	2-Chlorophenol
95-63-6	1,2,4-Trimethylbenzene *
95-94-3	1,2,4,5-Tetrachlorobenzene
95-95-4	**2,4,5-Trichlorophenol**
959-98-8	Endosulfan I
96-12-8	1,2-Dibromo-3-chloropropane; DBCP
96-18-4	1,2,3-Trichloropropane
97-63-2	Ethyl methacrylate
98-06-6	tert-Butylbenzene *
98-82-8	Isopropylbenzene *

F1: Help | F2: Reindex | F3: Toggle Sort | Enter: Select Item | Esc: Quit

FIGURE 3c
2,4,5-TRICHLOROPHENOL SORTED BY CAS NUMBER

Appendix IX Name	2,4,5-Trichlorophenol		
CAS Name	Phenol, 2,4,5-trichloro-		
CAS Number	95-95-4		
Empirical Formula	C6-H3-Cl3-O		
Molecular Weight	197.45 g/mol		--
Boiling Point	252 °C		--
Melting Point	68-70 °C		--
Specific Gravity	1.678 @ 25C		--
Solubility	1.19 E 03 mg/L	25 °C	01
Vapor Pressure	2.9 E-05 atm	25 °C	04
Henry's Law Constant	1.76 E-07 atm·m^3/mol		04
Log Kow	3.06		05
MCL		NA mg/L	--
Possible SW-846 Methods	Method:↑ 8270 EQL:	10 ug/L	--

F1: Help | F2: Reference List | F3: View Structure | PgUp/PgDn | ↑/↓ | Esc

FIGURE 4.
MULTIPLE VALUES FOR POSSIBLE SW-846 METHODS

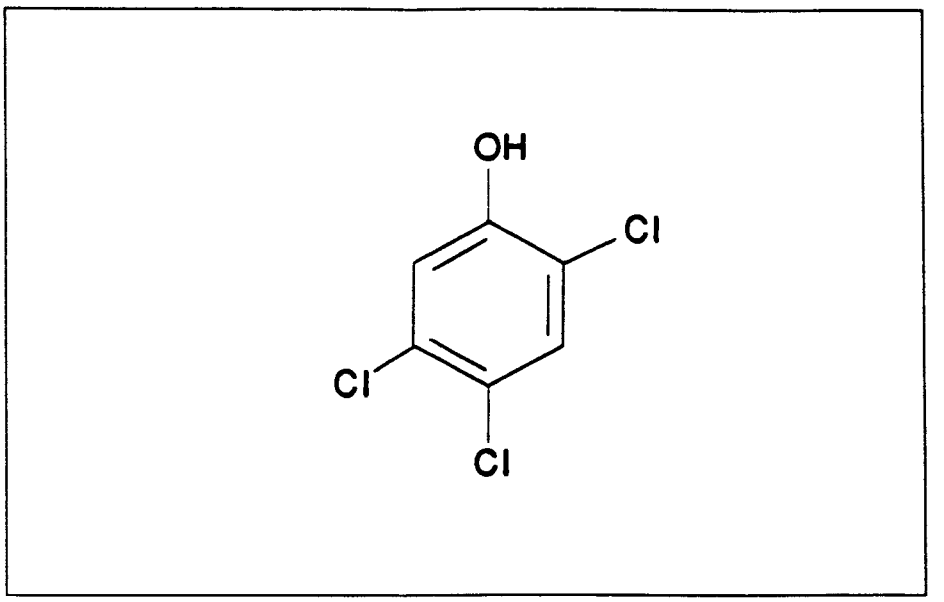


FIGURE 5.
CHEMICAL STRUCTURE FOR 2,4,5-TRICHLOROPHENOL

Code	Data Source
01	Weast, Robert C., ed. 1986
02	Budavari, Susan, ed. 1989.
03	Aldrich Chemical Company. 1990.
04	Montgomery, John H. 1990 and 1991.
05	Verschueren, Karel. 1983.
06	Howard, Philip H., ed. 1991.
07	USEPA. October 1986.

Enter: Select Item - Display Detail | Esc

FIGURE 6a.
LIST OF REFERENCES

Code	Data Source
01	Weast, Robert C., ed. 1986
02	Budavari, Susan, ed. 1989.
03	Al
04	Mo
05	Ve
06	Ho
07	US

Weast, Robert C., ed. 1986. "CRC Handbook of Chemistry and Physics," 67th Edition. CRC Press, Inc., Boca Raton, Florida, 2406 pp.

↑,↓,PgUp,PgDn: Scroll Source Detail | Esc

FIGURE 6b.
COMPLETE REFERENCE CITATION

77 Rationale for the Design of Cost-Effective Groundwater Monitoring Systems in Limestone and Dolomite Terranes: Cost-Effective as Conceived is Not Cost-Effective as Built if the System Design and Sampling Frequency Inadequately Consider Site Hydrogeology

James F. Quinlan, Principal Hydrogeologist, Quinlan & Associates, Inc., Box 110539, Nashville, Tennessee, 37222; Gareth J. Davies, Hydrogeologist, Ozark Underground Laboratory, Protem, Missouri 65733; and Stephen R. H. Worthington, Instructor, Department of Geography, McMaster University, Hamilton, Ontario, L8S 4K1, Canada

Abstract: If one assumes that the purpose of a monitoring well is to detect the presence or absence of contaminants draining from a facility, if one has the goal of doing so reliably and successfully, and if one must accomplish this goal in carbonate rocks, then it cannot be accomplished by the conventional technique of drilling several down-gradient wells — except by improbably good luck.

Where there is carbonate rock, in most settings there is also karst and a karst aquifer. The only way to design a reliable monitoring system for a facility in a karst terrane is to determine where it drains to. Such drainage can only be established by well-designed, properly performed, and correctly interpreted tracer tests to springs and cave streams to which the facility drains and to wells which intercept their flow lines. [Such interception is difficult to accomplish and must be proven by tracing.] In a karst, any so-called monitoring point, until and unless it has been shown by tracing to function as such, is a monitoring point in name only. The springs to which a karst aquifer (and a facility) drains may have significant storm-related variation in discharge and water quality. Sampling of these springs and other monitoring points must be done at a frequency that reliably senses these variations. Regular annual, semi-annual, or quarterly sampling is incapable of doing so — again, except by improbably good luck.

The cost-effectiveness and reliability of a monitoring system in a karst aquifer is directly proportional to the extent to which its hydrogeology and flow dynamics are understood. The hydrogeology must be studied on a regional scale. One of the aquifer parameters useful for the design of a monitoring system in any type of aquifer is estimated flow velocity, a parameter that can be used to estimate hydraulic conductivity at at a regional scale. In carbonate aquifers the measurement of hydraulic conductivity is scale-dependent over many orders of magnitude and directly proportional to the scale of the investigation, as shown in Figure 1. When the representative elementary volume [REV] is at the scale of a pumping test, such well tests can be excellent for evaluating water supply potential of an aquifer. But when concern is with contaminant movement, then the whole catchment is the appropriate scale of investigation. Only a tracer test can represent aquifer-scale worse-case contaminant velocities.

INTRODUCTION

Current RCRA [Resource Conservation and Recovery Act] and CERCLA [Comprehensive Environmental Response, Conservation, and Liability Act (Superfund)] regulations require the installation of wells for groundwater monitoring of all sites — regardless of their rock types. The following assumptions are implicitly made by designers of monitoring-well systems:

1. The aquifers are isotropic and homogeneous.
2. Flow is in a plume to be intersected by the well.
3. Flow is dispersive, as a result of advection, hydrodynamic dispersion, and molecular diffusion.

These assumptions are generally valid in granular aquifers and in many finely fractured aquifers. In limestone and dolomite (carbonate) terranes— nearly all of which are karst terranes and have karst aquifers — these three assumptions are either presumed to be valid or an alternative assumption is made:

4. Flow is to a cave stream (often more than one) that:
   a. Drains the site to be monitored.
   b. Is intercepted by the well.

In most karst terranes, the first two assumptions are always wrong. Assumption 3 is correct. Dispersion may occur in the X,Y, and Z directions and will be predominant in one of them; diffusion into the rock matrix is usually trivial, but there are exceptions.* Assumption 4a is usually right, but 4b is almost always wrong.

It is appropriate to define the terms *karst* and *karst aquifer*:

> *Karst:* A landscape and its subsurface characterized by surface water flow and groundwater flow through caves (or other dissolutionally enlarged cavities) and a variable suite of distinctive surface landforms and hydrologic features. These include the following nine types of features, any one of which is diagnostic of karst:
>
> 1. Sinkholes (any closed depressions, with or without a discrete opening at their bottom, formed by dissolution and/or collapse of bedrock, with flushing and/or collapse of soil into a subjacent cavity), and internal drainage to them
> 2. Dry valleys (in humid climates)
> 3. Springs (draining carbonate, sulfate, or halide rocks)
> 4. Caves (open to the surface or encountered by drilling)
> 5. Sinking streams (that sink at a hole known as a *swallet*)
> 6. Dissolutionally enlarged joints and/or bedding planes (as seen in cores or outcrops)
> 7. Grikes (soil-filled, dissolutionally enlarged joints or grooves; also known as *cutters* or *soil karren*)
> 8. Karren (dissolutionally, subaerially, water-carved grooves on rock; commonly subparallel)
> 9. Significant loss of fluid circulation during drilling of wells
>
> *Karst aquifer:* An aquifer in which flow of water is or can be appreciable through one or more of the following: joints, faults, bedding planes, pores, cavities, and caves — any or all of which have been enlarged by dissolution of bedrock.

Most karsts are developed in carbonate rocks, but they also develop in gypsum, salt, carbonate-cemented sandstone, and (to a trivial extent) in other rocks.

A few examples of karst features 1 through 5 may be shown on a published topographic map, but most of them and features 6 through 9 can be found only by field work. If one looks in the field, and does so diligently, some of these nine features, perhaps all of them, will be found. Experience has repeatedly shown that if there is carbonate rock, there is almost certainly some type of karst and a karst aquifer (Quinlan *et al.*, 1992).

The apparent lack of some or all of the above nine karst-diagnostic features in a carbonate terrane, or their non-recognition, does not mean that a karst is not present. It commonly means that more field work or drilling is needed to find them. Similarly, the presence of just one of the features in areas where there are few outcrops is diagnostic of a karst because that one is usually representative of a much larger population. This is true because the scale of sampling is so coarse relative to the actual distribution of the karst features. The statistics of searching for (and finding)

---

* If the mean flow time is less than a month, the tracer has had insufficient time to penetrate deeply into the matrix. Nevertheless, diffusion cannot be ignored in the analysis of dye recovery (Maloszewski and Zuber, 1990, 1985). Correct interpretation of diffusion in moderate- to long-term tests is complicated, however, by the effects of bacterial decomposition on tracer dyes (Aley *et al.* 1993).

many of the more subtle and sparsely distributed features diagnostic of karst favor failure to find them.

Useful introductions to karst hydrogeology are the texts by Milanovic (1981), White (1988), Ford and Williams (1989), and Kresic (1993).

The consequences of accidental spills or of intentional or permitted discharges of harmful materials into karst aquifers are in many ways more severe than into other aquifers. Travel time is usually extremely rapid; attenuation is usually minimal (Field, 1988). Flow velocities in many karst terranes vary as much as 10 to 1500 ft per hour (~0.001 to 0.1 m/s) between the same two points — the latter, in response to storms — and are tens of thousands to several million times faster than those characteristic of many granular aquifers. The flow velocities are thousands of times more rapid than slug or pumping tests in wells in carbonate aquifers would indicate (Kiraly, 1975; Sauter, 1992; Smart *et al.*, 1992). Consequently, one can study karst aquifers more readily and interpret real data rather than synthetic data which are honorably (but sometimes erroneously) produced by computer simulations of flow in karst aquifers. Consequently also, there are groundwater monitoring problems and wellhead delineation problems unique to wells and springs in karst terranes. For monitoring, these problems include the following:

1. Where to monitor for pollutants
2. Where to monitor for background
3. When to monitor for pollutants and background
4. How to reliably and economically determine the answers to problems 1, 2, and 3.

We do not know why there is so little recognition of the unique hydrologic nature of karst in texts concerning hydrology, hydrogeology, groundwater monitoring, hazardous-waste site management, and remediation (as discussed by Quinlan *et al.*, 1992, p. 582-583), but the fact remains that karst is usually ignored by most engineers and hydrogeologists, be they regulators or consultants — in the U.S., Canada, and much of Europe. Accordingly, most of these professionals, whatever their education, lack formal training in karst hydrogeology and rarely have the opportunity to learn about it. Many are unaware of the significance of karst. Too many deny its existence or importance at a given site. Yet approximately 40% of the U.S. east of Tulsa is underlain by carbonate rocks; most of this 40% is karstic.

Our experience has repeatedly shown that unless special approaches to the study of facilities in carbonate terranes are taken, their monitoring programs yield data that are irrelevant to the purpose of monitoring — the denial by professionals of the need for such special approaches notwithstanding. This paper and publications by Quinlan (1989, 1990), Aley (1986), Ewers (1992), Alexander *et al.* (1992), Edwards and Smart (1989), Smart (1985), Field (1988), and Quinlan and Ewers (1985) describe these approaches. They have been written because there is overwhelming proof that most carbonate rocks are karstified. This karstification affects the validity of monitoring efforts in them and it requires special approaches.

The lack of reliable monitoring in karst aquifers has many origins. These include:

1. Many of the regulators who wrote the RCRA and CERCLA regulations were unfamiliar with the complexities of karst .
2. Sometimes there is an unthinking literal interpretation of the regulations, both by regulators and by consultants.
3. Some attorneys (and others) tend to become uncomfortable about the implications of off-site monitoring that is sometimes all that is economically feasible.
4. Some consultants, fearful of losing a client's future business, report only that which they think the client wants to hear. They intentionally suppress potentially embarrassing facts and/or ignore clues that may lead to them.

GROUNDWATER FLOW IN CARBONATE ROCKS

Porosity is the percentage of the total volume of rock or sediment that is void space. In limestones and dolomites, the initial or primary porosity can be high or low, depending on the depositional environment in which the rock formed, and the subsequent history of burial and of exposure to the atmosphere and *in-situ* dissolution and recrystallization (Scholle *et al.*, 1983; Tucker and Wright, 1990). Changes in depositional environment during sedimentation, such as interruptions caused by alterations in sea level, or temporary fluctuations in water depth or energy, cause differences in rock texture, generally as partings or distinct bedding planes in what became the rock.

As these rocks are eventually uplifted and as overlying rocks are eroded, stresses are released and vertical fractures known as joints develop, commonly normal to bedding planes. Faults develop where there was movement of rocks relative to each other. Fractures and faults comprise secondary porosity.

Carbonate rocks are soluble in meteoric waters, most of which are slightly acidic, and most carbonate rocks contain sulfide or sulfate minerals that oxidize to produce sulfuric acid *in situ*, thus enhancing dissolution of the rock. As the rocks are subaerially exposed, water infiltrates and dissolution along joints, faults, and bedding planes creates tertiary porosity. Such dissolution creates flow pathways for groundwater, thus producing a karst aquifer (White, 1988; Ford and Williams, 1989). Exposed bedding planes and joints are readily exploited by chemically aggressive meteoric waters that produce underground flow paths with a length that may be many tens of miles. They form an integrated network of shafts, tubes, fractures, and conduits (Palmer, 1991; White, 1988; Ford and Williams, 1989; Worthington, 1991).

If a unit volume of rock is assumed, the efficiency of the movement of groundwater through the void spaces in it is a function of the degree of interconnection of the void spaces. A measure of this efficiency, the hydraulic conductivity, is defined as the volume of fluid (usually water) that will move through a medium in a unit of time under a unit hydraulic gradient through a unit area measured perpendicular to the flow.

Laminar flow in a granular rock such as a sandstone with pores and narrow fissures can be described by Darcy's Law:

$$Q = K\,i\,A$$

where Q is the discharge, K is the hydraulic conductivity, i is the hydraulic gradient, and A is the cross sectional area.

Laminar flow through fissures or small tubes is described by the Hagen-Poiseuille equation:

$$Q = \pi \rho g r^4 i / (8 \eta)$$

where ρ is the fluid density, g is the acceleration due to gravity, r is the radius, and η is the dynamic viscosity of the fluid. Flow in most carbonate aquifers is often in pipe-full conduits and is turbulent. Accordingly, it can be described by the Darcy-Weisbach equation:

$$Q = (8\,g\,R\,i\,A^2 / f)^{0.5}$$

where R is the hydraulic radius of the conduit (area ÷ wetted perimeter), A is the passage cross-sectional area, and f is the friction factor. Fissure or conduit width has the greatest influence on discharge in both the Hagen-Poiseuille and the Darcy-Weisbach equations. Note that K is not relevant to flow described by either of these equations.

Older carbonate rocks (pre-Cenozoic) have been subjected to long periods of diagenesis which has generally reduced their porosity to a few percent at most. In these rocks, flow is most likely to be concentrated along joints, faults, and bedding planes. Solutional enlargement produces conduits which may have cross sectional areas large enough to permit turbulent flow.

Conversely, karstification is less likely in younger carbonates where lack of burial has allowed high porosities (10%+) to be maintained. For instance, the limestones of Florida and Puerto Rico are Cenozoic, have high porosities, and have considerable flow through their pores. Nevertheless, aquifer characterization, using Darcy's Law, has only been successfully accomplished in the unconfined parts of the Floridan aquifer by using "coarse-mesh" digital models on a regional scale (Johnston and Bush, 1988). In those areas in central and northern Florida, flow is to a series of major springs. Scuba divers have penetrated some of these springs, following water-filled conduits for distances of up to 3 km, sometimes at depths in excess of 100 m below the water table (Farr, 1991). One system has 16 km of mapped underwater passage accessible from a total of 19 entrances and to a depth of 75 m (Irving *et al.*, 1992). Other mapped systems are equally impressive (Wilson and Skiles, 1988). Such daring exploits are compelling evidence that conduit flow is widespread in the unconfined parts of the Floridan aquifer.

The successful application of Darcy's Law to well-based groundwater monitoring in sand and gravel aquifers, and application of it to computer modelling of flow, does not mean that the same techniques can be applied to fractured-rock and karst aquifers. Most certainly, there is overwhelming evidence that computer models cannot be applied successfully to most karst aquifers (Palmer, 1992; Teutsch and Sauter, 1992; Sauter, 1992). By the time one has enough data to meaningfully model a karst aquifer, one no longer needs the model. For example, the work by Teutsch and Sauter (cited above) is based, in part, on 12,000 data values acquired during 10 years of geologic, hydrologic, and tracing studies.

SCALE EFFECTS OF HYDRAULIC CONDUCTIVITY

An aquifer in sand or gravel can be reasonably assumed to have hydrologic characteristics that can be described using Darcy's Law. Although nature never produces laboratory-like conditions similar to the sand-filled vessels used by Darcy, an assumption can usually be made with some confidence that flow is laminar and that conditions throughout the aquifer are approximately isotropic and homogeneous. A representative elementary volume (REV) of aquifer material would be relatively small because it could be reasonably assumed that, at the small scale of a 6-inch diameter monitoring well, hydrologic conditions in the aquifer would be adequately described, or the continuum approach would work (Domenico and Schwartz, 1990, p. 84). Therefore, in most sand and gravel aquifers, monitoring wells are generally reliable — if they intercept the plume and if they are screened in the proper interval.

The only void spaces in most fractured-rock aquifers which are significant for flow are the fractures. [For simplicity we deliberately ignore here the important concept of dual porosity (Maloszewski and Zuber, 1990; Wang, 1991; Wheatcraft and Cushman, 1991).] The density of these fractures would dictate whether a 6-inch monitoring well would adequately describe hydrologic conditions assuming, for instance, that the well had a 5-ft screened interval. The problem would be how many fractures (in three dimensions) would the screened interval in the well intersect? Also, would all of these fractures produce water? To have confidence in the efficiency of the well, the REV would obviously have to be much larger than in a sand and gravel aquifer because, at the same scale of a 6-inch monitoring well, it is very likely that far fewer fractures than equivalent pore spaces in a sand and gravel aquifer would be intersected.

It should be stressed that the hydraulic conductivity of the rock matrix of most fractured-rock aquifers is essentially trivial when compared to flow in a single fracture. Both Darcy flow conditions and Hagen-Poiseuille conditions would exist. In certain situations, flow could also be

turbulent. Wells are often less reliable for groundwater monitoring in fractured-rock aquifers than in granular aquifers because their distribution (their density or number per unit area) is sometimes insufficient and because their screened intervals are long relative to the total width of fractures they intersect. However, if a sufficiently large-scale approach is adopted, it can be reasonably assumed that the aquifer approximates a porous medium, and hydrologic parameters can be determined as for a granular aquifer.

A significant difference between fractured-rock and karst aquifers is the development of tertiary porosity in the latter, as already described. Not only are fractures utilized by groundwater flow, but specific sets of them are dissolutionally enlarged by it. In fact, there is constant dissolutional modification happening in a flow-field. Thus, over time, any one part of the aquifer may evolve from flow through pores (Darcy's Law) to laminar flow through fissures (Hagen-Poiseuille equation) to turbulent flow through conduits (Darcy-Weisbach equation) (Worthington, 1991).

In these circumstances, the REV is not on the macroscopic scales (centimeters to meters) which are valid in granular aquifers where computer modeling, using Darcy's Law, is reliable. Indeed, the REV of karst aquifers is equivalent to the entire groundwater basin (Ford and Williams, 1989, p. 211). This can be demonstrated by testing hydraulic conductivity at different scales.

In a granular aquifer, hydraulic conductivity [K] is independent of the scale of measurement. Thus data from rock cores taken from wells and from *in situ* slug or pumping tests will all yield approximately the same value of K, even though K may range over several orders of magnitude within the same aquifer (Dykaar and Kitanidis, 1992). However, variations in K with scale of investigation do occur in fractured rocks (Domenico and Schwartz, 1990, p. 84-87; Clauser, 1992). Such variation is even more pronounced in karst aquifers, as has been convincingly demonstrated by studies in Switzerland (Kiraly, 1975), Germany (Sauter, 1992; Teutsch and Sauter, 1992), and in Great Britain (Smart *et al.*, 1992; Edwards *et al.*, 1992). Averages from these and other data are shown in Figure 1. The hydraulic conductivity as measured by pumping tests is also dependent upon their duration (Streltsova, 1988, p. 366; Sauter, 1992).

The smallest scale shown in Figure 1 is that of a rock core taken from water wells (Kiraly, 1975; Sauter, 1992) or from petroleum wells (Archie, 1952; Murray, 1960). Mean K values of about 10^{-7} to 10^{-8} m/s in carbonates are similar to those for sandstone aquifers and reflect flow through pores.

Double packer tests measure the flow and pressure in a small interval of a well isolated by means of seals (packers). Slug tests involve the recovery of a well from an induced sudden change in its water level. Both of these methods yield K values which represent flow over a distance of some meters and in karst yield values that are routinely 100 to 1000 times greater than K values from cores in the same aquifers (Sauter, 1992; and Figure 1). These higher values reflect flow in small fissures.

Pumping tests involve removal of water from a well and produce K values which represent flow over tens to hundreds of meters. At this larger scale, larger fissures and small conduits are often encountered, so K is typically ten times larger than from slug tests in the same wells (Smart *et al.*, 1992; and Figure 1).

The largest scale of investigation is that of a complete catchment (typically 1 to 100 km in length). Water movement at this scale in karst aquifers is measured by tracer tests. Such tests yield velocities rather than hydraulic conductivities. From the Darcy equation it can be shown that these two parameters are related by:

$$v = K\,i / S_y$$

where v is water velocity, i is the hydraulic gradient, and S_y is specific yield, the proportional volume of the rock from which water will drain freely in an unconfined aquifer (Worthington,

1992). Typical values in karst aquifers are i = 0.001 to 0.02 and S_y = 0.005 to 0.02, so v and K are approximately equivalent (Worthington, 1991; Quinlan and Ray, 1989; Smart *et al.*, 1992). Nevertheless, derivation of K-values from tracer-test velocities is not valid because conduit velocities are almost always beyond the range of validity of Darcy's Law (Ford and Williams, 1989, p. 144; Worthington, 1992). Hundreds of tracer tests in karst have been conducted over distances >10 km, with dye injection into sinking streams and dye recovery at springs. The majority of these tests have yielded velocities in the range 0.001to 0.1 m/s (Ford and Williams, 1989; Worthington, 1991; Quinlan and Ewers, 1989). These tracer velocities are, on average, some 10 to 1000 times faster than pumping tests in these aquifers would indicate (Figure 1).

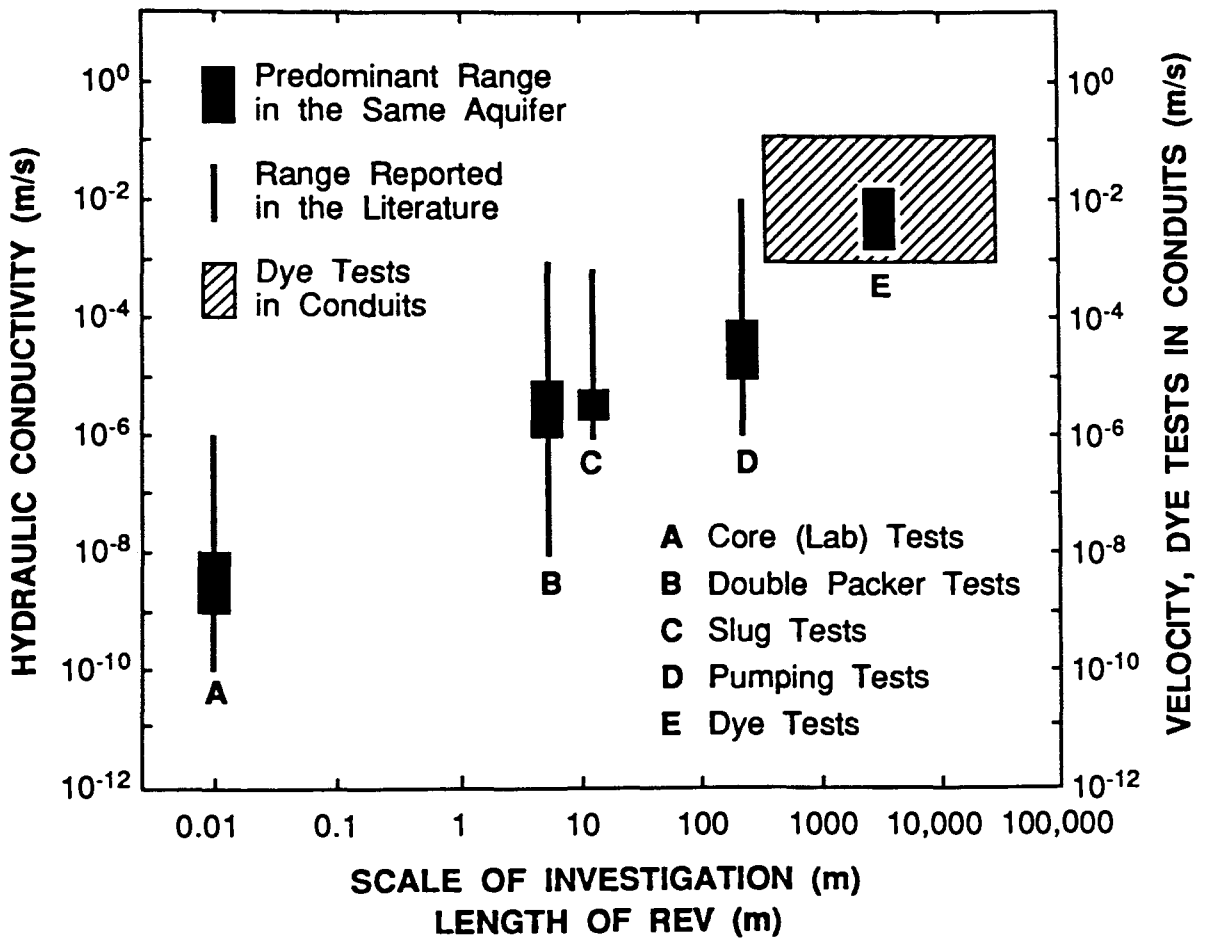


Figure 1. Range in hydraulic conductivities of carbonate aquifers as a function of scale of investigation. REV = representative elementary volume. The data shown by the heavy bars are from a Jurassic karst aquifer in the Swabian Alb of Germany, as described by Sauter (1992) and Teutsch and Sauter (1992). Other data are from references cited within text. The ruled rectangle shows the range of velocities occurring in dye tests from sinking streams to springs and is based on 1405 values from 25 countries (Worthington, 1992). This figure shows that the hydraulic conductivity of an unconfined karst aquifer is extremely dependent upon the scale of measurement. Also, tracer-test velocities, other than those which are from well-to-well, can be used as an estimator for worst-case aquifer-scale contaminant velocities. [Modified after Kiraly (1975) and Sauter (1992)]

The conclusion to be drawn from these results is that a hydraulic conductivity or velocity test in karst yields values that are only valid for the scale of the test, and that extrapolation to a larger scale will underestimate the true values by several orders of magnitude. These results are semi-consistent with those of Clauser (1992) for crystalline rocks, but whereas our Figure 1 shows the regional data on a continuation of the same trend, his Figure 1 shows the regional data on a plateau that is not a continuation of the initial trend. We interpret this plateau to be an artifact of the data and where they are subjectively plotted. There is no proof that any of his values are truly regional in scale.

To the best of our knowledge, no unconfined carbonate aquifer has ever been demonstrated to have similar range in K values at the core, packer test, slug test, pumping test, and tracer test scales.

The conceptual model that can be built up from the above tests and from the thousands of tracer tests that have been performed is that flow in carbonate rocks forms a tributary system. Percolation into the soil and down through the pores and narrow fissures in the uppermost bedrock proceeds at low velocities (10^{-8} to 10^{-2} m/s). Once the flow reaches a conduit, it then proceeds rapidly (10^{-3} to 10^{-1} m/s) to one or more springs. These dual ranges in velocity describe why the residence time of some of the dye (and pollutants) within an epikarst may be 10 to 100 or more times longer than when transit through an aquifer is solely from a sinking stream to a spring (Quinlan and Ray, 1992). Many, or possibly most, karst conduits terminate in distributary systems, so that flow from one conduit may reappear at two or more springs (Quinlan and Ray, 1989; Quinlan and Ewers, 1989; Worthington, 1991).

The low-velocity component of a carbonate aquifer system is short-circuited where there are sinkholes or sinking streams. In such cases, flow (and pollutants) have direct access to the conduit system, so that a toxic spill into a sinkhole may penetrate several miles into an aquifer within a period of hours. A graphic and serious example of high-velocity flow occurred at West Plains, Missouri, in 1978. The collapse of sewage lagoons there on May 28 released 94,000 m^3 of raw and partially treated sewage into the groundwater system. Some of the dye injected into the disappearing effluent reappeared twelve days later at Mammoth Spring, Arkansas, which is 23 miles away from the spill site. At least 700 illnesses were reported by residents drinking groundwater contaminated by this spill (Vineyard, 1981).

Wells are typically very unreliable monitoring devices in karst aquifers (Quinlan and Ewers, 1985; Quinlan, 1989, 1990; Ewers, 1992). At the scale of wells, features such as conduits are very difficult to find, even if they are quite large; Benson and La Fountain (1984) state that statistically it takes 1000 3-cm drill holes per acre to intercept a 2.5-m diameter cavity with 95% probability. The number of randomly or grid-fixed drill holes necessary to intercept a conduit with the same diameter would be smaller but would still be prohibitively expensive.

The only realistic axiom regarding conceptualization of a karst aquifer should be: Few, if any, assumptions about aquifer mechanics will be valid prior to measurement and tracing. It therefore is equally realistic to assume that conceptualization will be an evolutionary process and that many parameters have to be measured and field observations made before an accurate conceptualization is achieved. Indeed, many years of karst research have revealed that collection of data unfettered by assumptions about specific hypotheses is one of the more dependable tools in karst aquifer studies. If karst groundwater is to be understood, tracer tests are — without exception — necessary. Their use requires no assumptions about the aquifer to be valid; the tracer goes where it will. The only assumptions that have to be made relate to the tracing technique, test design, test execution, and test interpretation.

KARST AQUIFER HYDROGEOLOGY

It is not appropriate to assume that a karst aquifer does not exist in a carbonate rock because wells or cores do not indicate dissolution, or because Darcy conditions seem to be indicated, or because karst landforms are seemingly not present or not significant. Data from many countries of the world supply overwhelming evidence that where there is karst, there is also a karst aquifer (Quinlan *et al.*, 1992).

Recharge in karst is either directly onto a carbonate rock terrane (autogenic recharge) or from nearby non-carbonate rock terrane (allogenic recharge). Most allogenic recharge also eventually becomes concentrated at joint intersections where swallets (the sinking points of sinking streams) form; alternatively, autogenic recharge is distributed through many joints (Ford and Williams, 1989). A highly corroded zone of the upper bedrock (usually below residual soil), known as the epikarst, is also very important. Maximum fracture utilization is achieved to a depth of about 10 m, but the most efficient vertical drains below are formed only at intersections of master joints (Williams, 1983). Recharge effects are very important because they are a major cause of water-quality variation at springs (Newson, 1971).

Storage occurs in soil, seasonally flooded conduits and fractures, and in perennially saturated fractures, and is especially important in the epikarst. Storage effects in karst aquifers are difficult to quantify, although attempts have been made using spring recession and aquifer water-level analysis (Atkinson, 1977), and time-series (spectral) analysis (Mangin, 1984). Storage can very severely affect water quality for an entire groundwater basin because contaminants can be temporarily trapped in many fractures, cavities, and overflow conduits which, when they flood, reintroduce fresh pulses of contaminants to the springs or wells. In any karst aquifer, storage can prevent remediation because near-total removal of contaminants by pumped-wells is rarely, if ever, achievable (Quinlan and Ray, 1992; Travis and Doty, 1990; Freeze and Cherry, 1989).

The hydraulic gradients within karst aquifers commonly change one to two orders of magnitude with changes in flow. They decrease exponentially in a downstream direction (Worthington, 1991). Initial flow along bedding planes is down the hydraulic gradient but might not necessarily be down the stratal dip. Hydraulic gradients ensure that some flow must reach the lowest outcrop point of an aquifer and therefore could under-flow several springs or river valleys for considerable distances (Worthington, 1991).

Springs are typically parts of an underground distributary formed by falling external base level and yielding a vertical hierarchy (Ewers *et al.*, 1978; Quinlan *et al.*, 1978; Smart, 1983). This includes overflow springs that flow only during flood conditions and underflow springs that drain perennially. Full-flow springs that are the sole drain of an aquifer are quite rare. Underflow springs are difficult to find because they are commonly aggraded but, because they drain preferentially and perennially, they are very important for monitoring for pollutants. It is suggested by Worthington (1991) that all overflow springs have complementary underflow springs and that all streams in karst terranes gain or lose water from and to the subsurface.

Many karst springs have extremely large catchments. An example is Big Spring, Missouri, where the groundwater basin extends at least 43 miles, but travel time for dye, along the regional strike of the strata, takes only about two weeks (Aley, 1975).

Groundwater velocities in karst conduits are both substantial and highly variable. Low-flow velocities are typically 0.001-0.003 m/s and high-flow velocities usually reach about 0.1 m/s (Worthington, 1991; Quinlan, 1989). Repeated tracings between the same sinking stream and spring have shown that flow velocity in conduits is directly proportional to discharge (Stanton and Smart, 1981; Worthington, 1991, p. 34-35). These numbers emphasize, however, the unique nature of karst hydrogeology. The significance of a contaminant spill affecting a major spring and possibly drinking water supplies 40 miles away in two weeks, as described above, is the kind of

fact often ignored or unrecognized by consultants, regulators, and administrators unfamiliar with karst terranes.

FATE AND TRANSPORT OF CONTAMINANTS

Many contaminants that are spilled in karst terranes infiltrate rapidly through thin residual soils (Quinlan and Aley, 1987) and enter the groundwater system. The epikarst has only inefficient vertical connection with the conduit system below (Williams, 1983). If contaminants enter the epikarst, it is likely that they will be adsorbed onto soil particles and that they will also smear over rock surfaces. Even if the majority of contaminants travel in a dissolved phase through the groundwater system, a constant source of them tends to remain in the epikarst zone. Quinlan and Ray (1992) show that the concentrations of tracer dyes used as surrogates for pollutants in groundwater do not decline rapidly in springs draining the epikarst or in pumped wells that penetrate it, even after many years.

Ewers *et al.* (1992) show that if light non-aqueous phase liquids (LNAPL's) such as gasoline are involved, free-phase product can be carried to the water table, where it could float almost indefinitely. Water flowing through the floating product will produce a dissolved plume for as long as the floating product exists, but it might be sufficiently diluted so as to be undetectable at a nearby spring to which flow occurs. Alternatively, if the contaminant is a dense non-aqueous phase liquid (DNAPL), it will descend to the base of any fracture or conduit it enters. Any pathway that is made available, such as a newly drilled well, will typically allow the DNAPL to migrate deeper. It can be difficult and expensive to monitor for pesticides and herbicides, but Sabatini and Austin (1991) have shown that careful choice of two fluorescent dyes can effectively bracket the sorption and retardation properties of two of the more mobile herbicides. Various contaminants, including metals, are commonly sorbed onto clays and are typically transported with the suspended sediment load, which varies directly with discharge velocity. Sediments can be deposited on conduit floors and walls and can, therefore, produce long-term problems when they are periodically and repeatedly eroded and redeposited.

Measurement of variation of specific conductance, as a possible surrogate contaminant, can be extremely useful as an indicator in many karst aquifers of their transport characteristics in relation to aquifer mechanics (Quinlan *et al.*, 1992).

SPRING HYDROGRAPHS AND CHEMOGRAPHS

Traditional studies of karst springs have usually included plots of variation of discharge against time (hydrographs) and plots of variation of a chemical or physical parameter versus time (chemographs). The parameters have commonly included: hardness, stable isotopes, specific conductance, temperature, turbidity, and dissolved oxygen (Ford and Williams, 1989). Worthington (1991) showed that anions such as HCO_3^- and SO_4^{--}, as well as the traditional cations such as Ca^{++} and Mg^{++}, should also be measured routinely because they are useful indicators of aquifer mechanics.

Variation in the form of spring hydrographs in karst aquifers reflects not only variations in storm impulses but also differences in aquifers having predominantly vadose or phreatic flow, and autogenic or allogenic recharge. The shapes of spring hydrographs are numerous, with some being markedly oscillatory, peaked, or relatively flat and broad (Ford and Williams, 1989). Smart (1983) showed that, in the Canadian Rockies, different forms of hydrographs would occur for full-flow, overflow, and underflow regimes, and that the truncated segments of the hydrograph, when combined, could produce the complete hydrograph because there was a hierarchy of springs at different elevations, with many overflow springs and underflow springs. Worthington (1991) used the hydrograph recession exponent to estimate different aquifer boundary conditions between full-

flow, overflow, and underflow springs.

A frequency distribution for specific conductance of waters from different springs in France has shown that for porous aquifers, the distribution is unimodal with a relatively high specific conductance; for fissured aquifers, distribution is again unimodal but with relatively low conductance; and for karst aquifers, conductance is polymodal, with a wide range of values (Bakalowicz and Mangin, 1980). This is further proof that many different processes are operative in karst aquifers.

WHY MONITORING WELLS DO NOT WORK IN KARST TERRANES

Monitoring wells in karst terranes generally do not work as such for the same reason one does not win a state lottery with every ticket: The odds do not favor success. The odds for a monitoring well being successful are explained in terms of scale, however, not economics — although in both situations, one cannot afford to continue drilling (or playing) until success is attained. The extremely heterogeneous organization of groundwater flow in caves and dissolutionally enlarged fractures of a karst aquifer, an organization that is commonly dendritic or trellised and similar to that of tributaries of a surface river (Quinlan and Ray, 1989), is not adequately sensed by the number and size of wells drilled — except by improbably good luck. These facts compromise the presumed relevance and effectiveness of a conventional monitoring system based solely on wells. The wells yield water and data, but the samples are unlikely to sense drainage from the facility in question. Accordingly, the samples from such wells are most probably irrelevant. Certainly the cost of their analysis does not justify the gamble on their relevance.

The probability of a randomly located well intercepting a conduit draining from a site is similar to that of a dart thrown at a 30-foot wide wall map of the U.S. hitting the Mississippi River or one of its major tributaries. It could happen — and sometimes does — but don't bet on success. Neither you nor your employer can afford to do so.

The consequences of installing an ineffective monitoring well, missing pollutants that are going off-site, and missing the fact that a drinking water supply is adversely affected are serious. However, it is typically argued that such monitoring results indicate a "clean well" (*i.e.*, no contamination) or, if no cavities were intercepted or there was no loss of drilling fluid, non-existence of karst! Randomly located wells in karst terranes are known to be unreliable for monitoring, as explained above. In contrast, springs, wells, and cave streams, all of which have been confirmed by properly conducted tracing to drain from a facility, are known to be reliable (Quinlan and Ewers, 1985; Quinlan, 1989, 1990; Ewers, 1992). Accordingly, the motive for monitoring only via wells, and *not* on the basis of tracing to them or to springs, is commonly based on the fact that tracing raises issues beyond the interest and property boundaries of some of the parties involved.

RATIONALE FOR USE OF TRACER TESTS IN THE DESIGN OF MONITORING SYSTEMS IN KARST TERRANES

We make the assumption that the person or agency requiring a reliable system for monitoring groundwater in a karst terrane really wants to know what is happening. If this goal is sought, a series of well-designed, properly executed, and correctly interpreted tracer tests offers the best means of attaining it. This is true because their effectiveness is unconstrained by the numerous, often ill-founded assumptions made when using a well for monitoring (that the plume is intercepted by the well and at the correct depth, that the flow is unidirectional, etc.). The beauty of a tracer test lies in the minimal number of assumptions that must be made. The dye travels with the water and goes where it goes. [Yes, there are complications when one is trying to make predictions about DNAPL's and LNAPL's, and there are different retardation factors for different dyes, but these

factors, even if inaccurately represented, do not compromise the results of a tracer test. No other flow-prediction method is as reliable and as readily subject to empirical verification as is tracing.] The major assumptions made are that the tracer recovered is that of the test executor, that the field work and test design have been thorough, and that test execution has been done by reliable personnel. Other important assumptions are discussed by Quinlan (1989, p. 40-58; 1990).

The field and laboratory procedures for execution of a tracer test are relatively simple and straightforward (Aley *et al.*, 1993; Quinlan and Alexander, 1992). Nevertheless, as with most techniques, there are major elements of skill and experience that enhance the probability of success. Dye-tracing, like neurosurgery, can be done by anyone. But when either is needed, it is judicious and most cost-efficient to have it done by experienced professionals, those who have trained under the tutelage of an expert or those who have already made the numerous mistakes associated with learning and who have learned to avoid the procedural errors that could have economically and physically adverse consequences.

There are three types of tracer tests with dyes: qualitative (using either visual observation of the dye-plume or visual observation of dye eluted from passive detectors consisting of activated charcoal, semi-quantitative (using elutant from passive detectors and instrumental analysis with either a filter fluorometer or a scanning spectrofluorophotometer), and quantitative (using instrumental analysis of water samples, as discussed by Quinlan (1989, p. 32-34), Quinlan and Alexander (1992), Aley *et al.* (1993), Duley (1986), and Behrens (1988). Each type of tracer test can be best under different conditions.

No matter how superbly and efficiently conventionally located wells may be able to detect the migration of pollutants from a facility — if, by mere chance, they succeed in doing so, and assuming they would function so reliably — there is no way, other than by tracing, to identify correctly and conclusively on-site and off-site the places to which pollutants would flow. Stated another way, there is no way, other than by tracing or by regular frequent monitoring of numerous wells and springs both on-site and off-site, to discover the numerous consequences of leakage from a facility. This point is convincingly illustrated by the work of Aley (1986).

The uniqueness and relevance of tracer data for prediction of flow velocities is illustrated by the following case study. A detailed investigation, using geophysical logs, borehole video logs, lithologic core analysis, and unspecified aquifer tests was made of the dissolution porosity and permeability at a Florida site (Robinson and Hutchinson, 1991). Tracer tests were performed by injecting a fluorescent dye into the open-hole interval of a well and by measuring the movement induced by pumping 1000 gallons per minute at a well 200 feet away. Dye concentration at the pumped well was measured continuously with a filter fluorometer. Based on standard assumptions about flow in porous media and a porosity of 20%, the predicted arrival time for the dye should have been approximately 40 days, with a 4-day persistence time. Actual breakthrough time was 5 hours. The peak was at 22 hours, and the persistence time was 28 days. A second breakthrough of dye occurred at 36 days after injection and its persistence time was 8 days. This second breakthrough is not attributable to response to a storm (James Robinson, U.S.Geological Survey, Tampa, Fla., oral communication, December 1991). The bimodal distribution of tracer arrival time was interpreted to indicate dual porosity in the aquifer, but we suggest that bifurcation of a flow route, followed by rejoining of the trunk route, is a more plausible explanation (Tsang *et al.*, 1991; Ford and Williams, 1989, p. 226-228).

This case study illustrates the heterogeneity of the Floridan aquifer and the impossibility of using carefully (and expensively) acquired parameters to make correct predictions about travel times in karst aquifers. Most importantly, it shows that the assumption of uniform distribution of porosity and attendant Darcian flow, as has been proposed in current strategies of wellhead protection for the Floridan aquifer (DeHan, 1992), are probably not valid. Again, a conceptual model based on Darcian flow inadequately corresponds to reality. There is no substitute for a tracer test.

A tracer investigation should be designed to test all possible flow destinations from an input point — those which are logical, illogical, and semi-inconceivable — rather than to test just a hypothesis of flow from "A" to "B". Indeed, one of the measures of a person's tracing experience is the ability to differentiate between the impossible and the semi-inconceivable, and knowing when and how to do more than the obvious. Knowing where the tracer does *not* go can be as important as knowing where it does go.

WHERE TO MONITOR FOR POLLUTANTS

The American Society for Testing and Materials (ASTM) has a task group that is currently writing a standard guide for the design of groundwater monitoring systems in karst and fractured rock terranes (McCann and Quinlan, 1992).

The easiest reliable points at which to monitor groundwater quality in a karst terrane are springs and cave streams shown by dye-tracing to drain from the facility to be evaluated (Quinlan and Ewers, 1985; Quinlan, 1989, 1990; Ewers, 1992). [Non-toxic fluorescent dyes are used as tracers because they combine maximum detectability (some as low as 0.1 part per trillion) with minimum analytical cost.] A preferable alternative for monitoring points is a suite of wells that intercept cave streams known (by tracing) to flow from the facility to the spring (or springs) that drain the groundwater basin in which it lies. Such cave streams may be difficult or impossible to find with traditional geophysical techniques, but streaming potential has great promise (Kilty and Lange, 1992; Lange and Kilty, 1992).

A second alternative for monitoring is an intermittent (overflow) spring that can be pumped — but again, only if tracing has demonstrated its hydrologic connection to the facility in question.

A third alternative for monitoring points is a set of wells located in fractured rocks, preferably along fracture traces or at fracture-trace intersections. These wells are usable *only* if — like any well or spring to be used for monitoring in a karst — tracer tests show a connection with the facility under base-flow as well as flood-flow conditions. Randomly-located wells could also be used if, again, tracing has first proven a connection from the facility to each of them to be used and done so under various flow conditions.

Success in tracing to randomly located wells can be maximized if they are pumped continually to discharge at a low rate, say 1 gpm, through a passive detector for dye for weeks or months. In most settings this small amount of water can be wasted onto the ground at a reasonable distance, say 50 ft, from any building or structure, with no adverse effect. Dye detectors are changed weekly.

At most locations in karst terranes, proper and reliable monitoring (using springs, cave streams, and wells traced positively) can only be done several miles away from the facility. Monitoring sites (points) closer to a facility are more desirable because dilution of pollutants is less, but they are more difficult and more expensive to find and to evaluate.

WHERE TO MONITOR FOR BACKGROUND

Springs, cave streams, and wells in settings also geochemically similar to the traced monitoring sites are the only suitable places to meaningfully monitor background. This is true, however, only when these places have been shown by carefully designed, repeated dye-traces, done under conditions ranging from base flow and flood flow, *not* to drain from the facility to be monitored.

Background data at a new facility can also be obtained from wells that are monitored before, during, and after storms for an adequate period (often at least a year) prior to commencement of its

operation. Analysis of continuous records of stage and perhaps specific coonductance in these wells can be used to select storm-related sampling frequencies and for possible differentiation of wells into several categories. Traces should be run during that year-long period, using dyes as a "surrogate pollutant" to test the ability of the various wells to adequately monitor for pollutants. If a well does not show a positive dye-detection after allowance is made for flow velocity, the well does not comprise an effective monitoring system. If none of the wells or an insufficient number of wells to which dye-traces are attempted test positive, an *effective* monitoring system does not exist; one probably does not adequately understand the hydrogeology of the facility.

WHEN TO MONITOR FOR POLLUTANTS AND BACKGROUND

In order to reliably characterize the natural, storm-related water-quality variability of a spring in a conduit-flow system, sampling may have to be done much more frequently than was customary in the past. There are two reasons why this is so.

1. Velocities in karst conduits and the discharge of karst springs commonly vary in response to storms by a factor of 10 to 100, with a response time similar to surface rivers. Water quality is primarily a function of discharge (as in surface rivers), so a sampling program that ignores these discharge variations is of limited use (Quinlan *et al.* 1992; Worthington, 1991).
2. The correct interpretation of data from springs and wells, for determination of proper sampling frequency, cannot be done with justifiable confidence unless it is known that the results were not subject to *aliasing*, a phenomenon whereby a high-frequency signal can be wrongly interpreted as a low-frequency signal or trend because the sampling frequency was less often than it should have been (Gottman, 1981, p. 16). A method proposed for determination of proper sampling frequency and prevention of aliasing is given by Quinlan *et al.* (1992). In karst aquifers, at springs and wells that have a significant response to storm and melt-water events, it is essential to use this method or a similar one in order to determine the appropriate sampling frequency.

ECONOMIC FACTORS

A well-designed monitoring system, properly installed, diligently operated, and correctly interpreted, is far less expensive than litigation and assumption of liability if the monitoring system is inadequate. A tracer test is often cheaper than installing one monitoring well in bedrock, a well which is not likely to be relevant to the problem of monitoring. One cannot afford *not* to do things properly. Accordingly, tracing as part of the design of a monitoring system for a karst aquifer is likely to be more cost-effective than any other approach.

ETHICAL FACTORS

The professional hydrogeologist or engineer working for a client should be doing so as a diagnostician, not as an advocate. [This does not preclude vigorous defense of conclusions reached objectively.] Carefully designed, properly executed, and correctly interpreted tracer tests are unambiguous and can withstand the scrutiny of all. They can be challenged, but their logic is irrefutable and unassailable. When they are inadequately designed, executed, and interpreted, all parties are either compromised or victimized. Other aspects of ethics in groundwater tracing are discussed by Quinlan and Davies (1992).

SUMMARY

This paper shows that groundwater monitoring in karst terranes is highly dependent upon a

thorough understanding of the geology and hydrology around and beneath the facility being monitored. Karst hydrogeology is complex and requires measurement of hydrologic parameters at the correct scale, which is essentially, at minimum, the size of the drainage basin being investigated.

There can be many reasons why groundwater monitoring in karst terranes has in the past been poorly designed and performed. One of them is the suggestion that karst is rare. For whatever reason, a totally inappropriate approach was adopted. Notwithstanding, there is evidence that anywhere in the world where carbonate or other soluble rocks are found, there is not only karst but a karst aquifer. It cannot be emphasized too strongly or too often that investigation at a small scale in a karst terrane will underestimate not only hydraulic conductivity but probably much else. Karst aquifers and the springs that discharge groundwater from them are moderately sensitive or are often hypersensitive to long-term, if not semi-permanent contamination (Quinlan *et al.* 1992).

Groundwater monitoring in karst terranes should be based on the results of well-designed, properly conducted, and correctly interpreted tracer tests to identify springs, cave streams, and wells that drain from a site. Such places of discharge are potential monitoring points that are unfettered by the implicit assumptions made for an isotropic and/or homogeneous aquifer. Springs, cave streams, and traced wells that intercept them are more reliable and cost-effective at answering the most important question that has to be answered, *"Where* should one monitor for pollutants and background?" The tracing-guided monitoring strategy we recommend is soundly based on theoretical considerations, the results of hundreds of tracer tests, hundreds of miles of cave mapping, drilling many wells to intercept cave streams, and interpretation of water-quality data.

The next major question to be answered is *"When* should one monitor for pollutants and background?" Depending on what the hydrologic response is at a spring, as observed through several storm-events and determined from observation of discharge and preferably continuous monitoring of its specific conductance, the *when* to monitor for pollutants can be answered. The optimal sampling frequency must be storm-related but can only be determined after this initial study of spring response is made. If the proper determination of sampling frequency is not made, the sampling-consequent phenomenon of *aliasing* is likely to occur. It can be an effect that no amount of resampling at an insufficient frequency can rectify. At a minimum, expensive analytical and other monitoring costs are for naught.

The authors cannot think of any reason that the peculiaraties of karst cannot be addressed effectively. We know they can be. But it requires more than one site visit and more than four monitoring wells (one upgradient, three downgradient). However complex the task may seem (and which it actually is), it is not likely that it can be simplified — which is exactly what is done by a monitoring approach based upon wells. Such an approach is often less effective (including less cost-effective) than the tracer-guided approach which we know is the only reliable way to answer the important *where* and *when* questions.

ACKNOWLEDGEMENTS

The assistance of Marcia Williams in producing this manuscript is greatly appreciated. So also are the technical reviews by Tom Aley and the masterful editorial talents of A. Richard Smith.

REFERENCES CITED

Alexander, E.C., Jr., Alexander, S.C., Huberty, B.J., and Quinlan, J.F. 1992. The Oronoco Landfill Dye Trace III: Results from a Superfund remedial investigation in a glaciated diffuse-flow karst, *in* Quinlan and Stanley (1992). p. 417-429.

Aley, T. 1975. A predictive hydrologic model for evaluating the effects of land use and management on the quantity and quality of water from Ozark springs. Ozark Underground

Laboratory, Protem, Mo. [Republished in Missouri Speleology, 1978. 18:1-185.]
Aley, T. 1986. Complex radial flow of ground water in flat-lying, residuum-mantled limestone in the Arkansas Ozarks. Environmental Problems in Karst Terranes and Their Solutions Conference (1st, Bowling Green, Ky.), Proceedings. National Water Well Association, Dublin, Ohio. p. 159-170.
Aley, T., Quinlan, J.F., Alexander, E.C., Jr., and Behrens, H. 1993. The Joy of Dyeing: A Compendium of Practical Techniques for Tracing Groundwater, Especially in Karst Terranes. National Ground Waters Association, Dublin, Ohio. [in prep.]
Archie, G.E. 1952. Classification of carbonate rocks and petrological considerations. American Association of Petroleum Geologists, Bulletin. 36:278-298.
Atkinson, T.C. 1977. Diffuse flow and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain). Journal of Hydrology. 35:93-110.
Bakalowicz, M., and Mangin, A. 1980. L'aquifère karstique. Sa definition, ses characteristiques et son identification, *in* Hydrogéologie: Interactions entre l'eau souterrain et son milieu. Société Géologique de France, Mémoire hors-série no. 11. p. 71-79.
Behrens, H. 1988. Water tracer chemistry — a factor determining performance and analytics of tracers, *in* Symposium on Underground Water Tracing (5th, Athens, Greece, 1986), Proceedings. p. 121-133.
Benson, R.C., and La Fountain, L.J. 1984. Evaluation of subsidence or collapse potential due to subsurface cavities. Multidisciplinary Conference on Sinkholes Conference (1st, Orlando, Fla.), Proceedings. Balkema, Rotterdam, The Netherlands. p. 201-215.
Clauser, C. 1992. Permeability of crystalline rocks. Eos, May 26, 1992. 73(21):233, 237-238.
DeHan, R.S. 1992. Lessons from the Florida wellhead protection story. Annual Underground Injections Practices Council Meeting (Corpus Christi, Texas), Proceedings. 15 p. [in press]
Domenico, P.A., and Schwartz, F. 1990. Physical and Chemical Hydrogeology. Wiley, New York. 824 p.
Duley, J. W. 1986. Water tracing using a scanning spectrofluorometer for detection of fluorescent dyes, *in* Environmental Problems in Karst Terranes and Their Solutions Conference (1st, Bowling Green, Ky.), Proceedings. National Water Well Association, Dublin, Ohio. p. 389-406.
Dykaar, B.B. and Kitanidis, P.K. 1992. Determination of the effective hydraulic conductivity for heterogeneous porous media using a numerical spectral approach. 1. Method, and 2. Results. Water Resources Research. 28(4):1155-1178.
Edwards, A.J., Hobbs, S.L., and Smart, P.L. 1992. Effects of quarry dewatering on a karstified limestone aquifer: A case study from the Mendip Hills, England, *in* Quinlan and Stanley (1992). p. 77-92.
Edwards, A.J., and Smart, P.L. 1989. Waste disposal on karstified Carboniferous Limestone aquifers of England and Wales. Engineering and Environmental Aspects of Sinkholes and Karst Conference (3rd, St. Petersburg, Fla.), Proceedings. Balkema, Rotterdam, The Netherlands. p. 165-182.
Ewers, R.O., Quinlan, J.F., and Ford, D.C. 1978. The origin of distributary and tributary flow within karst aquifers [abs.]. Geological Society of America, Abstracts with Programs. 10:398-399.
Ewers, R.O. 1992. The response of landfill monitoring wells in limestone (karst) aquifers to point sources and non-point sources of contamination, *in* Quinlan and Stanley (1992). p. 529-540.
Ewers, R.O., Duda, A.J., Estes, E.K., Idstein, P.J., and Johnson, K.M. 1992. The transmission of light hydrocarbon contaminants in limestone (karst) aquifers, *in* Quinlan and Stanley (1992). p. 287-306.
Farr, M. 1991. The Darkness Beckons. Cave Books, St. Louis. 280 p.
Field, M.S. 1988. The vulnerability of karst aquifers to chemical contamination. Hydrological Science and Technology. 4(1-4):130-142.
Ford, D.C., and Williams, P.W. 1989. Karst Geomorphology and Hydrology. Unwin Hyman, Boston. 601 p.

Freeze, R.A., and Cherry, J.A. 1989. What has gone wrong? Ground Water. 27(4):458-464.

Gottman, J.M. 1981. Time Series Analysis: A Comprehensive Introduction for Social Scientists. Cambridge University Press, Cambridge. 400 p.

Irving, S., Norkus, T., Schile, S. 1992. Current exploration of the NSS WKPT. National Association for Cave Diving, Journal. 24(2):22-23,25.

Johnston, R.H., and Bush, P.W. 1988. Summary of the hydrology of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama. U.S. Geological Survey, Professional Papers 1403-A. 24 p. [Professional Papers 1403-B through H, by various authors, discuss specific regions underlain by the aquifer; 1403-I describes and interprets the geochemistry.]

Kilty, K. T., and Lange, A.L. 1992. Electrochemistry of natural potential processes in karst, *in* Quinlan and Stanley (1992). p. 163-177.

Kiraly, L. 1975. Rapport sur l'état actuel des connaissances dans le domaine des caractères physiques des roches karstiques, *in* Burger, A., and Dubertret, L., eds. Hydrology of Karstic Terrains. International Association of Hydrogeologists, Paris. International Union of Geological Sciences, Ser. B, no. 3. p. 53-67.

Kresic, N. 1993. Quantitative Karst Hydrogeology, with Elements of Groundwater Protection [translation from Serbo-Croatian in progress] Lewis, Boca Raton, Fla. *ca.* 200 p.

Lange, A.L., and Kilty, K.T. 1992. Natural-Potential Responses of Karst Systems of the Ground Surface, *in* Quinlan and Stanley (1992). p. 179-196.

Maloszewski, P., and Zuber, A. 1985. On the theory of tracer experiments in fissured rocks with a porous matrix. Journal of Hydrology. 79:333-358.

Maloszewski, P., and Zuber, A. 1990. Mathematical modeling of tracer behavior in short term experiments in fissured rocks. Water Resources Research. 26(7):1517-1528.

Mangin, A. 1984. Écoulement en milieu karstique. Annales des Mines. 191(5-6):135-142.

McCann, M.C., and Quinlan, J.F. 1992. Development of an ASTM standard guide for the design of ground-water monitoring systems in karst and fractured rock terranes, in Quinlan and Stanley (1992). p. 542-551.

Milanovic, P.T. 1981. Karst Hydrogeology. Water Resources Publications, Littleton, Colo. 434 p.

Murray, R.C. 1960. Origin of porosity in carbonate rocks. Journal of Sedimentary Petrology. 30: 59-84.

Newson, M.D. 1971. A model of subterranean limestone erosion in the British Isles based on hydrology. Institute of British Geographers, Transactions. 54:51-70.

Palmer, A.N. 1991. Origin and morphology of limestone caves. Geological Society of America, Bulletin. 103(1):1-21.

Palmer, A.N. 1992. Opportunities and pitfalls in the computer modeling of karst aquifers (abs). Friends of the Karst (13th meeting, Cookeville, Tenn.), Abstracts, p. 20-21.

Quinlan, J.F. 1989. Ground-Water Monitoring in Karst Terranes: Recommended Protocol and Implicit Assumptions. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nev. EPA/600/X-89/050 88 p. [DRAFT; final version to be published in 1992]

Quinlan, J.F. 1990. Special problems of ground-water monitoring in karst terranes, *in* Nielsen, D.M. and Johnson, A.I., eds. Ground Water and Vadose Zone Monitoring. ASTM Special Technical Publication 1053. American Society for Testing and Materials [ASTM], Philadelphia. p. 275-304.

Quinlan, J.F., and Alexander, E.C., Jr. 1992. Practical Tracing of Groundwater, with Emphasis on Karst Terranes. 2nd ed. Geological Society of America, Short-Course Manual. [in prep.]

Quinlan, J.F., and Aley, T. 1987. Discussion of "A new approach to the disposal of solid waste on land", by R.C. Heath and J. H. Lehr. Ground Water. 25(5):615-616.

Quinlan, J.F., and Davies, G.J., 1992. Ethical aspects of tracing: A guide for consultants, regulators, and students (abs). Friends of the Karst (13th Meeting, Cookeville, Tenn.), Abstracts. p. 23-24. [Extended abstract available from the senior author]

Quinlan, J.F., and Ewers, R.O. 1985. Ground water flow in limestone terranes: Strategy rationale and procedure for reliable, efficient monitoring of ground water quality in karst areas. National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring (5th, Columbus, Ohio), Proceedings. National Water Well Association, Worthington, Ohio. p. 197-234.

Quinlan, J.F., and Ewers, R.O. 1989. Subsurface drainage in the Mammoth Cave area, *in* White, W.B., and White, E.L., eds. Karst Hydrogeology: Concepts from the Mammoth Cave Area. Van Nostrand, New York. p. 65-103.

Quinlan, J.F., Ewers, R.O., and Saunders, J.W. 1978. Distributary flow within karst aquifers: Description, occurrence, and function of groundwater dispersal conduits and later stages of their development [abs.] Geological Society of America, Abstracts with Programs. 10:475.

Quinlan, J.F., and Ray, J.A. 1989. Groundwater Basins in the Mammoth Cave Region, Kentucky. Friends of the Karst, Occasional Publication No. 2. Friends of the Karst, Mammoth Cave, Ky. [map]

Quinlan, J.F., and Ray, J.A. 1992. Groundwater remediation may be achievable in some karst aquifers that are contaminated, but it ranges from unlikely to impossible in most: I. Implications of long-term tracer tests for universal failure in goal achievement by scientists, consultants, and regulators, *in* Quinlan and Stanley (1992). p. 553-558.

Quinlan, J.F., Smart, P.L., Schindel, G.M., Alexander, E.C., Jr., Edwards, A.J., and Smith, A.R. 1992. Recommended administrative/regulatory definition of karst aquifer, principles for classification of carbonate aquifers, practical evaluation of vulnerability of karst aquifers, and determination of optimum sampling frequency at springs, *in* Quinlan and Stanley (1992). p. 573-635.

Quinlan, J.F., and Stanley, A., eds. 1992. Hydrology, Ecology, Monitoring, and Management of Ground Water in Karst Terranes Conference (3rd, Nashville, Tenn., 1991), Proceedings. National Ground Water Association, Dublin, Ohio. 793 p.

Robinson, J.L., and Hutchinson, C.B. 1991. Ground-water tracer tests in west-central Florida [abs.]. American Institute of Hydrology, Annual Meeting (Orlando, Fla.), Abstracts. p. 39.

Sabatini, D.A., and Austin, T.A. 1991. Characteristics of Rhodamine WT and fluorescein as adsorbing ground-water tracers. Ground Water. 29(3):341-349.

Sauter, M. 1992. Assessment of hydraulic conductivity in a karst aquifer at local and regional scale, *in* Quinlan and Stanley (1992). p. 39-57.

Scholle, P.A., Bebout, D.G., and Moore, C.H., eds. 1983. Carbonate Depositional Environments. American Association of Petroleum Geologists, Memoir 33. 708 p.

Smart, C.C. 1983. The hydrology of the Castleguard karst, Columbia icefields, Alberta, Canada. Arctic and Alpine Research. 15: 471-486.

Smart, P.L. 1985. Applications of fluorescent dye tracers in the planning and hydrological appraisal of sanitary landfills. Geological Society of London, Quarterly Journal of Engineering Geology. 18:275-286.

Smart, P.L., Edwards, A.J., and Hobbs, S.L. 1992. Heterogeneity in carbonate aquifers: Effect of scale, fissuration, lithology, and karstification, *in* Quinlan and Stanley (1992). p. 373-388.

Stanton, W.I., and Smart, P.L. 1981. Repeated dye traces of underground streams in the Mendip Hills, Somerset. University of Bristol Speleological Society, Proceedings. 16(1):47-58.

Streltsova, T.D. 1988. Well Testing in Heterogeneous Formations. Wiley, New York. 412 p.

Teutsch, G., and Sauter, M. 1992. Groundwater modeling in karst terranes: Scale effects, data acquisition, and field validation. *in* Quinlan and Stanley (1992). p.17-35.

Travis, C.C., and Doty, C.B. 1990. Can contaminated aquifers at Superfund sites be remediated? Environmental Science and Technology. 24(10):1464-1466.

Tsang, C.F., Tsang, Y.W., and Hale, F.V. 1991. Tracer transport in fractures: Analysis of field data based on a variable-aperture channel model. Water Resources Research.

27(12):3095-3106.
Tucker, M.E., and Wright, V.P. 1990. Carbonate Sedimentology. Blackwell, Oxford. 482. p.
Vineyard, J.D. 1981. Guidebook to karst and caves of the Ozark region of Missouri and Arkansas. International Congress of Speleology (8th, Bowling Green, Ky.), Guidebook. p. 33-68.
Wang, J.S.W. 1991. Flow and transport in fractured rocks. Reviews of Geophysics, Supplement, Contributions in Hydrology. U.S. National Report 1987-1990. p. 254-262.
Wheatcraft, S.W., and Cushman, J.H. 1991. Hierarchical approaches to transport in heterogeneous porous media. Reviews of Geophysics, Supplement, Contributions in Hydrology. U.S. National Report 1987-1990. p. 263-269.
White, W.B. 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press, New York. 464 p.
Williams, P. W. 1983. The role of the subcutaneous zone in karst hydrology. Journal of Hydrology. 61:45-67.
Wilson, W. L., and Skiles, W.C. 1988. Aquifer characterization by quantitative dye tracing at Ginnie Spring, northern Florida. Environmental Problems in Karst Terranes and Their Solutions Conference (2nd, Nashville, Tenn.), Proceedings. National Water Well Association, Dublin, Ohio. p. 121-141.
Worthington, S.R.H. 1991. Karst Hydrogeology of the Canadian Rocky Mountains. PhD thesis, Geography. McMaster University. 370 p.
Worthington, S.R.H. 1992. Groundwater flow velocities in limestone terranes. [in prep]

78 RELEASABLE CYANIDE; DYSFUNCTIONAL REGULATION

Joe Lowry, Chief, Chemistry Branch; Marcela Siao, Chemist; Charles Ramsey, Chemist; and John Fowler, Chemist; U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, Colorado.

Abstract: A releasable hydrogen cyanide threshold limit of 250 mg/Kg, is currently recommended as a means to the identification of RCRA reactivity characteristic hazardous wastes. However, the experimental design of the releasable methodology is inadequate for hydrogen cyanide. Furthermore, the calculation of the recommended threshold limit is faulty underestimating the hazard. Recommendation of such guidance lacking in scientific merit is ill advised because it contributes to dysfunctional regulation.

INTRODUCTION

The purpose of the present work lies primarily in a critical analysis of the Agency's guidance for the identification of reactivity characteristic hazardous waste through testing for releasable cyanide. The present guidance contained in SW-846 [1]., provides a test method and a guidance threshold limit of 250 mg/Kg. The threshold limit is derived from a mathematical relationship between a mismanagement scenario and the test method. The regulatory genesis of the guidance states; "It is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment"[2].

Regrettably, the releasable cyanide test method suffers from rather disappointing performance and the mathematical relationship that derives the threshold limit is in error, both attributable to the neglect of Henry's Law. Clearly, the surest way to overcome these deficiencies is to understand them fully. With a full understanding, it should be possible to devise a regulatory testing strategy that is valid and rational.

MISMANAGEMENT SCENARIO

The mismanagement scenario causes a truckload of waste (6130 kg) to be discharged into a pit containing acidic waste. Of concern is if the waste contains sufficient cyanide or sulfide to cause the toxic gas concentration in the air over the 225 m^2 pit to exceed the respective OSHA standards. The toxic gas is allowed to disperse to a height of 4 m over the pit, a volume of air of 900 m^3. The OSHA standard for hydrogen cyanide is 10 mg/m^3, thus 9,000 mg hydrogen cyanide would need to be generated and released to cause the 900 m^3 of air to exceed the OSHA standard. The given mass of waste would need to be at least 1.47 mg/kg hydrogen cyanide to cause this exceedance. Furthermore, the scenario calculates that it should take 10 seconds to pass a given volume of air over the 15 m long pit which is the time given to generate and release the toxic gases. The scenario then corrects the waste concentration for differences between the test method time of 1800 seconds

and the 10 seconds given in the scenario by multipling 1.47 mg/kg by 180 to give a product of 264 mg/kg releasable cyanide. Moreover, the scenario adds a margin of safety and recommends an action level of 250 mg/kg.

The above calculation assumes the rates of release of hydrogen cyanide by the test method and the mismanagement scenario are the same as evidenced by the correction for difference in the times of the experiments. Henry's law states the solubility of a gas is proportional to its partial pressure above the solution [3]. Henry's Law is often expressed as,

$$K=P/X$$

where K is Henry's constant, P is the partial pressure (torr) of hydrogen cyanide and X is the mole fraction of hydrogen cyanide in water. Henry's constant, K, is 4000 at 18°C and 7.6 mm Hg when X is 0.0019 mole fraction in water [4]. This means that at equilibrium and at one atmosphere (760 mm Hg), the air will be 1% hydrogen cyanide and the aqueous hydrogen cyanide concentration 0.106 M.

Transposing this equilibrium to the SW-846 releasable cyanide method where equivalently 7.2 L of nitrogen are passed over one liter of acidic water, the 7.2 L of nitrogen will cause the removal of 0.072 L of hydrogen cyanide from one liter of 0.106 molar hydrogen cyanide solution. The volume of 0.072 L is equal to 0.0032 moles (0.072 L /22.4 L/M) while the initial aqueous hydrogen cyanide in one liter would be 0.106 moles. Therefore, the predicted release of hydrogen cyanide is just 3% (100% x 0.0032/0.106) at 18°C.

Similarly, when the equilibrium is transposed to the mismanagement scenario where equivalently 1.5 L of air are over one liter of acidic aqueous waste in the pit, assuming a volume of 600,000 L of aqueous waste in the pit, the 1.5 L of air will cause the removal of 0.015 L of hydrogen cyanide from one liter of 0.106 molar hydrogen cyanide solution. The volume of 0.015 L is equal to 0.000667 moles hydrogen cyanide. Therefore, the predicted release of hydrogen cyanide is 0.62% at 18°C.

The above equilibrium calculations demonstrate that the release of aqueous hydrogen cyanide to air will be different between the scenario and test method, simply because the volume of air to volume of aqueous solution is different. The scenarios time correction does not address this fact. Based just on the air to water volume ratio difference the test method should cause the release of 4.8 times more hydrogen cyanide than the scenario. Furthermore, the amount of hydrogen cyanide released will be different because the aqueous solution hydrogen cyanide concentrations will be different. The test method places 10 grams of waste in 250 mL of acidic aqueous solution (40 g/L) while the scenario places 6130 Kg of waste in 600,000 L of acidic aqueous waste (10.2 g/L). Therefore, combining the air to water volume ratio factor and the concentration factor, the test method should release 18.8 times more hydrogen cyanide than the scenario. Which means the threshold limit for hydrogen cyanide should be 27.6 mg/Kg (1.47 mg/Kg

times 18.8) rather than 264 mg/Kg or perhaps 25 mg/Kg rather than 250 mg/Kg in consideration of the scenarios safety factor.

Because the present recommend threshold limit is based on such easily discernible faulty science, enforcement premised on this limit can be faced with challenges concerning scientific validity leading to exclusion as evidence which is dysfunctional regulation.

TEST METHOD

As briefly discussed, the test method's air to water volume ratio if at equilibrium would cause to be measured only 3% of the hydrogen cyanide generated by the waste. In consideration of the regulatory genesis stated above, where the amount of generated toxic gas is of concern, it would seem that the test method's performance is inadequate. The SW-846 test method, only measures the amount of toxic gas generated and released to air under the conditions and design of the test method. The total amount of toxic gas generated is the amount dissolved in the aqueous test solution plus the amount released into the test's volume of nitrogen. The following expression is the reaction and equilibriums of concern.

$$\text{Waste} + H_3O^+ \Leftrightarrow HCN_{(aqueous)} \Leftrightarrow HCN_{(air)}$$

Analytically, the design of the test method is also inadequate. Consider that the test method requires that an analyst demonstrate proper performance of the test by obtaining better than a 50% recovery on a sodium cyanide standard. However, as calculated above even if equilibrium was reached only a 3% recovery would be achievable. In our laboratory, analysts achieve recoveries of between one to two percent which indicates the test method does not achieve equilibrium or the published Henry's constant does hold at the lower concentration. Moreover, both theoretically and experimentally the method's performance criteria can not be met, meaning test results can not be validated or confirmed, negating their evidentary value for enforcement which means dysfunctional regulation.

Now that it is understood that the test methods poor performance is in large part due to its low nitrogen to water volume ratio, modification of the method to increase the ratio should improve performance. At our laboratory experiments were conducted which confirm increasing the ratio increases the recovery of hydrogen cyanide. At a ratio of 341 L/L recoveries of around 50% were obtained. A plot of the ratio versus recovery plateaus at the higher recoveries, thus at 900 L/L, a recovery of about 92% is observed. Thus modification of the method such that greater than 900 liters of nitrogen per liter of reaction solution should provide acceptable analytical performance. It should be mentioned that the reaction vessel aqueous volume must be fixed which is consistent with the design of the first version of the SW-846 method but not the second version of the method.

Our laboratory has conducted experiments at nitrogen flow rates of 600 mL/min. The limiting factor on flow rate is the volume of the trapping impinger. At a reaction vessel aqueous volume of 250 mL and a nitrogen flow rate of 600 ml/min, an experiment time of 375 minutes is needed to provide a ratio of 900 L/L. However, if the reaction vessel aqueous volume is decreased to 50 mL, the time is shorten to 75 minutes. Our laboratory designed an apparatus some years ago for total cyanide that is well suited for this lower volume[5]. Experimentation with this apparatus provided similar results to the SW-846 methods apparatus.

Notably, there are other method design factors that must be considered. It is imperative and consistent with the regulatory genesis that the pH be made 2. The first version of the SW-846 method limits the equivalence of acid which in our experience with electroplating wastes is often insufficient to lower the reaction vessel aqueous solutions pH to 2. The second version of the SW-846 method does not place this limitation on the equivalence of acid.

Furthermore, the manner of pH adjustment may be critical. If the pH is adjusted with a small volume of acid followed by a volume adjustment with water, the cofactors of aqueous volume and ionic strength will cause more hydrogen cyanide to be released and perhaps generated than if a small volume of acid was added after the addition of a volume of water. A few experiments were conducted in our laboratory where the reaction vessel aqueous solution was made 4 M with sodium chloride. Essentially a "salting out" experiment, the volume of nitrogen required to give a 50% recovery was reduced by a third.

For a few samples, our laboratory has observed higher releasable cyanide recoveries than normal. These samples contained considerable caustic which upon acidification created substantial heat and evolution of carbon dioxide. Generally, Henry's constant decreases with increasing temperature. For example, Henry's constant for hydrogen sulfide decreases by a factor of two going from 25°C to 50°C [3]. A decrease in the constant means a greater recovery for the test method. Consideration might be given to modification of the method to heat the reaction vessel to 50°C or 60°C to shorten the test times.

CONCLUSIONS

An analysis forwarding agruments critical of the present guidance for reactivity characterization leads us to the following conclusions.

(i) The threshold limit recommended for hydrogen cyanide was incorrectly calculated and should be ten times lower.

(ii) The test method measures only a small fraction of the hydrogen cyanide gas generated at pH 2 and method performance criteria can not be achieved.

(iii) The guidance is unsuitable for enforcement and is in effect dysfunctional regulation.

Furthermore, although not detailed, guidance for hydrogen sulfide may be similarly flawed.

While expressing here criticisms regarding the use of the present releasable cyanide guidance for hazardous waste characterization, we are nevertheless confident that we have provided fundamental study and experimentation, most essentially, to the development of scientifically sound and functional regulatory guidance. Until such time, regulation would be better facilitated by return to the former guidance, primarily dependent on the opinion of a toxicologist or chemist.

REFERENCES

[1] U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd Edition, Office of Solid Waste and Emergency Response, Washington, D.C., (1986).

[2] U.S. Environmental Protection Agency, *Protection of the Environment*, Code of Federal Regulation, Title 40, Part 261.23(a)(5), (1991).

[3] W.H. Hamill, R.R. Williams, and C. MacKay, *Principles of Physical Chemistry* , Englewood Cliffs, N.J., Prentice-Hall, Inc., (1966), pp 20.

[4] U.S. Environmental Protection Agency, *Summary Review of Health Effects Associated with Hydrogen Cyanide*, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Research Triangle Park, North Carolina, EPA/600/8-90/002F (May 1990), pp 7.

[5] M.L. Siao, T.J. Meszaros, and J.H. Lowry, The Determination of Cyanide in Environmental Samples by a Midi-Distillation Procedure, 31st Rocky Mountain Conference, Denver, CO (1989).

79 DESIGN CONSIDERATIONS FOR AN AUTOMATED ON-LINE AIR SAMPLING SYSTEM

G. Broadway and E. Woolfenden, Perkin-Elmer Ltd, Beaconsfield, Bucks., UK and
J. Ryan and I. Seeley, The Perkin Elmer Corporation, Wilton, CT.

ABSTRACT: Ambient air determination of volatile organic compounds (VOCs) that arise from industrial emissions or automotive exhausts presents the environmental chemist with a number of challenges. The pollutants, present at ppb levels, must be collected, concentrated, separated and identified. This paper describes a design of a fully automated system for continuous air monitoring and presents data collected from that system. Trapping of VOCs below C_5 on charcoal or polymeric adsorbents is normally performed at sub-ambient temperatures. Such temperatures usually require large amounts of liquid cryogen which is expensive to acquire and difficult to handle at field air monitoring stations. Evaluation of adsorbents capable of trapping volatile organics at -30°C has been performed using Peltier electrical cooling. Thus the described on-line air monitoring system eliminates the need for cryogen. Trapped volatile organics are released from the adsorbents by thermal desorption. Separation and identification, critical parts of the system on-line air monitoring system, are performed by a multidimensional chromatographic non-polar capillary column and an Al_2O_3 column in series. This system permits the 42 compounds listed in EPA method TO-14 and as well as volatile hydrocarbons from C_2 to C_8 to be separated in a single analytical run. By using such multidimensional systems, it is possible to achieve a complete separation in 40 minutes.

INTRODUCTION

The 1990 Clean Air Act Amendments requires ambient air be monitored for concentrations of ozone and its precursors. Certain volatile organic compounds, including light hydrocarbons and aromatics, are generally regarded as precursors to ozone formation over urban and industrial areas and may be present in the atmosphere at low ppb concentrations. Sampling ambient air may be performed in a number of ways. Whatever method is chosen, it is usually necessary to perform some preconcentration step on the sample before analysis by gas chromatography is feasible. The most common methods are collection in evacuated, passivated canisters or by drawing air through a tube containing an adsorbent. Both techniques have drawbacks; passivated canisters suffer in that they are suited only to short term "spot" samples whereas the tubes are more suited to time weighted averaged sampling over longer periods. Neither technique is suitable for the detection of diurnal variations in ambient concentration of volatile organic compounds.

The system described in this paper enables automatic sampling of ambient air at regular intervals throughout the day. Such sampling is likely to be required at relatively remote non-laboratory locations. Therefore, one major requirement of the system was that sampling and subsequent chromatographic separation should not require liquid cryogens. The system uses a commercially available apparatus which can also be used for analysis of both passivated canisters and sampling tubes.

METHODOLOGY

A schematic of the system is shown in Figure 1. Air is sampled using a Perkin-Elmer ATD-400 thermal desorption instrument equipped with a standard injection accessory (valve 2). The standard ATD-400 glass-lined stainless steel tubing was modified to allow a sample of ambient air to be pulled through the electrically cooled trap (which is incorporated in the ATD-400) for a fixed time period using a small pump. A Tylan mass flow controller was incorporated in the system to ensure that the air volume sampled remained constant. A separate valve (valve 1) has also been incorporated into the system enabling a standard gas mixture to be sampled at regular intervals for calibration. Although the packed trap can tolerate relatively large amounts of water [1], a Nafion dryer has been included between the first and second valves to reduce the amount of moisture reaching the Peltier cold-trap. The performance of such a dryer has been described previously [2].

After the sampling period, valve 2 is switched so that carrier gas is directed through the trap. Simultaneously, the trap is rapidly heated to transfer the adsorbed compounds to the gas chromatographic column. The performance characteristics of the trap have been described previously [3] and it has been shown that by using an adsorbent filled trap, a temperature of -30 °C may be used to retain compounds with boiling points in the order of -90 °C [4,5] and eliminates the need for liquid cryogen for this application.

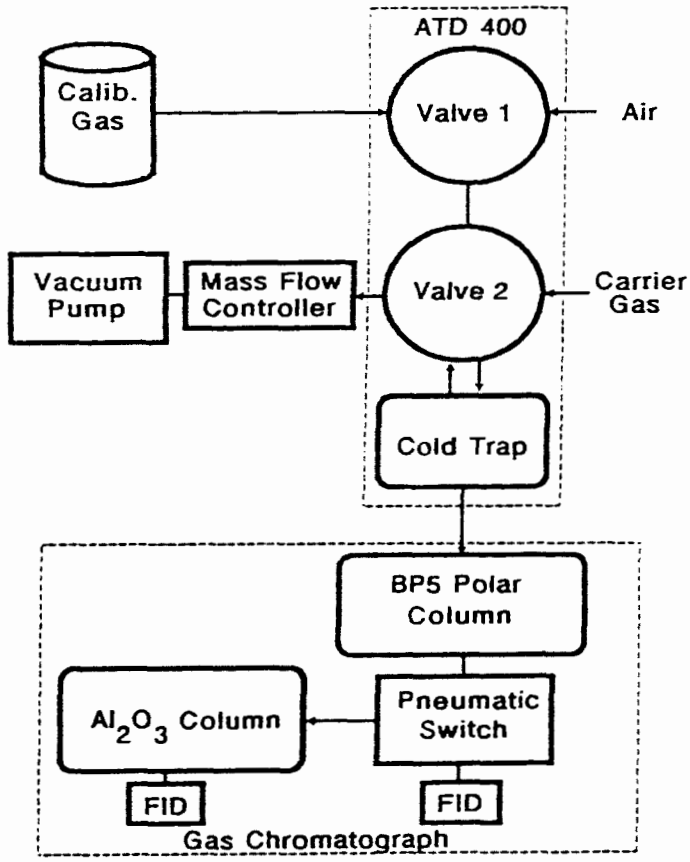


Figure 1. Principle components of the air sampling system.

To enable the gas chromatographic separation to take place at super ambient temperatures, a two-column system has been developed based on the Deans' principle of remote pressure switching [6]. The hardware used is identical to that described by Johnson [7,8], but employs a 50m x 0.22mm id 1.0um BP5 precolumn and an analytical column, 50m x 0.32 mm Al_2O_3 column deactivated with Na_2SO_4.

The second column was chosen in preference to the more common Al_2O_3/KCl deactivated column because the column manufacturer states that the former is more tolerant of moisture that the latter. The separation of a 60 component USEPA evaluation sample mixture using this column configuration is shown in Figure 2 with the component identification listed in Table 1.

RESULTS AND DISCUSSION

System evaluation was performed using a 60 component mixture of hydrocarbons and halocarbons listed for the USEPA Atlanta field studies as ozone precursors. The components were present at a concentration of 10ppb (v/v) and were humidified to 75% R.H. To trap all sample components, the trap was packed with a mixed bed of two carbon-based adsorbents. A weaker adsorbent was used to retain the less volatile components and was followed by a stronger adsorbent for the lower boiling compounds. During trap heating, the gas flow through the trap was reversed to backflush the VOCs from the adsorbent bed into the precolumn. In the evaluation, two factors were of greatest concern.

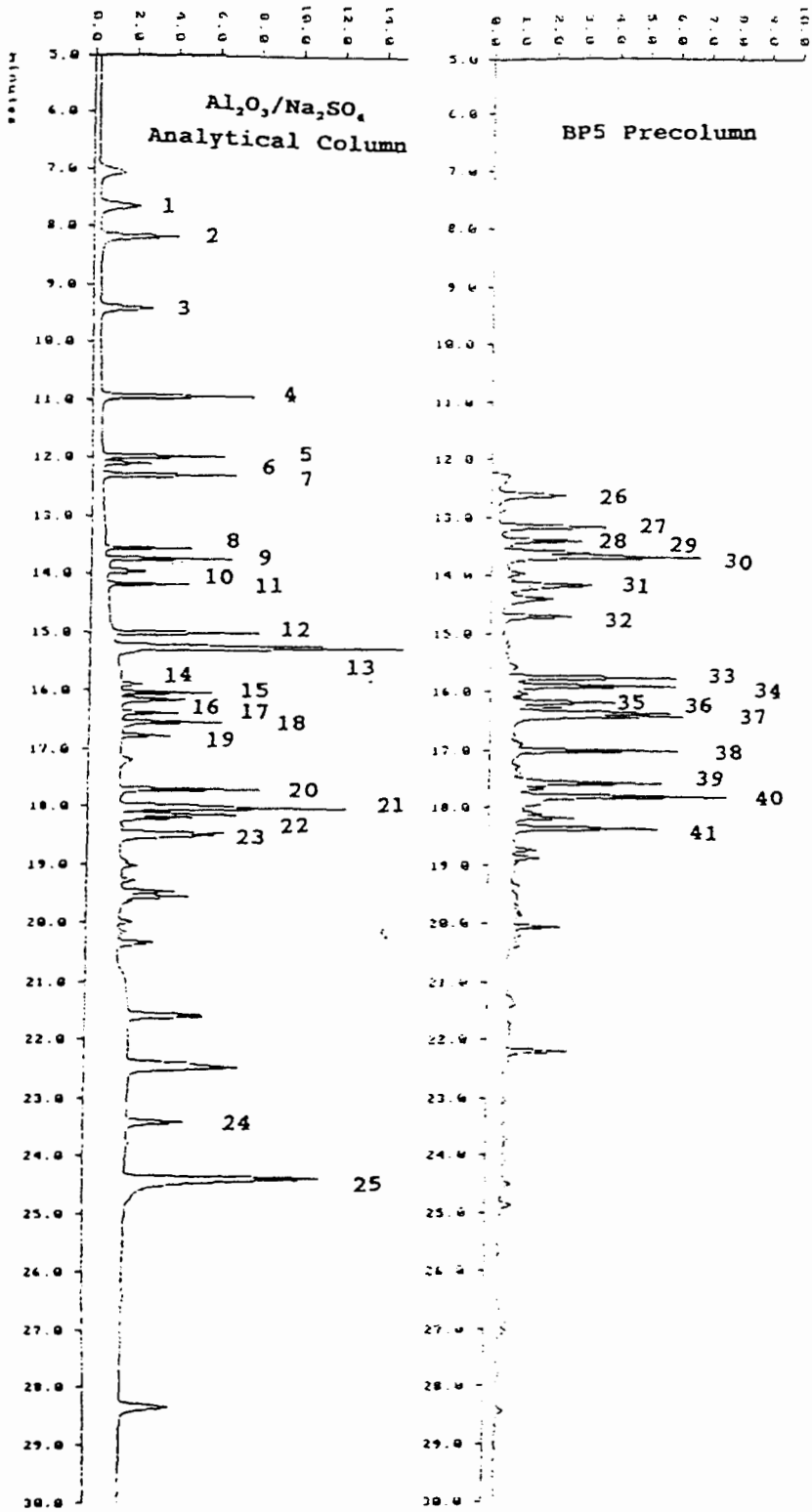


Figure 2. A 60 component ozone precursor standard mixture at 10ppb and 75% R.H. Sample collected for 15 minutes at 20mL/min, trapped at -30°C. Trap heated at 40°C/sec to 400°C and held for 10 minutes. GC conditions: precolumn - 50m x 0.22mm 1.0um BP-5, analytical column - 50m x 0.32 mm Al_2O_3 column deactivated with Na_2SO_4, oven 40°C for 5 minutes programmed at 15°C/min to 200°C for 15 minutes.

Peak No.	Component
1	ethane
2	ethylene
3	propane
4	propylene
5	iso-butane
6	acetylene
7	n-butane
8	trans-2-butene
9	1-butene
10	iso-butene
11	cis-2-butene
12	iso-pentane
13	n-pentane
14	3-methyl-1-butene
15	2-methyl-2-butene
16	trans-2-pentene
17	2,2-dimethylbutane
18	1-pentene
19	cis-2-pentene
20	methylcyclopentane
21	2-methylpentane
22	3-methylpentane
23	2-methylhexane and 3-methylhexane
24	n-heptane
25	benzene
26	methylcyclohexane
27	2,3,4-trimethylpentane
28	toluene
29	2-methylheptane
30	3-methylheptane
31	n-octane
32	perchloroethylene
33	ethyl benzene
34	p-xylene and m-xylene
35	styrene
36	o-xylene
37	n-nonane
38	iso-propylbenzene
39	n-propylbenzene
40	1,3,5-trimethylbenzene
41	1,2,4-trimethylbenzene

Table I. Component identification for Figure 2.

First, it was important that the trap retain all components of interest through the whole sampling period. Second, it was important that all of the sample be released to the gas chromatograph when the trap was heated. Trap breakthrough was determined by measuring the peak area counts for increasing volumes of sample introduced to the trap. The C_2 to C_4 hydrocarbons, being most volatile and therefore most likely not to be strongly retained, were studied for breakthrough. This was determined to be where area counts cease to increase with increasing volumes of sample. Figure 3 shows the effect of increasing the sample volume for C_2 and C_3 hydrocarbon. For the volumes studied, there was no evidence of breakthrough for C_3 and C_4 hydrocarbons. It is evident that breakthrough of ethylene occurs around 1000mL. Ethane continued to increase in a linear manner to at least 2000mL, the largest volume measured. If the safe sampling volume is considered to be one-half of the breakthrough volume, samples of up to 400 mL may be taken if it is important to determine either acetylene or ethylene. If these components are not of interest, volumes of 1000mL or more may be taken.

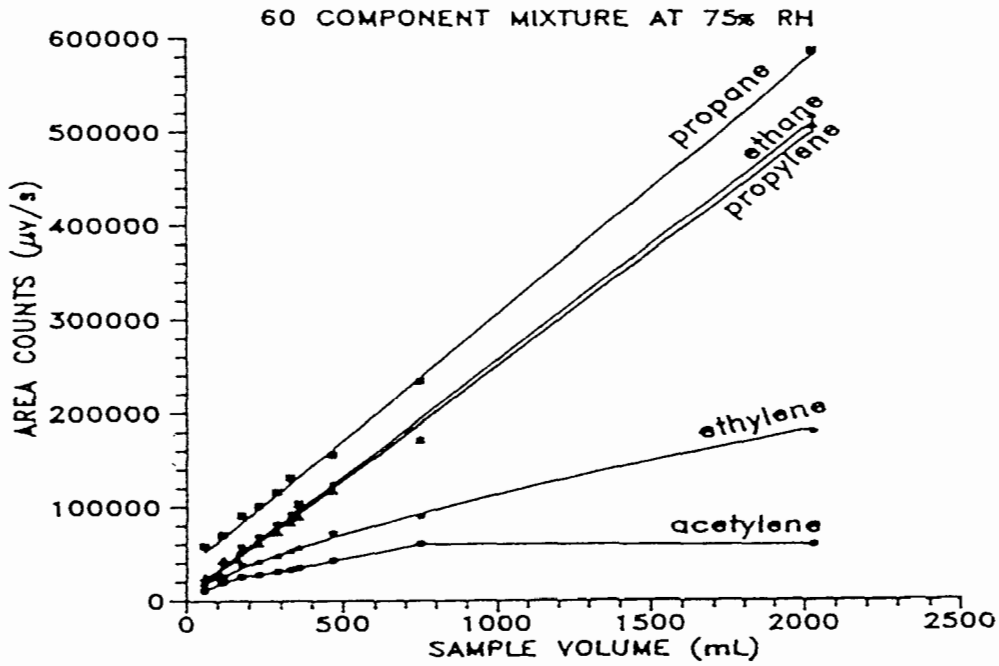


Figure 3. Sample volume vs. chromatographic area counts

To establish if all components were released from the Peltier device, the trap was heated a second time and the chromatographic run examined for residual traces of each compound. When the trap was held at its upper temperature of 400 °C for 10 minutes, no carryover could be detected.

If a 400 mL sample is taken, it is estimated from the peak areas of the 10ppb sample that the detection limit is in the order of low ppb or even sub-ppb levels. However, this will also be dependent on other interfering components in the sample at a particular site. If the C_2 hydrocarbons are not of interest, then the sample volume may be increased with a corresponding reduction in the detection limit.

The repeatability of the system has been found to be in the order of $\pm$10%. Table II shows data for a number of representative compounds in the 60 component sample mixture.

	ethane	benzene	toluene	octane	perchloro ethylene	o-xylene
	333	684	233	263	125	319
	336	600	226	303	109	308
	298	551	218	233	95	283
	284	638	203	222	88	272
	284	535	197	218	92	296
	273	528	196	217	94	283
mean	301	589	212	243	100	293
sd	24.70	57.04	14.22	31.22	12.65	16.28
rsd	8.2%	9.7%	6.7%	12.9%	12.6%	5.6%

Table II. Reproducibility of selected component quantification using on-line air sampling system.

SUMMARY.

This work shows that the system described is a convenient means of sampling air and has been evaluated using a 60 component mixture of hydrocarbons known to be precursors to ozone formation in the urban environment. By using a packed cold-trap containing a mixed bed of carbon based adsorbent, a safe sampling volume of 400 mL can be used for C_2 determinations at -30 °C. The sampling volume determines the detection limit which, for the standard 60 component mixture, is on the order of low ppb to sub-ppb levels. The system described uses commercially available instrumentation and is suitable for tube type samplers and canisters as well as direct ambient air sampling. By using a Peltier-cooled trap and a two-column chromatographic system, the need for liquid cryogenic cooling is eliminated, allowing a wide boiling range of compounds to be separated in 30 minutes or less. Eliminating cryogen in field sampling is desirable.

REFERENCES

1. Perkin-Elmer Thermal Desorption Application Note 29.
2. Piell, J.D., Oliver, K.D., McClenny, W.A. JAPCA,37:(1987),pp 244-248.
3. Broadway, G.M., Trewern, T., Proc. 13th Intl. Symp. on Capillary Chrom., Vol 1, pp 310-320.
4. Kristensson, J., Schrier, (Ed), Proc. Analysis of Volatiles, International Workshop, Worzburg, F.R.G., 28-30th Sept. 1983, pp 375-378.
5. Broadway, G.M., Proc 9th Australian Symp. on Analytical Chemistry, Sydney 1987, Vol 1., pp 375-378.
6. Deans, D.R., Chromatographia 1 (1968), pp 18.
7. Johnson, G.L., Tipler, A., Proc. 8th Intl. Symp. on Capillary Chrom., Vol 1, pp 540-549.
8. Johnson, G.L., Tipler, A., Crowshaw, D., Proc. 10th Intl. Symp. on Capillary Chrom., Vol 2, pp 971-985.

80 REVIEW OF ARMY RESEARCH ON WELL CASINGS USED IN GROUNDWATER MONITORING

Louise V. Parker, Research Physical Scientist, and Alan D. Hewitt, Research Physical Scientist, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire 03755-1290.

ABSTRACT: Our laboratory has conducted several studies that have focused on either the effects of well-casing materials on groundwater chemistry or the ability of these materials to withstand high concentrations of organic solvents in aqueous solutions. Static studies have examined the sorption of organics and the sorption and leaching of metals from four well-casing materials. The four types of well casings tested are stainless steel 304 (SS 304), stainless steel 316 (SS 316), polyvinylchloride (PVC), and polytetrafluoroethylene (PTFE).

With respect to sorption and leaching of metals, studies have been conducted under both low and high dissolved oxygen conditions. These studies indicate that neither stainless steel 304 or 316 should be used when monitoring for inorganic constituents because these materials can sorb cations and anions and leach several metal constituents. PVC generally showed considerably less interaction with the inorganic constituents of the sample than the stainless steel casings did. PTFE was inert, except for very slow sorption of Pb.

Studies that examined sorption of aqueous solutions of organics by the four materials indicated that SS 304 and SS 316 were the most inert materials. In contrast, substantial loss of hydrophobic organics occurred in samples exposed to PTFE casings within 24 hours. Losses were also found with PVC, but the rate and extent were slow enough so that it did not appear that sorption by PVC casings or screen would be of concern.

Two studies have looked at the effects of high concentrations of organic solvents in aqueous solution on the integrity of rigid PVC. The first examined the effect of a mixed solution of four organic solvents on SS 304, SS 316, PVC, and PTFE casings over a 6-month period. Each organic was at a concentration one-fourth its solubility in water. For all the materials, no changes in surface structure could be associated with exposure to these high concentrations of organic solvents even after 6 months. In the other study, small pieces of rigid PVC casing were exposed to methylene chloride solutions at various concentrations for periods up to 33 days. We concluded that rigid PVC would only be degraded by very high concentrations of methylene chloride, i.e. > 3300 mg/L.

Our results are compared with other published studies.

INTRODUCTION

Concern regarding the use of polyvinylchloride (PVC) vs polytetrafluoroethylene (PTFE) vs stainless steel well casings for groundwater monitoring has centered around two issues: 1) the effect these materials

may have on sample integrity either by sorbing analytes of interest or by leaching contaminants and 2) the resistance of these materials to degradation by the environment. Our laboratory has conducted several studies that have looked at these effects. This paper reviews our findings and compares this material with other published studies.

EFFECT OF MATERIALS ON SAMPLE INTEGRITY

Sorption of Organics. Our first study (Parker et al. 1990) examined the sorption of organics and metals by four well-casing materials (PVC, PTFE, stainless steel 304 (SS 304), and stainless steel 316 (SS 316)). With respect to the organic part of this study, these four materials were exposed to a mixed solution (20 ppm) of 10 organics under sterile conditions. The organics were hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5-trinitrobenzene (TNB), cis- and trans-1,2-dichloroethylene (CDCE and TDCE), *m*-nitrotoluene (MNT), trichloroethylene (TCE), chlorobenzene (CLB), and *o*-, *p*-, and *m*-dichlorobenzene (ODCB, PDCB, and MDCB). The selection of these compounds was based on the compound's molecular structure, solubility in water, octanol-water partition coefficient (Kow value), and retention time (using reversed-phase HPLC). Samples were analyzed and discarded after 1, 8, 24, and 72 hours, 7 days, and 6 weeks.

Figure 1 shows the results for TCE. Neither stainless steel casing affects the concentration of TCE, even after 6 weeks. This was true for all of the organics studied. However, the rate and extent of loss of TCE was greater for PTFE than for PVC. This was also true for all the other compounds that were sorbed by PTFE, which includes CDCE, TDCE, CLB, ODCB, MDCB, and PDCB. For these compounds, there was a 10% loss in 8 to 24 hours in samples exposed to PTFE, although it took 1 to 6 weeks to see an

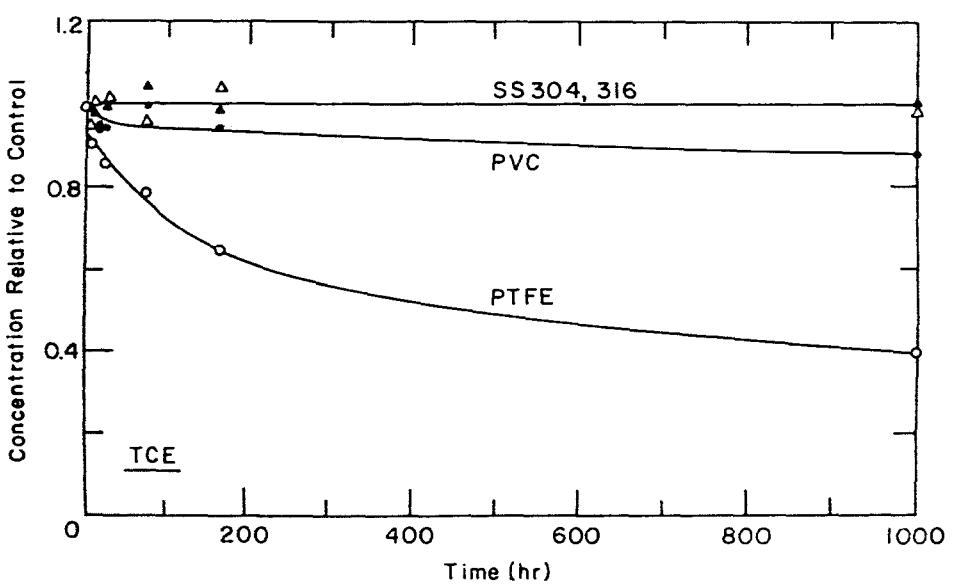


Figure 1. Sorption of TCE by SS 304, SS 316, PVC, and PTFE well casings (from Parker et al. 1990).

Table 1. Time for 10% Loss of Selected Organics (from Parker et al. 1990).*

Compound	PTFE	PVC
RDX	> 6 wk	> 6 wk
TNB	> 6 wk	> 6 wk
CDCE	6 wk(20%)	6 wk(20%)
TDCE	24 hr	1 wk
MNT	1 wk	< 6 wk
TCE	8 hr	6 wk
CLB	24 hr	6 wk
ODCB	24 hr	6 wk
PDCB	8 hr	1 wk
MDCB	8 hr	1 wk

* Sample times: 0, 1, 8, 24, 72 hours, 7 days, and 6 weeks.

equivalent loss in samples exposed to PVC (Table 1). MDCB and PDCB were sorbed to the greatest extent, 74% loss after 6 weeks. Two analytes, RDX and TNB, were not sorbed by any of the casings, even after 6 weeks.

We were able to correlate the loss of hydrophobic organic constituents in the solutions exposed to PTFE casings with the substance's Kow value. The greater the Kow, or the more hydrophobic the substance, the greater the tendency to be sorbed by PTFE. However this correlation overestimates losses for more polar organics. While it is difficult to extrapolate this test data to a sampling situation, we felt the rate of loss of several organics when exposed to PTFE was rapid enough that it could impact the integrity of a sample.

This study agrees well with similiar studies conducted at the University of Waterloo. Gillham and O'Hannesin (1990) conducted a study, also under sterile conditions, that looked for sorption of several aromatic hydrocarbons (ppm levels) by several materials used in sampling groundwater. These materials included stainless steel, rigid and flexible PVC, and PTFE, among others. Figure 2 is typical of their findings and shows the results for benzene. There is no loss with stainless steel, very slow loss with rigid PVC, more rapid loss with PTFE, and very rapid loss with flexible PVC. For PTFE, a 10% loss of most of the organics occured within 6 hours, but it took 12 to 24 hours to see a similiar loss with rigid PVC (Table 2). For flexible PVC, however, sorption of these compounds equaled 10% within 5 minutes. These results clearly show the importance of distinguishing between flexible and rigid PVC. Previous studies by Barcelona et al. (1985) are often cited as a justification for using PTFE rather than PVC. They noted extremely rapid sorption by PVC and slower rates for PTFE. However, what many readers fail to discern is that this study was conducted using flexible PVC.

Reynolds and Gillham (1986) had relatively similar results for a series of halogenated alkanes and alkenes (Table 3). Here, loss was not always greater for PVC than for PTFE but biocide was not used in this

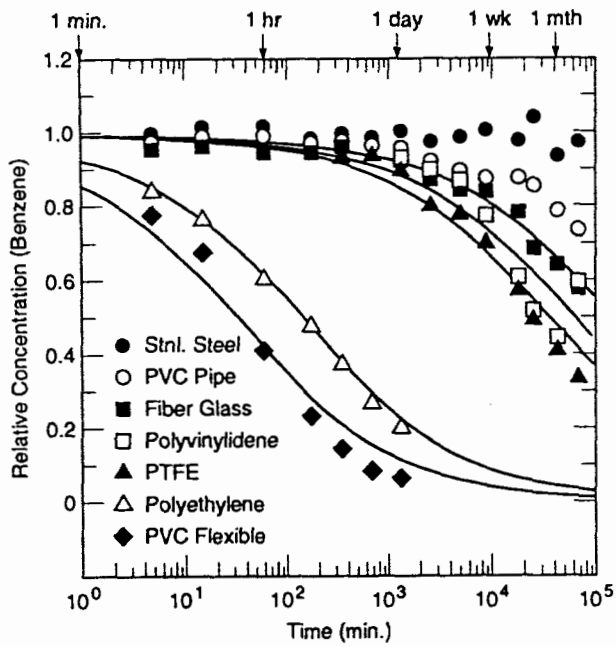


Figure 2. Sorption of benzene by materials used in groundwater monitoring (from Gillham and O'Hannesin 1990).

Table 2. Time (hours) for Concentration to be Significantly Different from 1.0 (from Gillham and O'Harresin 1990).*

	Benzene	Toluene	Ethyl-benzene	*m*-xylene	*o*-xylene	*p*-xylene
SS	> 1344	> 1344	> 1344	> 1344	> 1344	> 1344
PVC (rigid)	48–96	24–48	12–24	12–24	12–24	12–24
PTFE	24–48	3-6	1-3	3-6	6-12	1-3
PVC (flexible)	0-01	0.1	0-0.1	0-0.1	0-0.1	0-0.1

* Approximately a 10% loss. 1344 hr = 56 days

Table 3. Time for a 10% Loss of Organics (from Reynolds and Gillham 1985).

	1,1,1–trichloroethane	Tetrachloro–ethane	Bromoform	Hexachloro–ethane	Tetrachloro–ethylene
PTFE	~ 1 day	~ 2 wk	> 5 wk	~ 1 day	< 5 min
PVC	~ 5 wk	~ 2 wk	~ 3 days	~ 1 day	~ 1 day

Table 4. Time (days) for 50% Loss of Organics
(from Reynolds et al. 1990).

	1,1,1-trichloroethane	Tetrachloro-ethane	Bromoform	Hexachloro-ethane	Tetrachloro-ethylene
SS	> 35	> 35	31	32	> 35

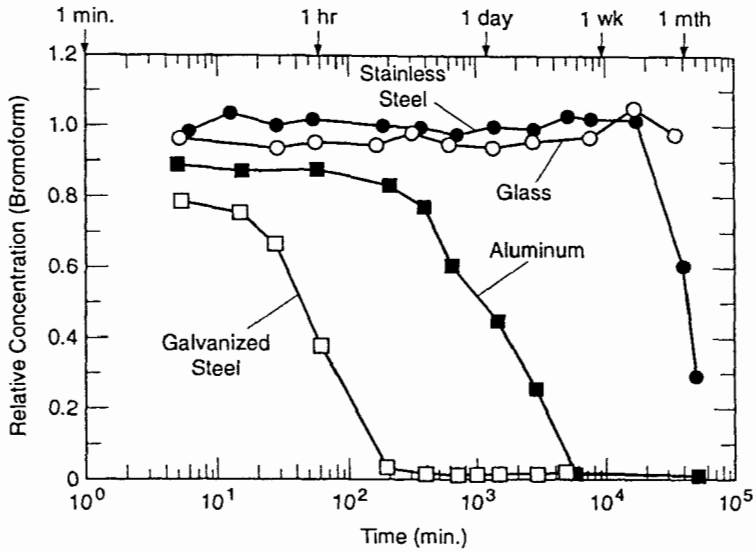


Figure 3. Sorption of bromoform by stainless steel, galvanized steel, glass, and aluminum (from Reynolds et al. 1990).

study and thus biological activity cannot be ruled out. However, the most significant finding of this study is the very rapid sorption of tetrachloroethylene by PTFE; loss was 10% within 5 minutes. This loss is as rapid as that seen in the previous study with the flexible PVC and is rapid enough that biological activity can most likely be ruled out.

Reynolds et al. (1990) exposed stainless steel and several other metals to aqueous solutions similar to those used in the previous study. Substantial losses of the two most highly halogenated compounds (bromoform and hexachloroethane) were observed in solutions exposed to these metals (Table 4). As seen in Figure 3, the loss of these two compounds occurs rapidly after a 2-week lag. The authors attributed this loss to reductive hydrogenolysis resulting from leaching of transition metal ions (such as Cr, Mn, Fe, and Ni) from the stainless steel. Based on our inorganic leaching studies (Hewitt 1989, Hewitt 1992), this explanation is entirely plausible, although losses due to biological activity cannot be ruled out.

In the previous studies, losses of organics were attributed to absorption within the polymer matrix rather than adsorption by the surface. If losses were due to adsorption and the extent of this depended upon the number of available sites, one would predict that the percent

loss would be greater at lower concentrations. We are currently conducting studies to determine if there is any concentration effect. Our previous study used a 20-ppm solution, while our current studies use 10- to 20-ppb concentrations of the same suite of organics. Thus far, we have looked at losses of RDX, TNB, MNT, TDCE, CDCE, and TCE and have found the percent losses are equivalent to losses seen previously for the two polymers. As in the previous study, we have seen no losses in samples exposed to either SS 304 or SS 316 under sterile conditions.

Sorption and Leaching of Metals. For the inorganic portion of our first study (Parker et al. 1990), the same four well-casing materials (PVC, PTFE, SS 304, and SS 316) were exposed to mixed solutions of arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) to determine if sorption occurred. Sample times were 0.5, 4, 8, 24, and 72 hours. Table 5 shows the time required for a 10% change in analyte concentration. We see that PVC and PTFE had no effect on the concentrations of either of the two metals (As, Cr) that are most likely present as anions. Perhaps this is because anions do not strongly associate with these types of plastic surfaces (Masse et al. 1981). The two stainless steel casings sorbed more than 10% of the As within 24 hours, and the SS 316 casings sorbed more than 20% of the Cr after 8 hours (Table 5).

Table 5. Time for 10% Change in Metal Concentrations (from Parker et al. 1990).*

	Loss						Gain	
	As		Cr		Pb		Cd	
PVC	> 72		> 72		4	(10%)	4	(13%)
PTFE	> 72		> 72		72		> 72	
SS 304	24	(12%)	> 72		4	(22%)	4	(17%)
SS 316	24	(15%)	8	(23%)	4	(20%)	4	(24%)

* Sample times: 0.5, 4, 8, 24, and 72 hr. Values in parenthesis are the actual amount lost.

With respect to the metals that exist as cations in solution, Pb was the most actively sorbed species, and even PTFE showed a 10% loss after 72 hours (Table 5). While loss of Pb was greater and more rapid for PVC than for PTFE, losses were much greater and more rapid for the two stainless steel casings than for PVC. In contrast to the sorption seen with the other three metals, Cd was leached from the PVC and stainless steel casings. However, again the stainless casings had a greater impact on the solution chemistry than PVC casings.

We also found a large standard deviation in the Cd and Cr data for the SS 316 and SS 304 samples and in the Pb data for the SS 316 samples. We attributed this variability to surface oxidation, which was visible on many of the stainless steel samples. Thus, we concluded that, when monitoring for metals, PTFE is clearly the best material and that PVC is a better second choice than either stainless steel casing. However, when

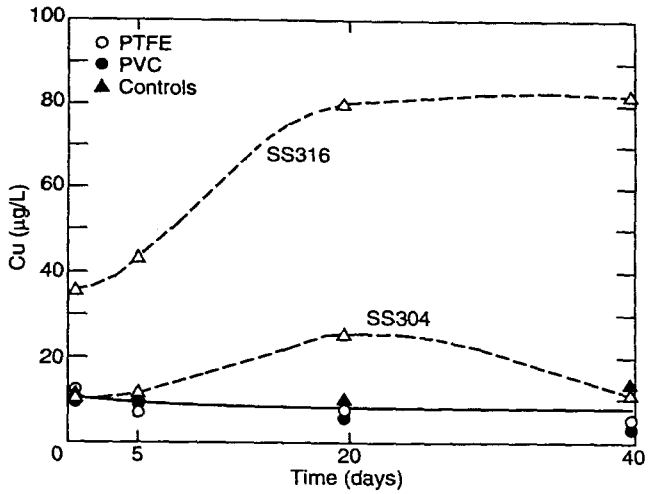


Figure 4. The effects of well casings on Cu concentrations (from Parker et al. 1990).

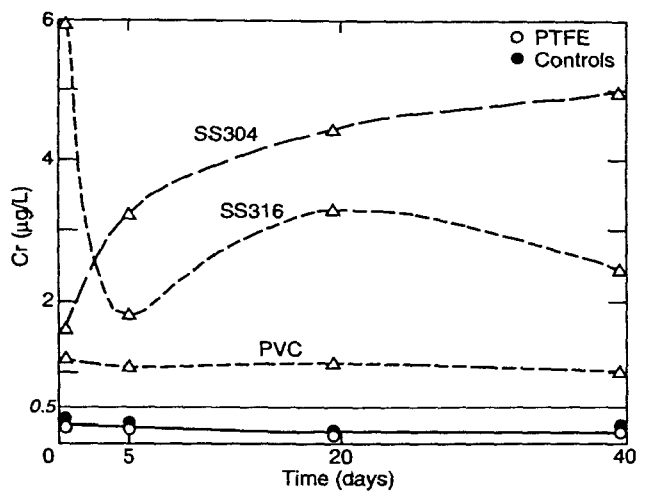


Figure 5. The effects of well casings on Cr concentrations (from Parker et al. 1990).

monitoring for both metals and organics, we concluded that PVC was the best compromise material.

Hewitt (1989) looked for leaching of nine metals in samples of well water exposed to the same four types of well-casing materials used in our previous study. The following metals were analyzed: Ag, As, Ba, Cd, Cr, Pb, Se, Hg and Cu. Sample times were 1, 5, 20, and 40 days. PTFE casings did not leach any of the nine metals at levels that were considered statistically significant when compared with controls that contained no casings. In contrast, PVC leached significant levels of Cr, Cd, and Pb; SS 316 leached significant levels of Cr, Cd, Pb, Ba, and Cu; and SS 304 leached significant quantities of Cr and Pb. With the exception of Pb, leached concentrations were always higher for the two stainless steel casings than for PVC. Figure 4 shows the concentration of Cu with time for samples exposed to the four casings. Copper concentrations showed a steady increase with time in the SS 316 samples. For Cr, the samples exposed to the SS 304 casings show a similar trend (Figure 5). The concentration of Pb in the SS 304 samples also increased for the first 20

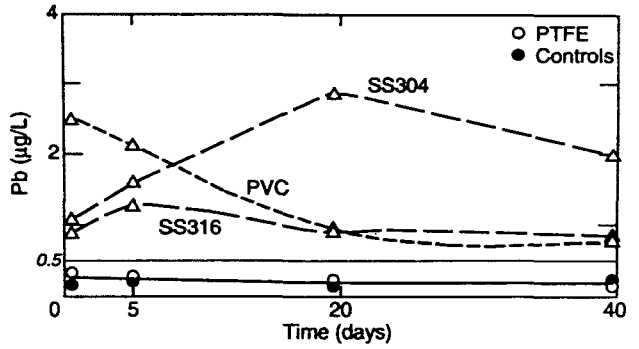


Figure 6. The effects of well casings on Pb concentrations (from Parker et al. 1990).

days, and Pb concentrations decreased with time in the PVC samples (Figure 6). We believe this indicates that the leaching of Pb is a surface phenomenon. Packham (1971) studied the leaching of lead stabilizers from PVC pipe and found that it was a surface phenomenon that could be substantially reduced by pretreatment with either alcoholic sodium hydroxide solution or a mixture of dilute nitric and perchloric acids.

Once again, there were very high variances in the stainless steel data. This variability was attributed to the surface oxidation that was observed on many, but not all, of these samples.

Since the oxidation observed in the previous studies was likely due to the high dissolved oxygen content of the well water, the next series of studies (Hewitt 1992) were conducted using well water with a low dissolved oxygen content. These experiments were conducted in a nitrogen atmosphere using well water that had been previously purged with nitrogen to remove the oxygen. This was done to simulate the more anoxic conditions found in a deep well. Sample times were 2, 8, 24, and 120 hours. Table 6 summarizes the results of the statistical analyses of the sorption and leaching studies for the 2-hour samples. It is clear that both stainless steel casings can have an impact on the concentrations of several metals in only 2 hours time. The same is also true for PVC with respect to levels of Pb.

Table 6. Materials Showing Significant* Change in Metal Concentration After 2 Hours – Low D.O. Study (from Hewitt 1992).

	Fe	Ni	Cd	Cu	Cr	Pb
Leaching	SS 316 SS 304	SS 316	SS 316 SS 304	SS 316	—	—
Sorption	—	—	—	—	SS 304	SS 316 SS 304 PVC

* By ANOVA

Again the variances were very high for samples exposed to the stainless steel casings even though there was no visible oxidation and these conditions should not have been corrosive. It is clear that the conclusions of this study are essentially the same as those found in the previous two studies: stainless steel can significantly alter metal concentrations within a few hours of contact, and PTFE and PVC are preferable when analyzing for metals.

DEGRADATION OF WELL CASINGS BY THE ENVIRONMENT

The conditions that cause the corrosion of stainless steel are well documented in the literature. These include: low pH, high dissolved oxygen content, presence of hydrogen sulfide, dissolved solids, high carbon dioxide, high chlorides, and the presence of sulfate-reducing bacteria (Aller et al. 1989, Driscoll 1986). While it is also commonly known that several pure (neat) organic solvents can degrade (swell) rigid PVC, the effects of high concentrations of these solvents in aqueous solution is not generally known.

Berens (1985) predicted the permeation of organics through PVC pipe based on samples of PVC exposed to a range of concentrations (activities) of these solvents. He noted that the solvent interaction parameter (χ) used in the Flory-Huggins equation could be used as a measure of the solvent or swelling power of a particular solvent. Table 7 gives the χ values for a number of organic solvents. In general, PVC is only softened by solvents with a χ value less than 1; the lower the number the greater the solvent/swelling power. A solvent with a χ value less than 0.5 can completely dissolve the polymer.

In these studies, Berens observed that the rate of penetration in PVC changed many orders of magnitude as the activity of the penetrant in the environment changed. He noted that at ambient temperatures, rigid PVC would only be softened by strong solvents or swelling agents of PVC (with $\chi = 0$) at activities > 0.5. For less aggressive solvents, even higher activities would be needed. Figure 7 shows the isotherms Berens derived using the Flory-Huggins equation for various values of χ and the approxi-

Table 7. Polymer-Solvent Interaction Parameters (x) for a Series of Organics (from Berens 1985).

Compound	X
Methylene chloride	< 0.53
Trichloromethane	9.64
1,1–dichloroethane	< 0.68
1,1,1–trichloroethane	0.85
Trichloroethylene	0.88
Tetrachloroethylene	1.17
Benzene	0.68
Toluene	0.83
Acetone	0.61

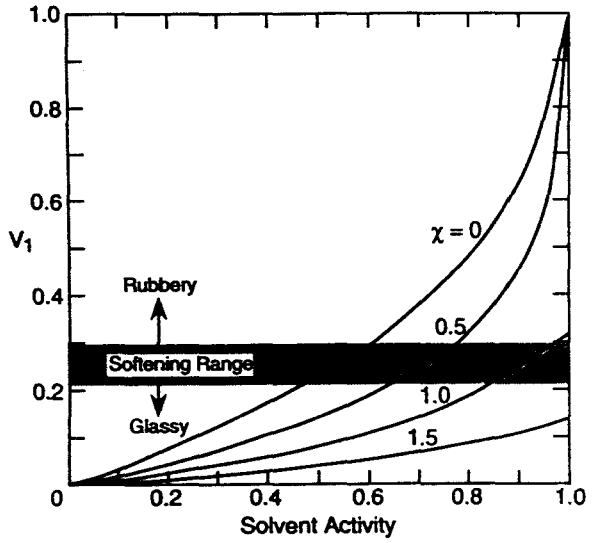


Figure 7. Flory-Huggins isotherms for different values of χ and the approximate softening range for PVC (from Berens 1985).

mate softening range for PVC. For example, for compound with $\chi = 0.5$, softening should occur in solutions with activities greater than 0.6.

For aqueous solutions, the solvent activity can be approximated by dividing the concentration of the compound in solution by its solubility in water. Thus for aqueous solutions of solvents to cause softening of rigid PVC, the solvent must be able to dissolve PVC and must exist in solution at a concentration that exceeds one-half its solubility in water. Thus Berens concluded that softening of PVC is only possible in the presence of nearly undiluted solvents or swelling agents of PVC.

One criticism of Berens' work is that he tested different activity solutions by dissolving the solvents in polyethylene glycol but never actually tested aqueous solutions of these solvents. We have conducted two preliminary studies addressing this issue and further studies are ongoing.

In the first study (Taylor and Parker 1990), we exposed pieces of PVC, PTFE, SS 304, and SS 316 to aqueous solutions of a mixture of toluene, tetrachloroethylene, o-dichlorobenzene, and p-dichlorobenzene. Each compound was at concentrations 0.25 time its respective solubility in water (approximate activity = 0.25). These casings were soaked in these solutions for times up to 6 months and then examined for changes in surface structure using a scanning electron microscope (SEM). No changes in surface structure were noted even in the PVC pieces that had been exposed for 6 months.

In the second study (Parker et al. 1992), small pieces of PVC well casing were exposed to aqueous solutions of methylene chloride at approximate activities of 0.2, 0.4, 0.6, 0.8, and 1.0, and controls (water only).

Table 8. Times for Softening of PVC in Solutions at Various Activities (from Parker et al. 1992).

Activity	Time to Pronounced Softening*	Time to Slight Softening
1.0	4 days	←
0.8	22 days	4 days
0.6	> 33 days	15 days
0.4	> 33 days	33 days
0.2	> 33 days	> 33 days
0.0	> 33 days	< 33 days

* Sample could be bent back on itself.

The samples were monitored for changes in weight gain, length, flexibility, and curvature. We also looked for any changes in surface structure using the SEM. The study ran for 33 days. The results agree reasonably well with Berens' predictions. Samples exposed to the highest activity solution (1.0) softened within the first 4 days, and samples exposed to the 0.8 activity solution were softened after 22 days (Table 8). As predicted, samples exposed to the lowest activity solution (0.2) showed no signs of softening. However, samples exposed to the 0.4 and 0.6 activity solutions showed some slight changes, indicating softening might occur eventually, especially at the 0.6 activity. Whether softening should occur at the 0.6 activity depends upon the actual χ value of methylene chloride. Berens estimated that this value is less than 0.53 but did not give an actual number. If χ is around 0.3, softening would be predicted for solutions with an activity of 0.6. Further longer term studies will be conducted shortly to better determine if softening occurs at 0.6 or 0.4. Conservatively, we can say that there should be no softening of rigid PVC in solutions of methylene chloride at activities below 0.2. This corresponds to a very high concentration of methylene chloride: 3340 mg/L. Thus, in most environmental situations, aqueous solutions of methylene chloride, or any other solvent, will not cause serious swelling or softening of PVC pipe.

SUMMARY

It is clear from these studies that neither PVC, PTFE, SS 304, or SS 316 is an inert material. Thus, selection of a material for a well casing should be done on a case by case basis based on site characteristics, such as depth of the well, expected pollutants, and the chemistry of the subsurface environment. The presence of neat or excessively high concentrations of PVC solvents would preclude using PVC, corrosive conditions would preclude using stainless steel, deep wells would preclude using PTFE, and extremely deep wells would preclude using PVC. With respect to trying to reduce the impact of a well-casing material on analyte concentration, stainless steel or PVC would be best if monitoring for hydrophobic organics, PTFE or PVC would be best if monitoring for metals, and PVC would be best if monitoring for both. A more thorough review with suggested guide-

lines for selecting materials used in samplers and casings can be found in Parker (1992-in press).

ACKNOWLEDGEMENTS

Thanks to Dr. Thomas Jenkins and Susan Taylor of our laboratory for their review comments and to our sponsor the U.S. Army Toxic and Hazardous Materials Agency, Martin H.Stutz, Project Monitor.

REFERENCES

Aller, L., Bennett, T.W., Hackett, G., Petty, R.J., Lehr, J.H., Sedoris, H., Nielsen, D.M., and Denne, J.E., *Handbook of suggested practices for the design and installation of ground-water monitoring wells*. National Water Well Association, Dublin, Ohio, 1989.

Barcelona, M.J., Helfrich, J.A., and Garske, E.E., "Sampling tubing effects on ground water samples," *Analytical Chemistry*, Vol. 57, 1985, pp. 460-464.

Berens, A.R., "Prediction of organic chemical permeation through PVC pipe," *Journal of the American Water Works Association*, 1985, pp. 57-65.

Driscoll, F.G., *Ground Water and Wells*, Johnson Division, St. Paul, Minnesota, 1986.

Gillham, R.W. and O'Hannesin, S.F., "Sorption of aromatic hydrocarbons by materials used in construction of ground-water in sampling wells," in *Ground Water and Vadose Zone Monitoring*, ASTM STP 1053, American Society for Testing and Materials, Philadelphia, 1990, pp. 108-122.

Hewitt, A.D., *Leaching of metal pollutants from four well casings used for ground-water monitoring*. CRREL Special Report 89-32, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H., 1989.

Hewitt, A.D., "Potential of common well casing materials to influence aqueous metal concentrations," *Ground Water Monitoring Review*, Vol. 12, No. 2, 1992.

Masse, R., Maessen, F.J.M.J., and DeGoeij, J.J.M., "Loss of silver, arsenic, cadmium, selenium and zinc traces from distilled water and artificial sea-water by sorption on various container surfaces." *Analytica Chimica Acta*, Vol. 127, 1985, pp. 181-193.

Packham, R.F., "The leaching of toxic substances from unplasticized PVC water pipe. Part III. The measurement of extractable lead in PVC pipes," *Water Treatment and Examination*, Vol. 20, No. 2, 1971, pp. 152-164.

Parker, L.V., Hewitt, A.D., and Jenkins, T.F., "Influence of casing materials on trace-level chemicals in well water". *Ground Water Monitoring Review*, Vol. 10, No. 2, 1990, pp. 146-156.

Parker, L.V., "Suggested Guidelines for the use of PTFE, PVC and stainless steel in samplers and well casings", *Current Practices in Ground Water and Vadose Zone Investigations*, ASTM STP 1118, David M. Nielsen and Martin N. Sara, Editors, American Society for Testing and Materials, Philadelphia, 1992 (in press).

Parker, L.V., Ranney, T.A., and Taylor, S., *Softening of Rigid Polyvinyl Chloride by High Concentrations of Aqueous Solutions of Methylene Chloride*, CRREL Special Report 92-12, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H., 1992.

Reynolds, G.W. and Gillham, R.W., "Adsorption of halogenated organic compounds by polymer materials commonly used in groundwater monitors," in *Proceedings of Second Canadian/American Conference on Hydrology. Hazardous Wastes in Ground Water: A Soluble Dilemma*, National Water Well Association, Dublin, Ohio, 1986, pp. 125-132.

Reynolds, G.W., Hoff, J.T., and Gillham, R.W., "Sampling bias caused by materials used to monitor halocarbons in groundwater," *Environmental Science and Technology*, Vol. 24, No. 1, 1990, pp. 135-142.

Taylor, S. and L.V. Parker, *Surface Changes in Well Casing Pipe Exposed to High Concentrations of Organics in Aqueous Solution*, CRREL Special Report 90-7, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H., 1990.

AUTHOR INDEX

Author Index

Author	Paper Number
Aleckson, K.A.	24
Allen, R.L.	8
Almasi, E.	52, 62
Armour, J.	25
Baker, R.	45
Bath, R.J.	72
Bean, R.M.	12
Beaty, R.D.	15
Beckert, W.F.	57, 63
Benedicto, J.	63
Bollman, M.	3
Brittain, R.	52
Brown, J.R.	76
Brozowski, E.	6
Bruce, M.L.	44, 55, 58
Burkitt, D.	44
Callahan, C.	3
Carl, J.	44
Carlson, R.E.	13
Carlston, R.	76
Carlton, J.E.	71
Carter, K.R.	9, 10, 11
Chen, P.H.	59
Colby, B.W.	40, 56
Combs, D.W.	71
Dandge, V.	25
Davies, G.J.	77
Del Mar, P.	43
Dias, F.	30
Dodhiwala, N.S.	63
Doerge, D.R.	51, 53
Doherty, L.C.	50
Doyi, R.	30
Dupes, L. J.	26
Dwight, D.S.	35
Dyer, F.F.	71
Dymerski, M.	27
Elkins, D.J.	37
Fadeff, S.K.	12
Fencl, M.	28
Fleeker, J.R.	14
Fowler, J.	78
Friedman, S.B.	5, 8
Garrett, J.H.	65
Gillet, C.	3
Goheen, S.C.	12
Graham, W.R.	4
Greenlaw, P.D.	72
Harrison, R.O.	13
Hasty, E.	66
Hecht, C.R.	60
Helms, C.L.	40
Henderson, G.	3
Herzog, D.P.	14
Hewetson, D.	25
Hewitt, A.D.	80
Hiatt. M.H.	42
Hill, B.	29
Hines, L.A.	17
Holley, J.	29
Hottenstein, C.S.	14
Hoyt, M.P.	21, 28
Huckins, J.N.	7
Hudek, J.	72
Hummel, M.	30
Iwanczyk, J.S.	4
Jassie, L.	66
Johnson, A.E.	76
Johnson, K.	31
Jones, C.	73
Jones, T.L.	61
Karnofsky, J.	28
Keeran, W.S.	59
Kendall, D.	75
Kester,P.	41
Killough, B.	44
Kingston, H.M.	66
Kirshen, N.	52, 62
Kocurek, D.	16
Kolopanis, J.W.	60
Kramer, R.	67
Lang, K. T.	2
Lawruk, T.S.	14
Le Brun, G.	46
Lebo, J.A.	7
Lee, J.	23
Lesnik, B.	39
Levy, J.M.	54
Li, W.W.	47
Linder, G.	3
Lindquist, L.	30
Lopez-Avila, V.	61, 63
Lowry, J.	48, 78
Lucero, K. P.	2
Manning, W.B.	8
Marsden, P.	40
Matteson,J.	46
McCulloch, M.	12
Mealy, R.G.	18
Mehra, H.C.	32
Morrissette, S.E.	17
Myers,V.B.	76
Neptune, D.	22
Newberry, W.R.	73
Nwosu, J.	3
Ondracek, A.L.	71
Ott, S.	3
Parker, L.V.	80
Parsons, C.S.	56
Petty, J.D.	7
Phillips, I.A.	19
Phillips, R.E.	72
Poling, G.L.	33
Quinlan, J.F.	77
Ramsey, C.	48, 78
Rethwill, P.	46
Revesz, R.	66
Rhodes, J.E.	6
Riley, R.G.	12
Roberts, D.F.	59
Robertson, G.L.	23
Robinson, L.	71
Robitaille, G.E.	2
Romano, J.P.	69
Root, D.K.	47
Rosecrance, A.	34
Rubio, F.M.	14
Ryan, J.	79
Schoen, M.R.	15
Seeley, I.	79
Shirkhan, H.	65
Siao, M.	70, 78
Simon, Jr., J.R.	48
Smith, J.S.	6
Solch, J.G.	65
Spear, R.D.	72
Speis, D.N.	21
Spilkin, A.J.	74
Stephens, M.W.	44, 55, 58
Stewart, T.M.	8
Stokely, J.R.	71
Strattan, L.W.	70
Suarez, X.	73
Sutton, G.	64
Teasley, N.A.	71
Thomas, F.	60
Thompson, R.A.	33
Tiernan, T.O.	65
Tomayko, R.	58
Tomczak, L.M.	36
Unangst, F.J.	20
VanAusdale, W.A.	59
VanNess, G.F.	65
Wade, J.W.	71
Wagel, D.J.	65
Walters, G.	16
Wang, Y.J.	4
Warden, B.	30
Weichert, B.A.	45
Wilborn, D.	3
Williams, L.R.	1
Winslow, M.G.	45
Withers, T.A.	8
Wolf, M.K.	37
Yang, Z.	68
Youngman, D.R.	42
Zajicek, J.L.	7
Zawodny, P.	35
Zimmerman, M.	49
Zine, T.	44