PROCEEDINGS

THIRD ANNUAL SYMPOSIUM

United States
Environmental Protection Agency
Symposium
on

SOLID WASTE TESTING and QUALITY ASSURANCE

Volume II

JULY 13-17, 1987

WASHINGTON, D.C.
WESTIN HOTEL

Symposium Managed by American Public Works Association

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PROCEEDINGS INTRODUCTION

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

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

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

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HIERARCHICAL APPROACH TO THE ANALYSIS OF HAZARDOUS ORGANIC COMPOUNDS IN WASTE WATERS

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INTRODUCTION

The Resource Conservation and Recovery Act (RCRA)[1] specifies over 300 toxic organic compounds in its Appendix VIII listing which may be used to identify hazardous wastes. In response to a petition by the state of Michigan, the U.S. Environmental Protection Agency (EPA) has proposed the amendment of RCRA Appendix VIII by the addition of over 100 other organic compounds to give a total of over 400 organic constituents.[2] Gas chromatographic methods for determining organic compounds in wastes are given in SW-846, "Test Methods for Evaluating Solid Wastes". In many cases these methods are modifications of procedures for the determination of some, but not all, of the Appendix VIII and Michigan List compounds in wastewater. EPA is currently attempting to validate analytical methods for as many of these 400 plus compounds as possible. A hierarchical approach to these validation efforts is being pursued.

An example of a hierarchical approach to the development and validation of analytical methods for the determination of organic compounds in wastes is presented in Figure 1. This figure is presented to show the context in which the work reported here leads to subsequent method development activities. For example, compounds which are not amenable to determination by GC-MS are to be evaluated in future programs for the feasibility of alternate approaches including special GC conditions, derivatization prior to GC analysis, high performance liquid chromatography (HPLC), and/or non-chromatographic methods. Compounds which are amenable to GC-MS are to be subjected to further method performance evaluation.

Volatile compounds will be evaluated for amenability to the purge-trap-desorb (PTD) techniques described in Method 5030. For compounds which are not successfully recovered from an aqueous matrix using this procedure, alternate procedures such as heated PTD, direct liquid injection (DLI), or the Method 5020 headspace sample introduction technique can then be evaluated. Compounds which are successfully recovered using the Method 5030 room temperature PTD procedure can be included in a validation study of Methods 5030/8240 using procedures described in the Single Laboratory Method Validation Protocol which was developed at Battelle.

The semivolatile compounds shown to be amenable to GC-MS determination will be evaluated for amenability to the extraction procedures described

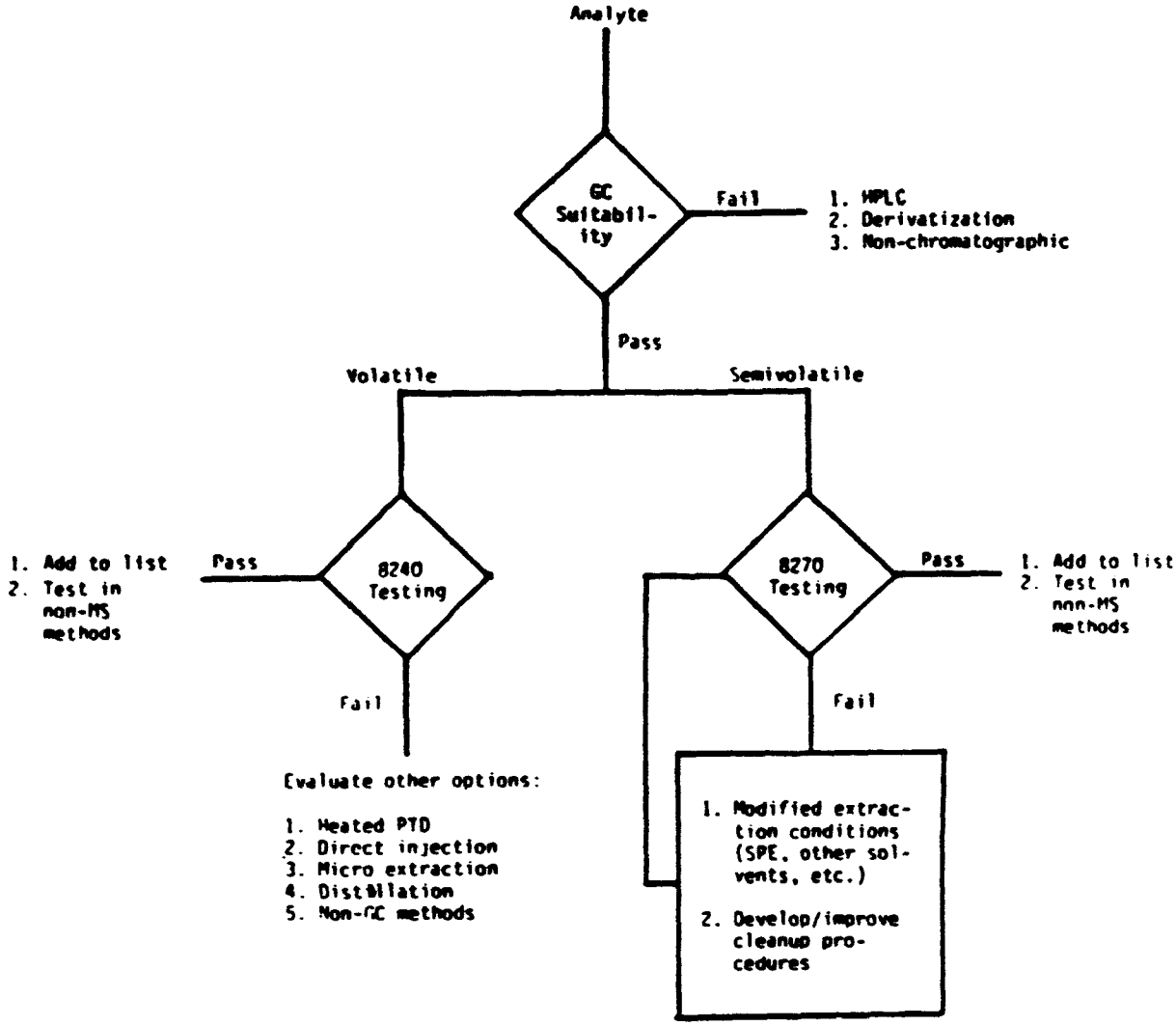

Figure 1. Hierarchical Approach for Analytical Method Development for Organic RCRA Analytes

in Method 8270. For compounds which are not successfully recovered from an aqueous matrix using this procedure, alternate extraction schemes and novel techniques, such as solid phase extraction (SPE), can be considered. Compounds successfully recovered using the Method 8270 extraction procedure can be included in evaluations of several sample cleanup procedures. These investigations will involve fortifying a wide variety of waste matrices with the compounds to permit selection of appropriate cleanup procedures for compounds/sample matrix combinations. Ultimately, these compounds will be included in a validation of Method 8270 using the Single Laboratory Method Validation Protocol.

Implementation of the hierarchical method development approach is expected to result in the development of a suite of analytical methods consisting of a limited number of procedures for the determination of a large proportion of the more than 400 organic compounds. This limited number of analytical procedures for extraction steps, cleanup steps, and determinative steps will form the core of a generic approach to the selection of appropriate analytical methods addressing hazardous wastes. The system will be generic in the sense that the specifications of type of analyte, type of matrix, and type of sensitivity and required specificity will generate, from the limited suite of component analytical procedures, the most appropriate set of analysis conditions.

The reduction in the number and variety of methods required to characterize wastes will provide cost benefits both to the government and to the regulated community. This generic approach will facilitate periodic updates as new information becomes available about specific analytes in specific matrices. Another advantage of this generic approach is that the areas requiring method modification or method development will be clearly identified. Consequently, this collection of research requirements can then be prioritized for resource allocation.

Results from the first phases of this approach are reported in this manuscript and presentation and in two other presentations by Battelle scientists. The first phase defines the scope of work for the research program and involves the identification of compounds which are amenable to GC separation and MS detection. These evaluations involved the analysis of standard solutions using the GC-MS conditions described in the Contractor Laboratory Protocol (CLP) for the application of SW-846 Methods 8240 and 8270 for volatile and semivolatile organic compounds, respectively. Compounds suitable for GC separation and MS detection were classified as candidates for further Method 8240 or Method 8270 testing.

Two subsequent phases were also explored. Volatile compounds determined to be amenable to gas chromatographic separation were evaluated for purging efficiency using three non-MS detection methods, SW-846 Methods 8010, 8015, or 8020. Using results from room temperature PTD and DLI experiments, purging efficiencies can be calculated. The purging efficiencies from room temperature PTD experiments, coupled with GC-MS

data for these compounds, can also be used to select those compounds to be validated by Method 8240.

Semivolatile organic compounds found suitable for GC separation and MS detection were further evaluated for Method 8270 suitability by determining their recovery from water and their seven day aqueous stability using a modified SW-846 Method 3510 extraction procedure. Compounds exhibiting acceptable recovery and stability are candidate compounds to be validated by Method 8270.

EXPERIMENTAL

GC-MS Suitability

The initial set of analytes consisted of organic compounds included in RCRA Appendix VIII[1] plus those included in the Michigan petition[2] minus the EPA priority pollutants. After eliminating redundancies in the two lists, remaining compounds were classified as to their predicted suitability for SW-846 Method 8240 (volatiles), Method 8270 (semivolatiles), or for their predicted inability to be determined by either method.

Sources for the selected analytes were identified in the following order of priority: 1) the EPA repositories of reference compounds and pesticides (EMSL - Las Vegas and RTP), 2) the EPA repository of certified solutions (EMSL - Cincinnati), and 3) commercial suppliers. GC-MS suitability studies were performed using analyte mixtures prepared after consideration of chemical reactivity.

Individual analyte concentrations in the volatile mixtures were 200 ug/mL for most of the analytes or 400 ug/mL for a few analytes predicted to exhibit lower response factors. Injections of volatile analytes provided a minimum of 300 ng of analyte on column. The concentrations of individual semivolatile analytes in the injection standards were 40 ug/mL. For analytes not detected on the first attempt, higher concentrations were employed, ranging from 50-400 ug/mL. Injections of semivolatile analytes provided a minimum of 80 ug of analyte to the splitless injection evaporator cavity. The usual packed GC column, 1 percent SP1000/Carbopack B (Supelco), was used for volatile compounds, and a 30 meter x 0.25 mm ID fused silica coated with 0.25 micron immobilized methyl phenyl silicone (J&W DB-5) was used for semivolatile compounds.

Internal standards specified in the CLP for both volatile and semivolatile analyses were used to provide measures for both GC relative retention indices and MS detection response factors. Surrogate standards specified in the CLP were included in volatile analyte mixtures but not for the semivolatile mixtures. The significantly greater number of these in the latter case would have made data interpretation more difficult without increased usefulness of the results obtained. The CLP GC and MS analysis conditions and MS quality control checks on ion source tuning were used in all cases.

Volatiles Purging Efficiency

The compounds included in this study were chosen from two sources, 1) volatiles listed for each of the three SW-846 Methods and 2) volatiles deemed suitable for GC separation from the GC-MS suitability studies.

Methods 8010, 8015, and 8020 provide packed-column gas chromatographic conditions for the determination of certain volatile organic compounds. Samples were analyzed using these Methods in conjunction with purge-trap-desorb, Method 5030 or direct liquid injection (DLI). Detection is achieved by a halogen specific detector for Method 8010, a flame ionization detector for Method 8015, and a photoionization detector for Method 8020.

Individual standard solutions were combined to form spiking mixtures that would avoid co-elutions. PTD analyses were performed after adding 3 uL of the spiking solution to 5 mL of water. Compound concentrations ranged from 40-800 ug/L and were estimated from previous experience to be high enough to give sufficient response for a reliable calculation of purging efficiency.

Semivolatiles Recovery and Stability

The compounds included in the original scope of Method 3510 performance testing are derived from Appendix VIII[3], the Michigan list[2] and the proposed Appendix IX and borderline chemicals lists.[4] After eliminating redundancies and compounds predicted to be unsuitable for this study, sources were sought for analytes from first, the EPA repositories of reference compounds and pesticides and second, commercial suppliers.

Individual stock and internal standard solutions were prepared. Spiking mixtures were designed to eliminate coelutions since flame ionization detection (FID) was used after GC separation. In addition, acidic and basic compounds were segregated to avoid chemical interactions; different GCs were used to analyze mixtures containing acids or bases.

Spiking mixtures were added to one liter aliquots of water and prepared for GC-FID quantitation using SW-846 Method 3510 modified for the base and acid extraction steps to use one 300-mL aliquot of methylene chloride for each step instead of three 60-mL aliquots in each extraction step. Peak identification was accomplished using an internal standard while quantitation resulted from external calibration. Compound mixtures were injected into a splitless injection evaporator cavity and separated with a 30 m x 0.25 mm ID fused silica capillary column coated with a 0.25 um film of immobilized methyl phenyl silicone (Supelco SPB-5).

Stability studies used the same analytical procedure for spiked water samples that had been stored at approximately 4 C in the dark for 7 days.

RESULTS AND DISCUSSION

GC-MS Suitability

After eliminating EPA priority pollutants from further consideration, 328 compounds were considered for suitability testing. After omitting compounds that were not obtainable and those which were believed to not be within the scope of work for this project, the remaining compounds were classified either as volatiles or semivolatiles.

The 54 volatile analytes tested with Method 8240 GC conditions are listed in Table 1 in which the status is indicated as satisfactorily detected (S), detected with a response factor versus benzene-D_6 below 0.02 (LR), or not detected (ND). Thirty-three analytes were satisfactorily detected and 6 were detected with low response factors. The very low response factors are predicted to result in unacceptably high method detection limit (MDL) values for Method 8240.

Table 1 also lists 15 volatile analytes that were not detected using the Method 8240 conditions. All of these non-detected analytes were analyzed at least twice, with the repeat analysis usually at 2 to 5-fold higher levels than the original 300 ng level. Three of those 15 analytes, hexachloropropene, tetranitromethane, and thiophenol, were thought to have failed to elute due to boiling points and/or polarities that were too high for the SP1000/Carbopack B column, and these compounds were retested using the Method 8270 (semivolatile analyte) conditions.

Non-detection of the hydrazines and aziridines (6 analytes) was probably due to extreme GC peak tailing on the SP1000/Carbopack B column. Five of these nitrogen bases were also tested with the semivolatile analytes. The sixth, N(2-hydroxyethyl)ethyleneimine, was not tested due to its extreme polarity.

2-Butanone peroxide apparently quantitatively decomposed to 2-butanone in the injector. Methyl mercaptan apparently coelutes with methanol on the SP1000/Carbopack B column and, in this case, would be substantially lost at the jet separator due to the presence of the methanol vapor displacement of the helium carrier. The remaining 4 undetected volatile compounds, 2 haloethers, methyl isocyante, and 2-methyllactonitrile, were not repeated in the semivolatile set since they were both too volatile to be recovered in a Kuderna-Danish (KD) distillation of extraction solvent and were also known to be chemically and/or hydrolytically labile.

The 185 semivolatile analytes plus the 8 volatile analytes to be retested with Method 8270 conditions are listed in Table 2. The status is indicated as satisfactorily detected (S), expected to be satisfactory for GC-MS determination based on other information (ES), detected with a response factor less than 0.02 versus phenanthrene-D_{10} (LR), or not detected (ND). There were 128 analytes detected with satisfactory response factors and 9 analytes detected with low response factors. All

9 of these analytes are highly polar and reasonably expected to be sensitive to thermal decomposition in the injection port.

Table 2 contains 11 analytes that are indicated with status "ES", which designates that non-detection of the analyte is considered anomalous. All 11 of these analytes were found to be suitably analyzed by gas chromatography in other projects. Thus, although MS data was not previously obtained, it seems reasonable to classify their non-detection in the present work as anomalous. Except for the two organophosphates, these anomalously non-detected Table 2 analytes are strongly basic molecules, so that a possible explanation for their non-detection would be that the GC column used was somewhat acidic precluding satisfactory elution.

The 45 analytes for which non-detection in the GC-MS data cannot be classified as anomalous are also listed in Table 2. Generally, these analytes are highly polar or are labile to decomposition before or during chromatography. Four of the 45 analytes are aromatic diamines, 1,2- and 1,3-phenylenediamine, 2,4-diaminoanisole, and 1,5-naphthalendiamine. These 4 analytes can probably be analyzed by fused silica GC if special precautions are taken to ensure good performance for basic materials. Ethylene thiourea (ETU) has been shown in previous work in our laboratory to be amenable to GC analysis using special conditions. For another six analytes (acrylamide, cycloheximide, 2-fluoroacetamide, niclosamide, oxydemeton-methyl, and thioacetamide) polarity, volatility and lability considerations apparently do not account for the non-detection, and, therefore, a more thorough attempt to develop GC-based methods might be successful. For the remaining 34 analytes, the causes of non-detection can be classified as one or more of the following: exceptionally high polarity, thermal or chemical lability, or insufficient volatility. Recommendations for further method development for these analytes focus on HPLC techniques, especially ion chromatography or post column derivitization methods.

Volatiles Purging Efficiency

Fifty-seven of the 84 volatile organic compounds included in these experiments produced a measurable recovery for room temperature PTD. The largest group of compounds, those classified as being suitable for Method 8010 evaluation, produced measurable purging efficiencies for 40 of the 53 compounds tested. Ten of the 21 Method 8015-classified compounds and 7 of 10 Method 8020-classified compounds could be detected at room temperature PTD conditions. Tables 3, 4, and 5 show the results for Methods 8010, 8015, and 8020 respectively.

There were 7 compounds (1,2-dibromo-3-chloropropane in Method 8010 experiments and 1,4-dioxane, isobutanol, 2-butanone, 4-methyl-2-pentanone, beta-propiolactone, and propionitrile in Method 8015) for which PTD recoveries were low enough (20% or less) to question their satisfactory validation using room temperature PTD methodology. Four of these compounds have undergone preliminary evaluation using heated PTD; the results will be reported at this symposium.

Precision, as measured by RSD, was 15% or more for only 11 of the 84 tested compounds. Chlorobenzene, chloroform, chloromethane, 1,1-dichloroethane, 1,2-dichloropropane, tetrachloroethylene, trichloroethylene, and vinyl chloride in Method 8010 all have recoveries in the 50-90% range while 1,4-dioxane, 4-methyl-2-pentanone and beta-propiolactone in Method 8015 all had low recoveries.

Semivolatiles Recovery and Stability

An average recovery or stability of less than 70% was considered an indicator of potential incompatibility for future validation testing since a compound must be adequately stored and extracted before being analyzed. Table 6 lists 41 compounds that did not fulfill both 70% criteria. Two of these compounds, dioxathion and dibenz(a,e)pyrene, were not detected in either sample extracts or calibration standards. Dioxathion is perhaps unstable to heat while apparently dibenz(a,e)pyrene did not elute from the GC column during data collection. Possible reasons for poor recovery and/or stability are given in Table 6 and include unfavorable distribution coefficients, hydrolysis during extraction or storage, and oxidation during extraction or storage.

The 115 compounds exhibiting suitable recovery and stability are listed in Table 7. While all 115 compounds are considered candidates for subsequent validation testing, 13 had poor reproducibility. Five compounds, 1,2:7,8-dibenzacridine, 3,3'-dimethoxybenzidine, p-dimethylaminoazobenzene, methyl parathion, and 4,4'-oxydianiline, had relative standard deviation (RSD) values for extraction efficiency greater than 15% on Day 0 and/or Day 7. Ten compounds, carbophenothion, 1,2:7,8-dibenzacridine, dichlorovos, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, fenthion, 4,4'-methylenebis(N,N-dimethylaniline), N-nitrosopyrrolidine, 1,4-phenylenediamine, and sulfallate, had RSD values greater than 15% for GC-FID response factors from the highest level calibration standard (100 ug/mL). Two compounds, 1,2;7,8-dibenzacridene and 3,3'-dimethoxybenzidine exhibited poor reproducibility for both recovery and response factor measures. These 13 compounds may prove not to be suitable for semivolatile analysis when validation studies are performed.

CONCLUSIONS AND RECOMMENDATIONS

The principal conclusion of the studies reported in this manuscript is that the hierarchical approach is a logical means for developing and validating analytical methods for the determination of organic compounds in wastes. Not only will this scheme allow for the logical evaluation of alternative analytical approaches, but the hierarchical system will allow new candidate compounds to be rapidly screened with a limited suite of component analytical procedures.

Recommendations for specific parts of the hierarchical approach discussed in this manuscript are:

- o Of the volatile organic compounds tested for GC-MS suitability and purging efficiency, the 57 listed in Table 8 are recommended for inclusion in SW-846 Method 8240 validation studies.

- o Based on their suitable GC-MS analysis, extraction, and stability, the 115 semivolatile organic compounds listed in Table 7 should be included in SW-846 Method 8270 validation studies. Preliminary experiments should include 1) extraction/stability studies at concentrations lower than the 500 ug/L values used in this investigation and 2) extraction of compounds under conditions milder than the strongly acidic and strongly basic conditions employed in Method 3510. Testing of the compounds failing extraction/ stability criteria may allow some of them to be included in subsequent validation experiments which use milder extraction conditions.

- o Based on results for semivolatile, non-priority pollutant organic compounds, the following changes to proposed Appendix IX are recommended. These compounds affected are contained in Table 9.

    - the 12 compounds listed in Table 9A should be removed from Appendix IX.

    - 3 compounds on the borderline list should be added to Appendix IX (see Table 9B).

    - 10 compounds from Appendix VIII that did not appear on proposed Appendix IX should be included on the Appendix IX list (see Table 9B).

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1. 40 Code of Federal Regulation, Part 261.
2. Federal Register, 49, No. 247, December 21, 1984, pp. 49784-49793.
3. Federal Register, 49, No 191, October 1, 1984, pp. 38786-38809.
4. Federal Register, 51, No. 142, July 24, 1986, pp. 26632-26642.

DISCLAIMER

Although the research described in this article has been funded 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.

TABLE 1. GC-MS SUITABILITY TESTING RESULTS FOR VOLATILE ANALYTES

No.	Substance	List(a)		CAS No.	RCRA Number	Status Code(b)
1	Acetonitrile	8		75-05-8	U003	S
2	Allyl alcohol	8		107-18-6	P005	S
3	Allyl chloride	8	M	107-05-1	U317	S
4	Benzyl chloride	8		100-44-7	P028	S
5	Bis-(2-chloroethyl) sulfide	8	M	505-60-2	P158	LR
6	Bis(chloromethyl) ether	8		542-88-1		ND
7	Bromoacetone	8		598-31-2	P017	S
8	2-Butanone peroxide	8		1338-23-4	U160	ND
9	2-Butanone	8		78-93-3		S
10	Carbon disulfide	8		75-15-0		S
11	Chloral hydrate	8		75-87-6	U034	LR
12	2-Chloroethanol		M	107-07-3	P133	LR
13	Chloromethyl methyl ether	8		107-30-2	U046	ND
14	Chloroprene	8	M	126-99-8	U276	S
15	3-Chloropropionitrile	8		542-76-7	P027	S
16	1,2-Dibromo-3-chloropropane	8		96-12-8		S
17	Dibromomethane	8		74-95-3		S
18	1,4-Dichloro-2-butene	8		764-41-0	U074	S
19	Dichlorodifluoromethane	8		75-71-8		S
20	1,3-Dichloro-2-propanol	8		96-23-1		S
21	1,2,3,4-Diepoxybutane	8		1464-53-5	U085	S
22	1,1-Dimethylhydrazine	8		57-14-7	U098	ND
23	1,2-Dimethylhydrazine	8		540-73-8	U099	ND
24	1,4-Dioxane	8		123-91-1	U108	S
25	Epichlorohydrin	8		106-89-8		S
26	Ethylene dibromide	8		106-93-4		S
27	Ethylene oxide	8		75-21-8	U115	S
28	Ethylenimine	8		151-56-4	P054	ND
29	Ethyl methacrylate	8		97-63-2	U118	S
30	Hexachloropropene	8		1888-71-7	U243	ND
31	N-(2-Hydroxyethyl)ethyleneimine		M	1072-52-2	U289	ND
32	2-Hydroxypropionitrile		M	78-97-7		LR
33	Isobutyl alcohol	8		78-83-1		S
34	Malononitrile	8		109-77-3	U149	S
35	Methacrylonitrile	8		126-98-7	U152	S
36	2-Methylaziridine	8		75-55-8	P067	ND
37	Methylhydrazine	8		60-34-4	P068	ND
38	Methyl iodide	8		74-88-4	U138	S
39	Methyl isocyanate	8		624-83-9	P064	ND
40	2-Methyllactonitrile	8		75-86-5	P069	ND
41	Methyl mercaptan	8		74-93-1		ND
42	Methyl methacrylate	8		80-62-6	U162	S
43	Pentachloroethane	8		76-01-7		S
44	2-Picoline	8		109-06-8	U191	S
45	Propargyl alcohol	8		107-19-7	P102	LR
46	β-Propiolactone		M	57-57-8	U302	S
47	Propionitrile	8		107-12-0	P101	S
48	N-Propylamine	8		107-10-8	U194	LR
49	Pyridine	8		110-86-1	U196	S
50	Styrene		M	100-42-5	U323	S
51	1,1,1,2-Tetrachloroethane	8		630-20-6		S
52	Tetranitromethane	8		509-14-8	P112	ND
53	Thiophenol	8		108-98-5	P104	ND
54	1,2,3-Trichloropropane	8		96-18-4		S

(a) 8 = Appendix VIII; M = Michigan list

(b) LR: low response factor
S: suitable for GC-MS analysis
ND: not detected in GC-MS data

TABLE 2. GC-MS SUITABILITY TESTING RESULTS FOR SEMIVOLATILE ANALYTES

No.	Substance	List(a)		CAS No.	RCRA Number	Status Code(b)
1	Acetophenone	8		98-86-2	U004	S
2	2-Acetylaminofluorene	8		53-96-3	U005	S
3	1-Acetyl-2-thiourea	8		591-08-2	P002	LR
4	Acrylamide	8		79-06-1		ND
5	Aldicarb	8		116-06-3		ND
6	2-Aminoanthraquinone		M	117-79-3	U264	S
7	Aminoazobenzene		M	60-09-3	U257	S
8	4-Aminobiphenyl	8	M	92-67-1	U274	S
9	3-Amino-9-ethylcarbazole		M	132-32-1	U253	ES
10	Amitrole	8		61-82-5	U011	ND
11	Anilazine		M	101-05-3	U333	S
12	Aniline	8		62-53-3		ES
13	o-Anisidine		M	90-04-0	U260	S
14	Aramite	8	M	140-57-8	U326	S
15	Auramine	8		492-80-8	U014	ND
16	Azinphos-methyl		M	86-50-0	P151	S
17	Barban		M	101-27-9	U280	LR
18	Benomyl		M	17804-35-2	U271	ND
19	p-Benzoquinone	8		106-51-4	U197	S
20	Bromoxynil		M	1689-84-5	U272	S
21	Brucine	8		357-57-3	P018	ND
22	Captafol		M	2425-06-1	U285	S
23	Captan		M	133-06-2	U266	S
24	Carbaryl		M	63-25-2	U279	S
25	Carbofuran		M	1563-66-2	U127	S
26	Carbophenothion		M	786-19-6	U148	S
27	Chlorfenvinphos		M	470-90-6	P143	S
28	4-Chloroaniline	8		106-47-8		S
29	Chlorobenzilate	8		510-15-6	U038	S
30	5-Chloro-2-methylaniline		M	95-79-4	U329	S
31	3-(Chloromethyl)pyridine hydrochloride		M	6959-48-4	U319	S
32	4-Chloro-1,3-phenylenediamine		M	5131-60-2	U305	ES
33	4-Chloro-1,2-phenylenediamine		M	95-83-0	U306	ES
34	Coumaphos		M	56-72-4	P130	S
35	p-Cresidine		M	120-71-8	U262	S
36	Crotoxyphos		M	7700-17-6	U238	S
37	Cupferron		M	135-20-6	U290	ND
38	Cycloheximide		M	66-81-9	P134	ND
39	2-Cyclohexyl-4,6-dinitrophenol	8		131-89-5	P034	LR
40	Cyclophosphamide	8		50-18-0	U058	ND
41	Demeton		M	8065-48-3	P155	S
42	Diallate	8		2303-16-4	U062	S
43	2,4-Diaminoanisole sulfate		M	39156-41-7	U307	ND
44	2,4-Diaminotoluene	8	M	95-80-7	U327	S
45	Diazinon		M	333-41-5	U313	ES
46	1,2:7,8-Dibenzacridine	8		224-42-0		S
47	1,2:4,5-Dibenzopyrene	8		192-65-4		S
48	Dichlone		M	117-80-6	U299	S
49	2,6-Dichlorophenol	8		87-65-0		S
50	Dichlorovos		M	62-73-7	P144	S
51	Dicrotophos		M	141-66-2	P146	S
52	Diethylstilbestrol	8		56-53-1	U086	S
53	Diethyl sulfate		M	64-67-5	U325	LR
54	Dihydrosafrole	8		56312-13-1	U090	ND
55	Dimethoate	8		60-51-5		S
56	3,3'-Dimethoxybenzidine	8		119-90-4	U091	LR
57	1,4-Dimethylaminoazobenzene	8		60-11-7	U093	S
58	7,12-Dimethylbenz(a)anthracene	8		57-97-6	U094	S
59	3,3'-Dimethylbenzidine	8		119-93-7	U095	S
60	1,1-Dimethylhydrazine	8		57-14-7	U098	ND
61	1,2-Dimethylhydrazine	8		540-73-8	U099	ND
62	α,α-Dimethylphenethylamine	8		122-09-8	P046	S
63	1,2-Dinitrobenzene	8		99-65-0		S
64	1,3-Dinitrobenzene	8		528-29-0		S

TABLE 2. (Continued)

No.	Substance	List(a)		CAS No.	RCRA Number	Status Code(b)
65	1,4-Dinitrobenzene	8		100-25-4		S
66	Dinocap		M	39300-45-3	U284	S
67	Dinoseb	8		88-85-7		S
68	Dioxathion		M	78-34-2	P153	S
69	5,5-Diphenylhydantoin		M	57-41-0		S
70	1,2-Diphenylhydrazine	8		122-66-7	U109	ND
71	Disulfoton	8		298-04-4		S
72	EPN		M	2104-64-5	P141	S
73	Ethion		M	563-12-2	P154	S
74	Ethyl carbamate	8		51-79-6	U238	S
75	Ethylenimine	8		151-56-4	P054	ND
76	Ethylene thiourea	8		96-45-7		ND
77	Ethyl methanesulfonate	8		62-50-0	U119	S
78	Famphur	8		52-85-7	P097	S
79	Fensulfothion		M	115-90-2	P156	S
80	Fenthion		M	55-38-9		S
81	Fluchloralin		M	33245-39-5	U330	S
82	2-Fluoroacetamide	8		640-19-7	P057	ND
83	Hexachlorophene	8		70-30-4	U132	S
84	Hexachloropropene	8		1888-71-7	U243	S
85	Hexamethyl phosphoramide		M	680-31-9	U312	S
86	Hydroquinone		M	123-31-9		S
87	Isodrin	8		465-73-6	P060	S
88	Isonicotinic acid hydrazide		M	54-85-3		ND
89	Isosafrole	8		120-58-1	U141	S
90	Kepone	8		143-50-0		S
91	Leptophos		M	21609-90-5	P140	S
92	Malathion		M	121-75-5	U324	S
93	Maleic anhydride	8		108-31-6	U147	S
94	Maleic hydrazide	8		123-33-1		ND
95	Mestranol		M	72-33-3	U301	S
96	Methapyrilene	8		91-80-5	U155	S
97	Methomyl	8		16752-77-5	P066	ND
98	p,p'-Methoxychlor	8		72-43-5		S
99	2-Methylaziridine	8		75-55-8	P067	ND
100	3-Methylcholanthrene	8		56-49-5	U157	S
101	4,4'-Methylenebis(2-chloroaniline)	8		101-14-4	U158	LR
102	4,4'-Methylenebis(N,N-dimethylaniline)		M	101-61-1	U255	ES
103	Methylhydrazine	8		60-34-4	P068	ND
104	Methyl methanesulfonate	8				S
105	N-Methyl-N-nitro-N-nitrosoguanidine	8		70-25-7	U163	ND
106	Methyl parathion	8		298-00-0		S
107	2-Methylphenol	8		95-48-7		S
108	3-Methylphenol	8		108-39-4		S
109	4-Methylphenol	8		106-44-5		S
110	Methylthiouracil	8		56-04-2	U164	ND
111	Mevinphos		M	7786-34-7	P131	S
112	Mexacarbate		M	315-18-4	P128	S
113	Mirex		M	2385-85-5	U297	S
114	Monocrotophos		M	6923-22-4	P147	S
115	Naled		M	300-76-5	U309	S
116	1,5-Naphthalenediamine		M	2243-62-1	U298	ND
117	1,4-Naphthoquinone	8		130-15-4	U166	S
118	1-Naphthylamine	8		134-32-7	U167	S
119	2-Naphthylamine	8		91-59-8	U168	ES
120	1-Naphthyl-2-thiourea	8		86-88-4	P072	ND
121	Niclosamide		M	50-65-7	U321	ND
122	Nicotine	8		54-11-5	P075	S
123	5-Nitroacenaphthene		M	602-87-9	U250	S
124	4-Nitroaniline	8		100-01-6		S
125	5-Nitro-o-anisidine		M	99-59-2	U263	S
126	4-Nitrobiphenyl		M	92-93-3	U275	S
127	Nitrofen		M	1836-75-5	U288	S
128	Nitrogen mustard	8	M	51-75-2	P132	ND

TABLE 2. (Continued)

No.	Substance	List(a)		CAS No.	RCRA Number	Status Code(b)
129	Nitroglycerine	8		55-63-0	P081	ND
130	5-Nitro-o-toluidine	8		99-55-8	U181	S
131	4-Nitroquinoline-1-oxide	8		56-57-5		S
132	N-Nitrosodibutylamine	8		924-16-3		S
133	N-Nitrosodiethanolamine	8		1116-54-7	U173	ND
134	N-Nitrosodiethylamine	8		55-18-5		S
135	p-Nitrosodiphenylamine		M	156-10-5	U287	ES
136	N-Nitroso-N-ethylurea	8		759-73-9	U176	ND
137	N-Nitrosomethylethylamine	8		10595-95-6		S
138	N-Nitroso-N-methylurea	8		684-93-5	U177	ND
139	N-Nitroso-N-methylurethane	8		615-53-2	U178	ND
140	N-Nitrosomorpholine	8		59-89-2		ES
141	N-Nitrosopiperidine	8		100-75-4	U176	S
142	N-Nitrosopyrrolidine	8		930-55-2		S
143	Octamethylpyrophosphoramide	8		152-16-9	P085	LR
144	Oxydemeton-methyl		M	301-12-2	P157	ND
145	4,4'-Oxydianiline		M	101-80-4	U303	S
146	Parathion ethyl	8		56-38-2		S
147	Pentachlorobenzene	8		608-93-5		S
148	Pentachloronitrobenzene	8		82-68-8		S
149	Phenacetin	8		62-44-2	U187	S
150	Phenazopyridine hydrochloride		M	136-40-3	U320	ND
151	Phenobarbital		M	50-06-6	U268	S
152	1,2-Phenylenediamine	8		95-54-5		ND
153	1,3-Phenylenediamine	8		108-45-2		ND
154	1,4-Phenylenediamine	8		106-50-3		S
155	N-Phenylthiourea	8		103-85-5	P093	ND
156	Phorate	8		298-02-2		S
157	Phosalone	8		2310-17-0		S
158	Phosmet		M	732-11-6		S
159	Phosphamidon		M	13171-21-6	P145	S
160	Phthalic anhydride	8		85-44-9	U190	S
161	Piperonyl sulfoxide		M	120-62-7	U270	S
162	Pronamide	8		23950-58-5		S
163	1,3-Propane sultone	8		1120-71-4	U193	ND
164	Propylthiouracil	8	M	51-52-5	U334	LR
165	Resorcinol	8		108-46-3		S
166	Rotenone		M	83-79-4	U273	ND
167	Saccharin	8		81-07-2	U202	ND
168	Safrole	8		94-59-7	U203	S
169	Strychnine	8		57-24-9		S
170	Sulfallate		M	95-06-7	U277	S
171	Terbufos		M	13071-79-9	P149	S
172	1,2,4,5-Tetrachlorobenzene	8		95-94-3		S
173	2,3,4,6-Tetrachlorophenol	8		58-90-2		S
174	Tetrachlorvinphos		M	961-11-5	U308	S
175	Tetraethyl dithiopyrophosphate	8		3689-24-5	P109	ES
176	Tetraethyl pyrophosphate	8		107-49-3		S
177	Tetranitromethane	8		509-14-8	P112	ND
178	Thioacetamide	8		62-55-5	U128	S
179	Thiofanox	8		39196-18-4	P045	ND
180	Thionazine	8		297-97-2	P040	S
181	Thiophenol	8		108-98-5	P104	S
182	Toluene diisocyanate	8		584-84-9	U223	S
183	o-Toluidine	8	M	95-53-4	U328	S
184	Trichlorfon		M	52-68-6	P139	ND
185	2,4,5-Trichlorophenol	8		95-95-4		S
186	O,O,O-Triethyl phosphorothioate	8		126-68-1		ES
187	Trifluralin		M	1582-09-8	U332	S

TABLE 2. (Continued)

No.	Substance	List(a)	CAS No.	RCRA Number	Status Code(b)
188	2,4,5-Trimethylaniline	M	137-17-7	U259	S
189	Trimethyl phosphate	M	512-56-1	U810	S
190	1,3,5-Trinitrobenzene	8	99-35-4	U234	S
191	Tris(2,3-dibromopropyl) phosphate	8	126-72-7	U235	LR
192	Tri-p-tolyl phosphate(c)	M	78-32-0		S
193	Warfarin	8	81-81-2	P001	ND

(a) 8 = Appendix VIII; M = Michigan list

(b) S - apparantly suitable for GC-MS analysis
LR - low response; response factor, versus phenanthrene-D10, less than 0.02
ND - not detected
ES - expected to be suitable for GC-MS analysis but not detected in this study

(c) Substituted for the non-specific mixture, tricresyl phosphate

TABLE 3. ROOM TEMPERATURE PTD RECOVERIES OF COMPOUNDS BY USE OF SW-846 METHOD 8010

No.	Substance	List(a)	CAS No.	Conc. (ug/L)	Recovery (percent)(b) Mean	RSD
1	Allyl chloride	9 B	107-05-1	40	88	2
2	Benzyl chloride	8	100-44-7	800	25	6
3	Bis(2-chloroethoxy)methane	9	111-91-1	(c)		
4	Bis(2-chloroethyl)sulfide	M	505-60-2	400	ND (d)	
5	Bis(2-chloroisopropyl)ether	9	108-60-1	(c)		
6	Bromoacetone	8	598-31-2	400	ND	
7	Bromobenzene	(e)	108-86-1	100	81	4
8	Bromodichloromethane	9	75-27-4	200	107	1
9	Bromoform	9	75-25-2	200	65	12
10	Bromomethane	9	74-83-9	100	77	12
11	Carbon tetrachloride	9	56-23-5	100	81	6
12	Chloroacetaldehyde	8	107-20-0	(c)		
13	Chloral hydrate	8	75-87-6	400	ND	
14	Chlorobenzene	9	108-90-7	100	51	20
15	Chloroethane	9	75-00-3	100	85	13
16	2-Chloroethanol	M	107-07-3	400	ND	
17	2-Chloroethyl vinyl ether	9	110-75-8	160	ND	
18	Chloroform	9	67-66-3	100	88	18
19	1-Chlorohexane	(e)	544-10-5	80	76	3
20	Chloromethane	9	74-87-3	100	73	18
21	Chloromethyl methyl ether	8	107-30-2	400	ND	2
22	Chloroprene	9 B	126-99-8	400	90	4
23	3-Chloropropionitrile	9 B	542-76-7	400	ND	
24	Chlorotoluene	(e)	95-49-8	80	83	4
25	Dibromochloromethane	9	124-48-1	80	109	5
26	1,2-Dibromo-3-chloropropane	9	96-12-8	160	14	8
27	1,2-Dibromoethane	9	106-93-4	80	71	6
28	1,2-Dichlorobenzene	9	95-50-1	160	83	1
29	1,3-Dichlorobenzene	9	541-73-1	80	82	2
30	1,4-Dichlorobenzene	9	106-46-7	160	80	2
31	1,4-Dichloro-2-butene	9	110-57-6	160	30	7
32	Dichlorodifluoromethane	9 B	75-71-8	80	109	1
33	1,1-Dichloroethane	9	75-34-3	100	86	16
34	1,2-Dichloroethane	9	107-06-2	200	103	1
35	1,1-Dichloroethylene	9	75-35-4	100	78	3
36	trans-1,2-Dichloroethylene	9	156-60-5	200	107	3
37	1,2-Dichloropropane	9	78-87-5	100	90	18
38	1,3-Dichloro-2-propanol	B	96-23-1	400	ND	
39	1,3-Dichloropropene	9	10061-01-5	400	100	1
40	Epichlorohydrin	8	106-89-8	400	ND	
41	Methylene bromide	9	75-95-3	40	78	4
42	Methylene chloride	9	75-09-2	100	86	14
43	Methyl iodide	9 B	74-88-4	80	87	3
44	Pentachloroethane	9	76-01-7	(f)		
45	1,1,2,2-Tetrachloroethane	9	79-34-5	200	102	2

TABLE 3. (Continued)

No.	Substance	List(a)	CAS No.	Conc. (ug/L)	Recovery (percent)(b) Mean	RSD
46	1,1,1,2-Tetrachloroethane	9	630-20-6	160	85	7
47	Tetrachloroethylene	9	127-18-4	100	51	17
48	1,1,1-Trichloroethane	9	71-55-6	200	97	4
49	1,1,2-Trichloroethane	9	79-00-5	40	83	5
50	Trichloroethylene	9	79-01-6	100	85	15
51	Trichlorofluoromethane	9	75-69-4	100	82	13
52	1,2,3-Trichloropropane	9	96-18-4	40	50	7
53	Vinyl chloride	9	75-01-4	100	81	16

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986 pp 26639-26642.
B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
M = Michigan list of chemicals proposed to be added to Appendix VIII to Part 261 and and published in the Federal Register, 49, No. 247, December 21, 1984, p 49793.
8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan Lists.
(b) Calculated from three replicates by comparing PTD vs DLI peak areas.
(c) Apparent decomposition in solution and/or on-column.
(d) ND = not detected.
(e) Included on SW-846 Method 8010 list but not present on proposed Appendix IX, borderline chemicals, Michigan, or Appendix VIII lists.
(f) Poor chromatographic behavior on the system used.

TABLE 4. ROOM TEMPERATURE PTD RECOVERIES OF COMPOUNDS BY USE OF SW-846 METHOD 8015

No.	Substance	List(a)	CAS No.	Conc. (ug/L)	Recovery (percent)(b) Mean	RSD
1	Acetonitrile	B	75-05-8	800	(c)	
2	Acrylamide	8	79-06-1	800	ND (d)	
3	Allyl alcohol	9 B	107-18-6	800	ND	
4	Carbon disulfide	9	75-15-0	200	ND	
5	1,2,3,4-Diepoxybutane	8	1464-53-5	800	ND	
6	Diethyl ether	(e)	60-29-7	200	90	11
7	1,4-Dioxane	9 B	123-91-1	800	1	100
8	Ethylene oxide	9 B	75-21-8	800	(f)	
9	Ethyl methacrylate	9	97-63-2	200	55	14
10	2-Hydroxypropionitrile	M	78-97-7	(g)		
11	Isobutanol	9	78-83-1	800	2	(b)
12	Malononitrile	9 B	109-77-3	800	ND	
13	Methacrylonitrile	9 B	126-98-7	800	37	(b)
14	Methyl ethyl ketone	9	78-93-3	200	14	12
15	Methyl mercaptan	(h)	74-93-1	200	(f)	
16	Methyl methacrylate	9	80-62-6	200	55	11
17	4-Methyl-2-pentanone	9	108-10-1	200	20	35
18	Paraldehyde	8	123-63-7	800	ND	
19	Propargyl alcohol	9 B	107-19-7	800	ND	
20	beta-Propiolactone	M	57-57-8	800	1	100
21	Propionitrile	9 B	107-12-0	800	7	14

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986 pp 26639-26642.
B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
M = Michigan list of chemicals proposed to be added to Appendix VIII to Part 261 and and published in the Federal Register, 49, No. 247, December 21, 1984, p 49793.
8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan Lists.

(b) Calculated from three replicates except for isobutanol and methacrylonitrile which had two replicates. Recovery calculated for PTD vs DLI peak areas.

(c) Interference from methanol, the solvent used to prepare the spiking solutions.

(d) ND = not detected.

(e) Included on SW-846 Method 8015 list but not present on proposed Appendix IX, borderline chemicals, Michigan, or Appendix VIII lists.

(f) Not retained on the trap used for SW-846 Method 8015.

(g) Poor chromatographic behavior under conditions specified by SW-846 Method 8015.

(h) Included on an earlier version of Appendix VIII, not on the August 6, 1986 revised list.

TABLE 5. ROOM TEMPERATURE PTD RECOVERIES OF COMPOUNDS BY USE OF SW-846 METHOD 8020

No.	Substance	List(a)	CAS No.	Conc. (ug/L)	Recovery (percent)(b) Mean	RSD
1	Benzene	9	71-43-2	200	77	8
2	Benzenethiol	9 B	108-98-5	(c)		
3	Ethylbenzene	9	100-41-4	200	94	1
4	2-Picoline	9 B	109-06-8	(c)		
5	Pyridine	9	110-86-1	(c)		
6	Styrene	9	100-42-5	200	86	7
7	Toluene	9	108-88-3	200	99	2
8	o-Xylene	9	(d)	200	92	8
9	m-Xylene	9	(d)	200	99	1
10	p-Xylene	9	(d)	200	98	1

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986 pp 26639-26642.
B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
M = Michigan list of chemicals proposed to be added to Appendix VIII to Part 261 and and published in the Federal Register, 49, No. 247, December 21, 1984, p 49793.
8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan Lists.

(b) Calculated for three replicates by comparing PTD vs DLI peak areas.

(c) Poor chromatographic behavior under conditions specified by SW-846 Method 8020

(d) Listed in proposed Appendix IX as, Xylene (total) with CAS No. 1330-20-7.

TABLE 6. COMPOUNDS WITH AVERAGE RECOVERIES AND/OR AQUEOUS STABILITIES LESS THAN 70 PERCENT

No.	Substance	List(a)	Percent Recovery	Percent Stability(b)	Comments(c)
1	Aramite(Isomers 1 and 2)	9		54,52	HS
2	Azinphos-methyl	M		62	HS
3	Benzenethiol	9 B	33	(d)	CP,OE,OS
4	p-Benzoquinone	9 B	0		OE
5	Captafol	M		55	HS
6	Captan	M		40	HS
7	Demeton-O	M		68	HS
8	2,4-Diaminoanisole sulfate	M	60		DC,OE
9	2,4-Diaminotoluene	M	42		DC,OE
10	Dibenzo(a,e)pyrene	9 B	(d)	(d)	LE
11	Dichlone	M	0		OE
12	Diethylstilbestrol	8		67	AW,OS
13	Dihydrosafrole	8		10	HS
14	Dimethoate	B	31		HE,HS
15	7,12-Dimethylbenz(a)anthracene	9		45	CP
16	1,4-Dinitrobenzene	9	14		HE
17	Dinocap	M		28	CP,HS
18	Dioxathion	M	(d)	(d)	CP
19	Ethyl carbamate	8	28		DC
20	Hexachlorophene	9		62	AW,CP
21	Isosafrole	9 B	46		DC
22	Malathion	M		5	HS
23	Maleic anhydride	8	0		HE
24	Malononitrile	9 B	9		CP,DC
25	4,4'-Methylenebis(2-chloroaniline)	9	33	0	OE,OS
26	Mexacarbate	M		68	HE,HS
27	Monocrotophos	M	26		HE
28	1-Naphthylamine	9		44	OS
29	Nicotine	8	67		OE
30	Pentachloroethane	9	64	4	HE,HS
31	1,2-Phenylenediamine	8	32		DC,OE
32	1,3-Phenylenediamine	8	19		DC,OE
33	Phosalone	(e)		65	HS
34	Phosmet	M		15	HS
35	Phosphamidon	M	63		HE
36	Phthalic anhydride	8	1	67	CP,DC,HE,HS
37	Resorcinol	9 B	10		DC,OE
38	Strychnine	8		55	AW,OS
39	Thioacetamide	8	1		DC
40	Toluene diisocyanate	8		6	HE
41	Trimethyl phosphate	M	60		HE

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986, pp. 26639-26642.

TABLE 6. (Continued)

B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
M = Michigan list of chemicals proposed to be added to Appendix VIII to Part 261 and and published in the Federal Register, 49, No. 247, December 21, 1984, p. 49793
8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan lists.

(b) Percent Stability = Ave Recovery (Day 7) x 100/Ave Recovery (Day 0).

(c) Comments:
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient.
HE = Hydrolysis during extraction accelerated by acidic or basic conditions.
HS = Hydrolysis during storage.
LE = Late eluting compound.
OE = Oxidation during extraction accelerated by basic conditions.
OS = Oxidation during storage.

(d) Compound not detected in either sample extracts or calibration standards.

(e) Included in an earlier version of Appendix VIII but not on the August 6, 1986 revised list.

TABLE 7. COMPOUNDS TENTATIVELY RECOMMENDED FOR INCLUSION IN SW-846 METHOD 3510(a)

No.	Substance	CAS No.	RCRA No.	List(b)
1	Acetophenone	98-86-2	U004	9
2	2-Acetylaminofluorene	53-96-3	U005	9 B
3	2-Aminoanthraquinone	117-79-3	U264	M
4	Aminoazobenzene	60-09-3	U257	M
5	4-Aminobiphenyl	92-67-1	U274	9
6	3-Amino-9-ethylcarbazole	132-32-1	U253	M
7	Anilazine	101-05-3	U333	M
8	Aniline	62-53-3		9 B
9	o-Anisidine	90-04-0	U260	M
10	Benzyl alcohol	100-51-6		9
11	Bromoxynil	1689-84-5	U272	M
12	2-sec-Butyl-4,6-dinitrophenol	88-85-7		9 B
13	Carbaryl	63-25-2	U279	M
14	Carbofuran	1563-66-2	U127	M
15	Carbophenothion(d)	786-19-6	U148	M
16	Chlorfenvinphos	470-90-6	P143	M
17	4-Chloroaniline	106-47-8		9
18	Chlorobenzilate	501-15-6		9
19	5-Chloro-2-methylaniline	95-79-4	U329	M
20	3-(Chloromethyl)pyridine hydrochloride	6959-48-4	U319	M
21	4-Chloro-1,2-phenylenediamine	95-83-0	U306	M
22	4-Chloro-1,3-phenylenediamine	5131-60-2	U305	M
23	Coumaphos	56-72-4	P130	M
24	p-Cresidine	120-71-8	U262	M
25	Crotoxyphos	7700-17-6	U238	M
26	2-Cyclohexyl-4,6-dinitrophenol	131-89-5	P034	8
27	Demeton-S	126-75-0		M
28	Diallate	2303-16-4	U062	B
29	Diazinon	333-41-5	U313	M
30	1,2:7,8-Dibenzacridine(c,d)	224-42-0		8
31	Dibenzofuran	132-64-9		9
32	1,2-Dibromo-3-chloropropane	96-12-8		9
33	2,6-Dichlorophenol	87-65-0		9
34	Dichlorovos(d)	62-73-7	P144	M
35	Dicrotophos	141-66-2	P146	M
36	3,3'-Dimethoxybenzidine(c,d)	119-90-4	U091	9
37	p-Dimethylaminoazobenzene(c)	60-11-7	U093	9
38	3,3-Dimethylbenzidine(d)	119-93-7	U095	9
39	1,2-Dinitrobenzene	528-29-0		8
40	1,3-Dinitrobenzene	99-65-0		8
41	Diphenylamine	122-39-4		9 B
42	5,5-Diphenylhydantoin	57-41-0		M
43	Disulfoton	298-04-4		9
44	EPN	2104-64-5	P141	M
45	Ethion	563-12-2	P154	M
46	Ethyl methanesulfonate	62-50-0	U119	8
47	Ethyl parathion	56-38-2		9
48	Famphur	52-85-7	P097	9

TABLE 7. (Continued)

No.	Substance	CAS No.	RCRA No.	List(b)
49	Fensulfothion	115-90-2	P156	M
50	Fenthion(d)	55-38-9		M
51	Fluchloralin	33245-39-5	U330	M
52	Hexachloropropene	1888-71-7	U243	9 B
53	Hexamethyl phosphoramide	680-31-9	U312	M
54	Isodrin	465-73-6	P060	9 B
55	Kepone	143-50-0		9 B
56	Leptophos	21609-90-5	P140	M
57	Mestranol	72-33-3	U301	M
58	Methapyrilene	91-80-5	U155	9
59	Methoxychlor	72-43-5		9
60	3-Methylcholanthrene	56-49-5	U157	9
61	4,4'-Methylenebis(N,N-dimethylaniline)(d)	101-61-1	U255	M
62	Methyl methanesulfonate	66-27-3		9
63	2-Methylnaphthalene	91-57-6		9
64	2-Methyl-5-nitroaniline	99-55-8	U181	9
65	Methyl parathion(c)	298-00-0		9
66	2-Methylphenol	95-48-7		9
67	3-Methylphenol	108-39-4		B
68	4-Methylphenol	106-44-5		9
69	2-Methylpyridine	109-06-8	U191	9 B
70	Mevinphos	7786-34-7	P131	M
71	Mirex	2385-85-5	U297	M
72	Naled	300-76-5	U309	M
73	1,4-Naphthoquinone	130-15-4	U166	9
74	2-Naphthylamine	91-59-8	U168	9
75	5-Nitroacenaphthene	602-87-9	U250	M
76	2-Nitroaniline	88-74-4		9
77	3-Nitroaniline	99-09-2		9
78	4-Nitroaniline	100-01-6		9
79	5-Nitro-o-Anisidine	99-59-2	U263	M
80	4-Nitrobiphenyl	92-93-3	U275	M
81	Nitrofen	1836-75-5	U288	M
82	4-Nitroquinoline-1-oxide	56-57-5		8
83	N-Nitrosodi-n-butylamine	924-16-3		9
84	N-Nitrosodiethylamine	55-18-5		9
85	p-Nitrosodiphenylamine	156-10-5	U287	M
86	N-Nitrosomethylethylamine	10595-95-6		9 B
87	N-Nitrosomorpholine	59-89-2		9
88	N-Nitrosopiperidine	100-75-4	U176	9
89	N-Nitrosopyrrolidine(d)	930-55-2		9
90	4,4'-Oxydianiline(c)	101-80-4	U303	M
91	Pentachlorobenzene	608-93-5		9
92	Pentachloronitrobenzene	82-68-8		9
93	Phenacetin	62-44-2	U187	9
94	Phenobarbital	50-06-6	U268	M
95	1,4-Phenylenediamine(d)	106-50-3		8
96	Phorate	298-02-2		9

TABLE 7. (Continued)

No.	Substance	CAS No.	RCRA No.	List(b)
97	Piperonyl sulfoxide	120-62-7	U270	M
98	Pronamide	23950-58-5		9
99	Safrole	94-59-7	U203	9
100	Sulfallate(d)	95-06-7	U277	M
101	Terbufos	13071-79-9	P149	M
102	1,2,4,5-Tetrachlorobenzene	95-94-3		9
103	2,3,4,6-Tetrachlorophenol	58-90-2		9
104	Tetrachlorvinphos	961-11-5	U308	M
105	Tetraethyl dithiopyrophosphate	3689-24-5	P109	9 B
106	Tetraethyl pyrophosphate	107-49-3		8
107	Thionazine	297-97-2	P040	9
108	o-Toluidine	95-53-4	U328	B M
109	2,4,5-Trichlorophenol	95-95-4		9
110	O,O,O-Triethyl phosphorothioate	126-68-1		8
111	Trifluralin	1582-09-8	U332	M
112	2,4,5-Trimethylaniline	137-17-7	U259	M
113	1,3,5-Trinitrobenzene	99-35-4	U234	8
114	Tri-p-tolyl phosphate	1330-78-5		M
115	Tris-(2,3-dibromopropyl) phosphate	126-72-7	U235	9 B

(a) Based on a compound having demonstrated both extractability and aqueous stability values equal to or greater than 70%.

(b) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986, pp. 26639-26642.
B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
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8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan lists.

(c) Compounds exhibiting either day 0 or day 7 recoveries with relative standard deviations greater than 15 percent.

(d) Compounds with calibration response factors having relative standard deviations greater than 15 percent.

TABLE 8. COMPOUNDS RECOMMENDED FOR INCLUSION IN SW-846 METHOD 8240 VALIDATION STUDY

No.	Substance	List(a)	CAS No.
1	Allyl chloride	9 B	107-05-1
2	Benzene	9	71-43-2
3	Benzyl chloride	8	100-44-7
4	Bromobenzene	(d)	108-86-1
5	Bromodichloromethane	9	75-27-4
6	Bromoform	9	75-25-2
7	Bromomethane	9	74-83-9
8	Carbon tetrachloride	9	56-23-5
9	Chlorobenzene(b)	9	108-90-7
10	Chloroethane	9	75-00-3
11	Chloroform(b)	9	67-66-3
12	1-Chlorohexane	(d)	544-10-5
13	Chloromethane(b)	9	74-87-3
14	Chloroprene	9 B	126-99-8
15	Chlorotoluene	(d)	95-49-8
16	Dibromochloromethane	9	124-48-1
17	1,2-Dibromo-3-chloropropane(c)	9	96-12-8
18	1,2-Dibromoethane	9	106-93-4
19	1,2-Dichlorobenzene	9	95-50-1
20	1,3-Dichlorobenzene	9	541-73-1
21	1,4-Dichlorobenzene	9	106-46-7
22	1,4-Dichloro-2-butene	9	110-57-6
23	Dichlorodifluoromethane	9 B	75-71-8
24	1,1-Dichloroethane(b)	9	75-34-3
25	1,2-Dichloroethane	9	107-06-2
26	1,1-Dichloroethylene	9	75-35-4
27	trans-1,2-Dichloroethylene	9	156-60-5
28	1,2-Dichloropropane(b)	9	78-87-5
29	1,3-Dichloropropene	9	10061-01-5
30	Diethyl ether	(e)	60-29-7
31	1,4-Dioxane(b,c)	9 B	123-91-1
32	Ethylbenzene	9	100-41-4
33	Ethyl methacrylate	9	97-63-2
34	Isobutanol(c)	9	78-83-1
35	Methacrylonitrile	9 B	126-98-7
36	Methylene bromide	9	75-95-3
37	Methylene chloride	9	75-09-2
38	Methyl ethyl ketone(c)	9	78-93-3
39	Methyl iodide	9 B	74-88-4
40	Methyl methacrylate	9	80-62-6
41	4-Methyl-2-pentanone(b,c)	9	108-10-1
42	beta-Propiolactone(b,c)	M	57-57-8
43	Propionitrile(c)	9 B	107-12-0
44	Styrene	9	100-42-5

TABLE 8. (Continued)

No.	Substance	List(a)	CAS No.
45	1,1,1,2-Tetrachloroethane	9	630-20-6
46	1,1,2,2-Tetrachloroethane	9	79-34-5
47	Tetrachloroethylene(b)	9	127-18-4
48	Toluene	9	108-88-3
49	1,1,1-Trichloroethane	9	71-55-6
50	1,1,2-Trichloroethane	9	79-00-5
51	Trichloroethylene(b)	9	79-01-6
52	Trichlorofluoromethane	9	75-69-4
53	1,2,3-Trichloropropane	9	96-18-4
54	Vinyl chloride(b)	9	75-01-4
55	m-Xylene	9	(f)
56	o-Xylene	9	(f)
57	p-Xylene	9	(f)

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986 pp 26639-26642.
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8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, borderline chemicals, or Michigan lists.

(b) Compounds with relative standard deviations of 15 percent or more.
(c) Compounds with mean recoveries of 20 percent or less.
(d) Included on SW-846 Method 8010 list but not present on proposed Appendix IX, borderline chemicals, Michigan, or Appendix VIII lists.
(e) Included on SW-846 Method 8015 list but not present on proposed Appendix IX, borderline chemicals, Michigan, or Appendix VIII lists.
(f) Listed in proposed Appendix IX as Xylene (total) with CAS No. 1330-20-7.

TABLE 9. RECOMMENDED CHANGES FOR SEMIVOLATILE ORGANIC COMPOUNDS ON PROPOSED APPENDIX IX

No.	Substance	List(a)	CAS No.
9A. Recommended Deletions			
1	Aramite(Isomers 1 and 2)	9	140-57-8
2	Benzenethiol	9 B	108-98-5
3	p-Benzoquinone	9 B	106-51-4
4	Dibenz(a,e)pyrene	9 B	192-65-4
5	7,12-Dimethylbenz(a)anthracene	9	57-97-6
6	1,4-Dinitrobenzene	9	100-25-4
7	Hexachlorophene	9	70-30-4
8	Isosafrole	9 B	120-58-1
9	Malononitrile	9 B	109-77-3
10	4,4'-Methylenebis(2-chloroaniline)	9	101-14-4
11	1-Naphthylamine	9	134-32-7
12	Pentachloroethane	9	76-01-7
13	Resorcinol	9 B	108-46-3
9B. Recommended Additions			
1	2-Cyclohexyl-4,6-dinitrophenol	8	131-89-5
2	Diallate	B	2303-16-4
3	1,2:7,8-Dibenzacridine(b,c)	8	224-42-0
4	1,2-Dinitrobenzene	8	528-29-0
5	1,3-Dinitrobenzene	8	99-65-0
6	Ethyl methanesulfonate	8	62-50-0
7	3-Methylphenol	B	108-39-4
8	4-Nitroquinoline-1-oxide	8	56-57-5
9	1,4-Phenylenediamine(c)	8	106-50-3
10	Tetraethyl pyrophosphate	8	107-49-3
11	o-Toluidine	B	95-53-4
12	O,O,O-Triethyl phosphorothioate	8	126-68-1
13	1,3,5-Trinitrobenzene	8	99-35-4

(a) 9 = Proposed Appendix IX to Part 264 as published in the Federal Register, 51, No. 142, July 24, 1986, pp. 26639-26642.
B = Borderline chemicals considered for additions to proposed Appendix IX to part 264 and published in the Federal Register, 51, No. 142, July 24, 1986, p 26637.
8 = Appendix VIII to Part 261 as revised and published in the Federal Register, 51, No. 247, August 6, 1986, pp. 28305-28310. Compounds so designated are not present on proposed Appendix IX, or borderline chemicals lists.

(b) 1,2:7,8-Dibenzacridine exhibits a day 0 recovery with relative standard deviation greater than 15%.

(c) Compounds with calibration response factors having relative standard deviations greater than 15%.

REVIEW OF STUDIES CONCERNING EFFECTS OF WELL CASING MATERIALS ON TRACE MEASUREMENTS OF ORGANIC COMPOUNDS

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ABSTRACT

This report analyzes the results of laboratory and field studies that allow a direct experimental comparison among commonly used monitoring well casing materials (stainless steel, Teflon, rigid PVC) in terms of their potential effects on measurements of trace organic compounds. Each of the studies analyzed attempts to determine experimentally how much -- if any -- sorption occurs, or what differences result among measured concentrations of a series of organic compounds.

Because the compounds tested were not consistent among all the studies -- although some of the same compounds were represented in several of them -- the analysis compares effects of the casing materials on sorption of different chemicals. The laboratory studies analyzed in this report all relate the measurements taken to a control, and the field investigation to measurements of the same trace compounds in adjacent wells constructed of different casing materials.

In comparing the measured trace concentrations to determine whether the well casing materials cause significant differences in results, a ratio was formulated to reflect the relative sorption effects of each of the materials; sensibly constant ratios over a reasonable range of trace concentrations would indicate few, or relatively minor, differences between the various materials, while varying ratios would indicate larger differences.

The report first reviews the methodology and results of each individual investigation analyzed; these results are then compared across studies through the averaged ratios; and conclusions are drawn about similarities and differences in sorption behavior. Additional observations about sample variation, effects of well purging, and limited measurements of non-volatile compounds are noted.

INTRODUCTION

This review compares the results of four studies that allow a direct experimental comparison of the potential effects of commonly used well casing materials (stainless steel, Teflon, and rigid PVC) on measurements of trace levels of organic compounds.[1,2,3,4,5]

Each of the four studies was designed to determine experimentally, for a water solution in contact with well casing materials (or coupons made from them), how much sorption occurs, or what differences results among measured concentrations, using several organic compounds. The tested organics were not identical in each of the studies, although several compounds are represented more than once. Three of these studies are laboratory experiments that relate the measurements to a control, while the fourth is a field study that compares measurements of the same trace concentrations on different casing materials in wells located close together.

If well materials affect trace level measurements significantly, then a ration can be formulated to reflect the relative sorption effects of the materials. Such a value should be sensibly constant over a reasonable range of trace level concentrations.

Although the exact procedures and the organic compounds measured differ among the studies, nevertheless any superiority of one well casing material over another ought to be observable if the studies are sufficiently sensitive. It is possible, of course, that at the trace levels measured -- 100 ppb to 20 ppb for the laboratory studies and subparts per billion for the field study -- other sources of variation so overwhelm the results that no meaningful differences can be observed, and this information is in itself useful.

LABORATORY STUDIES

Some preliminary observations about the varying lengths of the test periods in the laboratory studies are in order. The Reynolds and Gillham study tested only the effects on virgin materials over times up to 7 days. This approach is important in addressing the initial effect of a material on trace level measurements and on the mechanism of sorption. However, this approach does not mimic actual field protocol, such as followed by Barcelona. Barcelona *et al.* show that purging is essential to the correct operation of monitoring wells.

Both the ChemWaste and the Radian laboratory studies also incorporate a 7-day exposure period; however, beyond that they each add 1-hour and 24-hour re-exposures to represent results from both initial and much more closely calibrated samplings. These differences should be kept in mind throughout this review.

1. The Reynolds & Gillham Study. This laboratory study compared effects of six organic polymer materials -- PVC, Teflon, nylon, polypropylene, polyethylene, and latex rubber -- on a series of different trace level organics, ranging from 20 ppb to 45 ppb of 1,1,1 trichlorethane, 1,1,2,2 tetrachloroethane, hexachloroethane,

bromoform, and tetrachloroethylene. Samples were withdrawn from exposure at times varying from 10 minutes to 7 days and analyzed.

From the published results, the ratios of the concentrations of the chemicals in contact with Teflon and PVC coupons respectively can be calculated and compared for the five different compounds measured. These ratios, representing the relative effects of sorption on virgin materials, are presented in Table 1. This table indicates that, for four of the compounds measured, the Teflon/PVC ration is very close to 1, implying little difference among the materials' effects. The exception is tetrachloroethylene, which shows much greater sorption, and hence less sensitivity, for Teflon.

Table 1

RATIO OF CONCENTRATION MEASUREMENTS OVER TIME FOR DIFFERENT COMPOUNDS

Reynolds Study: TEF/PVC

Compound/Time	10 min.	Average 100 min. - 7 days	7 day
1,1,1 Trichloroethane	1.06	0.93	0.68
1,1,2,2 Tetrachloroethane	1.05	1.01	0.94
Hexachloroethane	1.08	1.07	1.30
Bromoform	1.06	1.17	1.68
Tetrachloroethylene	0.9	0.46	0.10
Average	1.03	0.93	0.94

In general, this shows typical differences at the 7-day time of ± 30%. Some of the chemicals are detected more easily with PVC (1,1,1 trichloroethane, 1,1,2,2 tetrachloroether, tetrachloroethylene) and some more easily with Teflon (hexachlorethane, bromoform). Based on this study alone, it would be difficult to establish clear superiority of either Teflon or PVC.

2. The ChemWaste Management Study. This study measured effects of coupons of stainless steel, Teflon, and rigid PVC on six organic compounds: methylene chloride, 1, 2 dichloroethane, trans-1,2 dichloroethylene, trichloroethylene, chlorobenzene, and toluene. The test solutions were prepared in the same way as for the Reynolds study; the organics were dissolved in a concentrated methane solution and then exposed to the coupons at two diluted concentrations of 50 ppb and 100 ppb.

Each casing material was first exposed for an initial 7 days (similar to Reynolds) after which the solutions from each coupon and control were sampled. The coupon materials were then re-exposed for

TABLE 2
CWM Report
RATIO OF CONCENTRATION MEASUREMENTS
OVER TIME FOR DIFFERENT COMPOUNDS
(50ppb nominal)
SS/PVC

	Reexposed		Initial
Compound/Time	1 hour	24 hour	7days
Meth Chl	1.02	1.07	0.92
1,2-DCE	1.05	1.08	0.92
1,2-DCY	0.98	1.12	1.00
Trichloroethylene	1.00	1.10	1.02
Toluene	1.05	1.13	0.88
Chlben	1.18	1.14	0.95
avg	1.05	1.11	0.95

TEF/PVC

	Reexposed		Initial
Compound/Time	1 hour	24 hour	7days
Meth Chl	1.02	0.94	0.89
1,2-DCE	1.03	0.94	0.90
1,2-DCY	0.98	0.93	0.76
Trichloroethylene	1.02	0.92	0.73
Toluene	1.03	1.06	0.79
Chlben	1.00	1.19	0.84
avg	1.01	1.00	0.82

TABLE 3
CWM Report
RATIO OF CONCENTRATION MEASUREMENTS
OVER TIME FOR DIFFERENT COMPOUNDS
(100ppb nominal)
SS/PVC

	Reexposed		Initial
Compound/Time	1 hour	24 hour	7days
Meth Chl	1.03	0.93	1.06
1,2-DCE	1.03	1.03	1.03
1,2-DCY	0.96	1.04	1.13
Trichloroethylene	1.03	1.03	1.11
Toluene	1.05	1.03	1.07
Chlben	1.06	1.04	1.13
avg	1.03	1.01	1.09

TEF/PVC

	Reexposed		Initial
Compound/Time	1 hour	24 hour	7days
Meth Chl	0.79	0.90	1.12
1,2-DCE	0.81	0.92	1.14
1,2-DCY	0.78	0.88	0.91
Trichloroethylene	0.80	0.87	0.89
Toluene	0.79	0.90	1.01
Chlben	0.97	0.90	1.04
avg	0.83	0.90	1.02

one hour and resampled. A third sampling was performed following a final 24-hour re-exposure.

Results from the initial 7-day conditioning period -- which may have very little significance since groudwater sampling protocols require purging wells prior to drawing samples -- show that PVC is a better measuring materials 12 times, while the Teflon or stainless steel is better 12 times.

To compare the remainder of the results, the concentrations of the other experimental exposure was used to calculate ratios. Table 2 shows the SS/PVC and TEF/PVC ratios for the 50 ppb nominal concentration, and Table 3 shows the same calculations for the 100 ppb nominal concentration, for all six of the tested chemicals.

There are not enough control samples or replicates in this study to estimate the standard deviation. The best that can be done is to compare the ratios. Inspection of Tables 2 and 3 shows that PVC and Teflon exhibit very similar behavior; the ratios are close to 1, a result similar to that from the Reynolds study (although the latter shows wider variation). Where the coupons were re-exposed for one hour, Teflon is slightly better (2-3%) at the 50 ppb nominal case for four chemicals and PVC slightly better (2-3%) for one chemical; at the 100 ppb nominal, PVC is better (20%) for all six chemicals. After 24 hours re-exposure, at the 50 ppb nominal PVC is better 6-8%) for four chemicals and Teflon better (6 to 20%) for two, while at the 100 ppb nominal PVC appears about 10% better for all six chemicals.

The re-exposure samples show stainless steel performing better once better (2-10%) than PVC ten times and PVC performing better once for each of the two nominal concentrations. For the 1-hour re-exposures, which are likely to most nearly represent a well monitoring protocol after purging, only one of the ratios (chlorobenzene for SS/PVC) is more than 5% greater than 1.

Without any estimate of uncertainties, it is impossible to know if the differences shown in this experiment (on the order of 10%) are significant.

3. The Radian Study. This study followed the same general protocol as the ChemWaste study, with several significant differences. The same six chemical compounds were used in the experiment but were dissolved to a nominal 100 ppb concentration in a water solution as a carrier, instead of methanol as for Reynolds and ChemWaste. The exposure periods were similar: an initial 7 days exposure of the well casing coupons, followed by 1-hour and 24-hour re-exposures. The 7-day and 24-hour re-exposures were held at 5°C, while the 1-hour re-exposure was at room temperature. Table 4 shows the

results of these analyses, with trichloroethylene deleted since it was not stable.

Table 4 also presents the results of the nine control samples, with averages and standard deviations. An analysis of variations showed that the controls were not drawn from different populations and thus can be averaged. Therefore the standard deviation gives an estimate of the variation likely to be seen in any set of measurements.

Inspection of Table 4 shows that, for the re-exposure experiments for the 20 paired differences possible between concentrations (of PVC and Teflon, and PVC and stainless steel) with the various coupons, no difference exceeds two standard deviations, and five exceed one standard deviation. For the initial 7-day exposure, none of the differences between PVC and Teflon are greater than two standard deviations.

However, the stainless steel results are quite unusual. The stainless steel concentrations are more than two standard deviations greater than the controls, as well as more than two standard deviations larger than both PVC and Teflon for all of the chemicals. It seems likely that some contamination has entered the system. The stainless steel coupons were used just as received from the manufacturer and may have contained cutting fluids or other organics which affected the spiking solutions; there was no control using a coupon without a spike to check for this. In any event, it appears that the 7-day stainless steel concentrations are highly suspect and should be redone.

As before, the ratios (SS/PVC and TEF/PVC) can be calculated from these data to establish relative sorption effects between the various compounds. The results, presented in Table 5, are similar to those from the ChemWaste Management study, yielding ratios very close to 1, except for the 7-day SS/PVC ones.

Table 5 also presents an estimated standard deviation for the ratios, based on the standard deviation of the control samples, rather than on the small number (3) of the replicates. While this is not a satisfactory statistical analysis, it gives an order of magnitude to the variations in the ratios which may be present due to uncertainties in the experiment. (A more complete statistical analysis will be performed.)

The results of the re-exposure show that, after one hour, PVC appears somewhat better than both Teflon (2-10%) and stainless steel (10-30%); however, the difference does not appear significant, never exceeding two standard deviations. After 24 hours, PVC appears better than Teflon (0 to 6%) but not as good as stainless steel (8-12%), although again neither set of differences appears significant.

TABLE 4
Radian Study
CONCENTRATIONS REMAINING IN SOLUTION
ppb

	ONE HOUR PVC	TEFLON	S.S.	AVG CONTRLS	STD
Meth Chl	129	127	119	127	16
1,2-DCE	68	64	48	57	10
1,2-DCY	109	100	96	103	9
Toluene	42	38	32	37	5
Chlben	67	60	55	58	8

	24 HOUR PVC	TEFLON	S.S.	AVG	STD
Meth Chl	117	118	131	127	16
1,2-DCE	53	51	57	57	10
1,2-DCY	103	97	104	103	9
Toluene	34	34	38	37	5
Chlben	56	54	62	58	8

	7 DAY PVC	TEFLON	S.S.	AVG	STD
Meth Chl	114	136	189	127	16
1,2-DCE	47	56	82	57	10
1,2-DCY	95	102	136	103	9
Toluene	31	35	69	37	5
Chlben	40	56	84	58	8

TABLE 5
Radian Study
RATIO OF CONCENTRATION MEASUREMENTS
OVER TIME FOR DIFFERENT COMPOUNDS
SS/PVC

	Reexposed 1 hour	std dev	24 hour	std dev	Initial 7days	std dev
Meth Chl	0.92	0.16	1.12	0.19	1.66	0.29
1,2-DCE	0.71	0.18	1.08	0.28	1.74	0.45
1,2-DCY	0.88	0.11	1.01	0.12	1.43	0.17
Toluene	0.76	0.15	1.12	0.22	2.23	0.45
Chlben	0.82	0.17	1.11	0.23	2.10	0.43
avg	0.82		1.09		1.83	

TEF/PVC

	Reexposed 1 hour	std dev	24 hour	std dev	Initial 7days	std dev
Meth Chl	0.98	0.17	1.01	0.18	1.19	0.21
1,2-DCE	0.94	0.24	0.96	0.25	1.19	0.31
1,2-DCY	0.92	0.11	0.94	0.11	1.07	0.13
Toluene	0.90	0.18	1.00	0.20	1.13	0.23
Chlben	0.90	0.18	0.96	0.20	1.40	0.29
avg	0.93		0.98		1.20	

It is difficult to conclude from this experiment that there is a consistent difference between stainless steel and PVC or Teflon and PVC. Based on the Radian study alone, if a well were purged and subsequently sampled within one hour, PVC would seem to be somewhat more sensitive than either stainless steel or Teflon, but not significantly so. Twenty-four hours after purging, the PVC is still somewhat more sensitive than Teflon but less sensitive than stainless steel -- again, not significantly so. While the initial 7-day stainless steel experiment appears flawed, Teflon is more sensitive after 7 days -- again, not significantly so.

C. Barcelona's Field Experiment

The experiment by Michael Barcelona and John Helfrich was designed to provide a comprehensive field study which tests the differences between three different well casing materials: PVC, stainless steel, and Teflon.[6] The experiment has potential advantages over the lab studies in that it investigates the detection of chemicals actually in the groundwater at two different contaminated sites.

At each site there were six wells, with one each of the three different casing materials in a cluster upgradient and one each of the three materials clustered downgradient of the site. Each of the wells at a given cluster was installed within two meters of the other two, thereby attempting to assure that each cluster was sampling the same groundwater.

Each site was sampled monthly, six times starting in May and extending through October. At each of the sites, samples were taken prior to purging the stagnant water.[7] The wells were purged until parameters such as pH stabilized, and then samples were taken for an extensive list of groundwater parameters that included pH, conductivity, temperature, alkalinity, and total iron, and for a series of organic compounds that included total non-volatile organic compounds (NVOC), methylene chloride, 1,1-dichloroethane (1,1-DCE), cis-1,2 dichloroethylene (c-1, 2-DCY), trichloroethylene, 1,1,1 TCE, and chlorobenzene.

The largest concentrations of total volatile halocarbons were detected at Site 2 down-gradient at a few parts per billion. However, the concentrations are so low that, in many cases, clear differences between concentrations at the different wells cannot be seen.

As Barcelona points out in the paper, there were problems at Site 1 with apparent grout contamination at both up- and down-gradient wells. This was a factor in the abnormally large pH levels seen in five out of the six wells at this site. The only well which apparently did not have high pH levels was the down-gradient PVC well. Such grout contamination obviously is of concern if it could

affect the measurement of organic constituents, since those are crucial to the determination of sorption effects. A fairly simple correlation of total NVOC with the pH values for the stainless steel and Teflon wells at Site 1 suggests that there may be a direct relationship between pH and the non-volatile organic compounds. The correlation coefficient was 0.5, with a possibility of 6%. Therefore, in reviewing the Site 1 data, the problems with pH must be kept in mind, since it is apparent that grout contamination occurred and the NVOC values may be affected as well. The wells at Site 2 apparently were constructed in such a way that there was no grout contamination, and the purged pH was as expected.

With respect to well casing material, no definitive conclusions can be drawn because the well casing effect is confounded with spatial variability and, at Site 1, with grout contamination. Each type of well casing is used only once for each experimental sampling. As a result, the differences seen could be a result of either well casing or spatial differences. A so-called mixed model analysis may be used to help disentangle the effects.

Prior to that, however, the data can be inspected to observe if any consistent differences across sites are apparent.

Table 6 shows the results of ratios calculated, as before, for SS/PVC and TEF/PVC for each chemical measured and a group of NVOC chemicals and Total Volatile Halocarbons (TVOC) for Sites 1 and 2 up- and down-gradient.

As can be seen, there are no consistent results indicating that PVC is inferior to the other two materials. For example, for NVOC at Site 1 down-gradient (with grout contamination) stainless steel and Teflon have superior detection capability, but at Site 1 up-gradient, where all wells have grout contamination, PVC is superior. Since, presumably, the differences should be the same, it is likely either spatial variability or grout contamination cause such a large variation.

If, therefore, attention is focused on Site 2 where volatile organics were detected, it can be seen that PVC is consistently superior to both Teflon and stainless steel, except for the non-volatiles. These values, however, have a significant variation and only the measurements for 1,1 DCE suggest that PVC is significantly (more than two standard deviations) superior to stainless steel and Teflon.

Indeed, the combination of time series data, the fixed spatial distances, and the material differences may allow a determination of errors due to spatial variability, which seem likely to be larger than those due to the analytical variability.

TABLE 6
Barcelona et. al.
Ratio of Groundwater Measurements
for Two Wells
SS/PVC

	Ratio Site 1 down	STD	Ratio Site 1 up	STD
NVOC	1.83	0.66	0.80	0.40
Meth.Chl.	1.98	0.95	4.25	5.65
	Site 2 down		Site 2 up	
NVOC	1.11	0.35	3.85	6.36
Meth.Chl.	0.90	0.44	0.91	0.39
TVOC	0.61	0.24		
12DCE+111TCE	0.70	0.39		
11DCE	0.43	0.16		
C12DCY	0.63	0.22		
average	0.73	0.30		

TEF/PVC

	Ratio Site 1 down	STD	Ratio Site 1 up	STD
NVOC	1.52	0.69	0.92	0.47
Meth.Chl.	1.35	0.92	1.46	1.49
	Site 2 down		Site 2 up	
NVOC	0.89	0.31	12.99	10.35
Meth.Chl.	0.80	0.31	0.98	0.59
TVOC	0.43	0.16		
12DCE+111TCE	0.58	0.12		
11DCE	0.62	0.13		
C12DCY	0.72	0.17		
average	0.67	0.20		

Table 7

COMPARISON OF SPECIFIC VOLATILE CHEMICALS
BETWEEN LABORATORY AND FIELD STUDIES

RATIOS OF CONCENTRATION MEASUREMENTS

SS/PVC

	Radian	CWM	CWM	Barcelona
1,2 DCE	0.71	1.03	1.05	0.70 ± .39*
c 1,2 DCY	0.88	0.96	0.98	0.63 ± .22

TEF/PVC

1,2 DCE	0.94	0.81	1.03	0.58 ± .12*
c 1,2 DCY	0.92	0.78	0.98	0.72 ± .17

* 1,2 DCE & 1,1,1 TCE

D. Comparison of Results

In comparing the different studies, this review has analyzed the ratios of SS/PVC and TEF/PVC derived from the experiments to assess whether one material is consistently better than another in measuring compounds common to the experiments. Table 7 compares 1,2 DCE and cis-1,2 DCY, two compounds measured (at 1-hour re-exposures) in the ChemWaste, Radian and Barcelona experiments (two laboratory and one field experiment). The results are generally consistent, although the Barcelona experiment suggests that PVC is somewhat better than is suggested by the Radian or ChemWaste studies. This implies that PVC would detect concentrations of the chemicals more efficiently than would the other two materials.

A second way to compare the study results is to average all of the chemicals in each of the experiments. Obviously, it is necessary to be very careful about averaging different chemical compounds with different sorption behaviors. But, since it is generally not known which compounds are likely to be in groundwater, averaging the ratios indicates what effects might occur with an unknown compound or suite of compounds in a groundwater situation. Table 8 shows average ratios for SS/PVC and TEF/PVC for two categories for the four studies reviewed. It assumes that the laboratory 1-hour re-exposures are roughly comparable to the Barcelona field experiment when the well is purged and that the 7-day exposures for Reynolds, ChemWaste and Radian are roughly comparable to the Barcelona field experiment when samples are taken under stagnant conditions.[8] If the average for the 1-hour re-exposure is considered for both SS/PVC and TEF/PVC, the ratios are determined by all four experiments are very similar.

There is somewhat more variation when looking at the 7-day stagnant situation for stainless steel and PVC. One reason for this may be the possibility of contamination in the Radian 7-day stainless steel experiment.

E. Conclusion

Based on this review of the existing studies, several conclusions are possible relating to the effects of well casing materials on the measurement of organic compounds, to apparent sample variations that occur in an actual measurement situation, and to judging the efficacy of various well materials.

- These four experiments suggest that, when groundwater is purged from a well, there are no consistent differences between the effects of stainless steel and PVC on volatile organic compound measurements. The laboratory experiments also show no significant differences between Teflon and PVC. In the field experiment, there is a small difference that may be significant,

Table 8

RATIO OF WELL CASING MATERIAL MEASUREMENTS
(average of all volatile organic compounds, laboratory & field tests)

	Radian	CWM	CWM	Reynolds	Barcelona	
1 hr. SS/PVC re-exposure (purged)	0.82	1.03	1.05	-	0.93*	(1,2)
1 hr. TEF/PVC re-exposure (purged)	0.93	0.83	1.01	-	0.81*	(1,2)
7 day SS/PVC (stagnant)	1.64+	1.09	0.95	-	0.46**	(2)
7 day TEF/PVC (stagnant)	1.16	1.02	0.82	0.94	0.63**	(2)

* Purged; numbers indicate sites
** Stagnant waters; number (2) indicates site 2
\+ Possible contamination of the SS values

showing that PVC may be more sensitive; if further work confirms this, PVC would detect volatile organics better than Teflon. If stagnant water is sampled, the comparison between studies is not so clear. Non-volatile chemicals, tested only in the Barcelona study, also do not show a significant difference across sites for any of the three casing materials.

- The effects of well materials on measurements of trace organic compounds need to be disentangled from sample variability. This variability may contribute an error larger than any error from analytical variability. Further investigation could shed light on whether this is an artifact of this particular field study -- which seems unlikely -- or is consistent at other waste sites.

- It seems clear that, in order to judge the efficacy of various well materials, comparisons must be made in the context of normal experimental variation. If it is to be judged that well material A has a different sorption than well material B, the difference in concentrations (reflecting different absorption behaviors) between them must be greater than the normal variation in the samples themselves. Further experiments could determine whether effects associated with the well easing material are larger than the 15% to 25% sample variation that seems likely.

Finally, a conservative position at the present may be to allow a choice of any of these three well casing materials: Teflon, stainless steel and PVC, at this time, excluding PVC could result in less detection of organic compounds.

FOOTNOTES

[1]Reynolds and Gillham, "Absorption of Halogenated Organic Compounds by Polymer Materials Commonly Used in Groundwater Monitors." Proceedings, Second [1985] Canadian-American Conference on Hydrogeology, Banf, Alberta, 1986, pp. 125-132.

[2]ChemWaste Management, Inc., "Absorption of Organics by Monitoring Well Construction Materials," unpublished technical note.

[3]Barcelona, Michael J. and John A. Helfrich. "Well Construction and Purging Effects on Ground-Water Samples," Environmental Science & Technology, Vol. 20, No. 11, 1179-84.

[4]Sykes, McAllister and Homolya. "Sorption of Organics by Monitoring Well Construction Materials." Radian Corporation (to be published).

[5]The review does not include a separate paper by Barcelona et al. that reported an investigation of the relationship between Teflon tubing and PVC tubing because, as Barcelona indicated, flexible PVC

tubing differs from rigid PVC pipe, and the sorption behavior is likely to differ greatly.

[6]The Teflon well at Site 2 was actually a Teflon/aluminum oxide dedicated sampler.

[7]With regard to well purging, Barcelona concluded that the experiment shows that purging is essential in order to eliminate spurious results from stagnant water. The investigation provides a useful data base for studying the necessity of purging.

[8]The stagnant conditions are not exactly the same, since the Barcelona experiment allowed 30 days exposure to the well casing materials, while the laboratory experiments had only 7 days; in addition, the Barcelona casings were not virgin materials.

APPLICATION OF WIDE-BORE CAPILLARY COLUMN TO THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY METHOD 8240

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ABSTRACT

Under the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (USEPA) has revised the regulations concerning the ground water monitoring for suspected contamination from hazardous waste treatment, storage and disposal facilities. Over 240 compounds are specified for monitoring in Appendix IX, with approximately 60 compounds having volatilities which would make them amenable to purge and trap techniques.

Method 8240 with the packed column suffers from limitations of resolving power and limited analyte range. In several cases, structurally similar compounds are not resolved, precluding positive identification or quantitation of the individual isomers. Also, the boiling range of compounds to be chromatographed is effectively limited to the dichlorobenzenes. Late eluting peaks become very broad and diffuse, and quantitation limits become higher.

Recently, large diameter capillary columns (0.5 mm ID) have become available with several phases specifically designed for retention and separation of volatile compounds. These columns afford the high resolving power of capillary columns with geometric and positional isomers well separated; at the same time, they accept high flow rates which make them compatible with the purge and trap apparatus. Additional benefits of the capillary column are a broadening of the analyte range, and a decrease in the analysis time. Good sensitivity is achieved for tetrachlorobenzene with an analysis time is achieved for tetrachlorobenzene with an analysis time of 32 mins, compared to an analysis time of 45 mins for dichlorobenzene on a packed column.

Accuracy and precision data are presented on the analysis of reagent water and publicly-owned treatment works (POTW) effluent using Method 8240 with a capillary column.

INTRODUCTION

Packed columns have been used for the separation of volatile organic compounds in the standard U.S. Environmental Protection Agency (USEPA) approved methods, such as Method 524 for drinking water analyses, Method 624 for wastewater contaminants and later Method 8240 for Resource Conservation and Recovery Act (RCRA) compounds. These methods have been effective when the number of measured

compounds was small; but with increasing monitoring regulations it has become apparent that packed columns can not provide the necessary column efficiency to resolve the many additional compounds of interest. Capillary columns offer sufficient efficiency to complete the separations.

Some attempts to use narrow-bore capillaries (<0.32 mm ID) for these analyses resulted in some success, but the methods lacked ruggedness due primarily to the problem of interfacing the purge and trap apparatus to the analytical column. The purge and trap requires relatively high flows for efficient desorption, 15-30 mL/min, whereas the column requires only a 2-3 mL flow for efficient operation. In addition, these columns have a thin film thickness which limits the analytical range to low concentrations.

More recently, wide-bore capillaries (>0.53 mm ID) having specialty phases designed for the retention and separation of volatiles have been introduced. When operated in the traditional capillary mode with a flow rate of 5-7 mL/min, the column offers the excellent separations and a greatly increased analyte range. Also, the columns have relatively thick liquid phases, 1.5 to w3m, to give a greater sample capacity. But a more practical mode of operation when a mass spectrometer is used is the "high-flow" mode, where column flows of 15 to 20 mL/min are utilized. At these flows only a small loss of column efficiency is noted, but the time of analysis is greatly shortened. In this mode, the column can be a direct substitution for the packed column for purgeable analyses.

The announced drinking water regulations of November 1985 provided the initial impetus toward development of a capillary column gas chromatography/mass spectrometer (GC/MS) method. The announcement cited 60 organic compounds for monitoring, with volatilities ranging from chloromethane (BP, -24°C) to 1, 2, 3-trichlorobenzene (BP, 219°C). These compounds were included in the scope of two packed column methods. The Agency proposed a packed column GC/MS method for the monitoring requirement. In addition, the monitoring regulations required an analytical range from 1/ µg/L for vinyl chloride to 200 µg/ L for 1,1,1-trichloroethane. In September, 1986, Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Cincinnati) proposed Method 524.2, providing single laboratory validation data on 58 of the volatile compounds. Method detection limits (MDL) for most compounds were less than 0.5 µg/L, indicating the necessary method sensitivity when a 25 mL sample is used.

The success with drinking water analytes led to investigate application of capillary column GC/MS to Appendix IX compounds. In our laboratory, and also through a contract with Battelle Columbus Laboratories, we have identified approximately 60 compounds which are amenable to purge and trap isolation and GC/MS detection. While many of these compounds are common with the drinking water method,

many new compounds are listed, several of which are beyond the volatility range previously described.

EXPERIMENTAL

Five mL aqueous samples were purged on a Tekmar LSC-2 concentrator under the conditions given in Table 1. Following concentration, the analytes were thermally desorbed directly onto a 60 m x 0.75 mm ID VOCOL capillary column maintained at 10°C in a Hewlett-Packard 5895 GC/MS. The column effluent was interfaced with the ion source through a jet separation. Column conditions and MS parameters are presented in Table 2.

Concentrated standards of the volatile analytes were obtained from the USEPA Repository or prepared from neat material in methanol at approximately 5000 µg/mL. From these concentrates spiking mixtures were produced containing each analyte at 50 µg/mL in methanol. A list of the method analytes from Appendix IX along with their retention times is given in Table 3.

Calibration for each analyte was accomplished by purging aqueous standards of the compounds spiked at 5, 10, 50 and 100 µg/L in Milli-Q water. The response factors at each level were calculated from the peak area of the ion chromatogram for that compound. For most compounds that ion was the base peak for the compound (Table 3), but in the few cases where the ion was common to co-eluting peaks, a secondary ion was selected. A linear fit was calculated for the detector responses. In all cases, the coefficient was 0.994 or greater, so that use of the average response factor was used over the entire range.

RESULTS AND DISCUSSIONS

Wide and narrow bore capillary columns shown to be effective for 58 compounds and included in the June final regulations.

Initial experiments for the Appendix IX list were to determine the purge characteristics of a number of potential analytes for which we had no prior data. From this list of potential analytes (Table 4) percent recovery and retention time data were gathered. Compounds having a purge recovery of 60% or greater were selected for further study.

Method accuracy and precision were determined by analyzing eight replicates of spiked reagent water at 10 µg/L of each component. The average recoveries relative to the purged standards for most components were in the range of 90-110% with relative standard deviations of 5 to 9%. Slightly lower recoveries were found for the vary gaseous halocarbons at 80-85%. A summary of these data is presented in Table 5. Only the meta- and p-xylene isomers were not

separated and quantitated; and are reported as single value of 20 µg/L for the isomer pair.

We have began to demonstrate the applicability of the method to the analysis of complex sample matrices. For example, a wastewater sample from a publicly-owned treatment works (POTW), a secondary effluent, was obtained from the Cincinnati Municipal Wastewater Plant. Since the sample was known to be biologically active, the sample was acidified with 1:1 HCl to pH 2 prior to spiking. As before, the target level for each analyte was 10 µg/L. This level was verified for all compounds except methylene chloride which appeared as a large contaminant peak at approximately 150 µg/L. The eight aliquots of spiked POTW were analyzed and the average recoveries calculated. Figure 2 presents chromatograms of the POTW samples. The upper trace depicts the unspiked POTW sample. Peaks marked with a "s" are internal standards or surrogate compounds. The lower trace is the chromatogram of the spiked sample. For most compounds the recoveries were slightly lower than those found from reagent water, ranging from 80 to 95%; again RSDs were in the range of 4 to 9% (Table 6). Notable exceptions to these recovery percentages are the dichlorobenzenes and trichlorobenzenes which appear as background contaminants. When corrections for these background levels are made the recoveries fall more into line with the other data.

SUMMARY

The applicability of wide-bore capillary columns to Method 8240 for some Appendix IX compounds has been demonstrated. The capillary column provides superior resolving power and a greatly increased range of analytes. Method accuracy and precision for most compounds are improved from those achieved with the packed column. We believe that the wide-bore capillary column is a means to provide better analytical data across all media. We are at present sponsoring formal single laboratory validation studies at Battelle with Appendix VIII and IX compounds in groundwater and leachate. Future plans inhouse call for us to demonstrate the method applicability to other wastewaters and municipal sludges.

Table 1. Purge and Trap conditions

Sample Volume - 5 mLs

Sample Temperature - Ambient (25°C)

Purge Time - 11 minutes

Purge Flow - 40 mL/min.

Desorption - 4 mins at 180°C

Desorption Flow - 15 mL/min.

Table 2. Chromatographic and Mass Spectrometric Conditions

Column - 60m x 0.75 mm ID (glass) VOCOL

GC Column Flow - 15 mL/min

GC Column Conditions - hold 5 mins at 10°C, then program to 180 at 6°C/min.

MS Scan Range - 45 to 300 amu

MS Scan Rate - 0.7 sec/scan

Table 3. CHROMATOGRAPHIC RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON APPENDIX IX LIST

ANALYTE	RETENTION TIME (mins)	ANALYTICAL IONS PRIMARY	SECONDARY
Dichlorodifluoromethane	1.55	85	87
Chloromethane	1.63	50	52
Vinyl chloride	1.71	62	64
Bromomethane	2.01	94	96
Chloroethane	2.09	64	66
Trichlorofluoromethane	2.27	101	103
1,1-Dichloroethene	2.89	61	96,63
Methylene Chloride	3.60	84	49,86
trans-1,2-Dichloroethene	3.98	96	61,98
1,1-Dichloroethane	4.85	63	65,83
Chloroform	6.40	83	85,47
1,1,1-Trichloroethane	7.27	97	61,99,117
Carbon Tetrachloride	7.61	117	119,44
Benzene	8.23	78	--
Trichloroethene	9.59	95	130,131
1,2-Dichloropropane	10.09	63	112
Bromodichloromethane	10.59	83	85,127
Dibromomethane	10.65	93	95,174
trans-1,3-Dichloropropene	11.98	75	49,110
Toluene	12.43	92	91,65
cis-1,3-Dichloropropene	13.22	75	49,110
1,1,2-Trichloroethane	13.41	97	83,61
Tetrachloroethene	13.74	166	129,94
Dibromochloromethane	14.39	129	127,131
1,2-Dibromoethane	14.73	107	109,188
Chlorobenzene	15.76	112	77,51
1,1,1,2-Tetrachloroethane	15.94	133	131,117
Ethylbenzene	15.99	91	106,51
p-Xylene	16.12	106	91
m-Xylene	16.17	106	91
o-Xylene	17.11	106	91
Styrene	17.31	104	78
Bromoform	17.93	173	171,254
1,1,2,2-Tetrachloroethane	18.72	83	131,85

Table 3. (Continued)

ANALYTE	RETENTION TIME (mins)	ANALYTICAL ION PRIMARY	SECONDARY
1,2,3-Trichloropropane	19.02	75	77
trans-1,4-Dichlorobutene-2	19.48	75	77,53
1,3-Dichlorobenzene	21.22	146	148,111
1,4-Dichlorobenzene	21.55	146	148,111
1,2-Dichlorobenzene	22.52	146	148,111
Hexachloroethane	23.22	117	201,166
1,2-Dibromo-3-Chloropropane	24.53	75	155,157
1,2,4-Trichlorobenzene	26.55	180	182,145
Hexachlorobutadiene	26.99	225	223
Naphthalene	27.17	128	--
Hexachloropropane	27.19	213	211,141
1,2,4,5-Tetrachlorobenzene	30.81	216	214,179
2-Chloronaphthalene	32.42	162	127

Table 4. ABSOLUTE RECOVERIES OF SOME APPENDIX IX COMPOUNDS BY PURGE AND TRAP GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

Compound	Retention Time (mins)	% Recovery
trans-1,3-dichloropropene	11.98	86
cis-1,3-dichloropropene	13.22	100
N-Nitrosodmetrylanino	13.64	0
trans-1,4-dichlorobutene-2	19.48	57
bis-(2-chloroethyl) ether	21.39	3
Hexachloroethane	23.22	102
Isophorene	25.39	0.9
Hexachloropropene	27.19	95
Hexachlorocyclopentadrene	30.57	43
1,2,4,5-Tetrachlorobenzene	30.81	78
2-Chloronaphthalene	32.44	51
Acenaphthylene	34.51	19
Acenaphthene	35.25	25
4-Chlorophenylphenyl ether	37.32	7
4-Bromophenylphenyl ether	40.17	0.3

Table 5. ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER DETERMINED WITH A WIDE BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Recovery[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	10	105	3.8	3.6
Bromodichloromethane	10	102	4.7	4.6
Bromoform	10	110	8.4	7.6
Bromomethane	10	100	9.1	9.1
Carbon tetrachloride	10	84	5.5	6.5
Chlorobenzene	10	101	5.0	4.9
Chloroethane	10	79	7.8	9.9
Chloroform	10	95	5.0	5.3
Chloromethane	10	98	4.8	4.9
1,2-Dibromo-3-chloropropane	10	94	5.7	6.1
Dibromochloromethane	10	102	5.6	5.5
1,2-Dibromoethane	10	108	6.0	5.6
Dibromomethane	10	105	5.6	5.3
1,2-Dichlorobenzene	10	101	5.1	5.1
1,3-Dichlorobenzene	10	99	8.1	8.2
1,4-Dichlorobenzene	20	103	5.3	5.2
Dichlorodifluoromethane	10	85	5.9	7.0
1,2-Dichloroethane	10	96	4.1	4.3
1,1-Dichloroethene	10	95	7.2	7.5
trans-1,2-Dichloroethene	10	104	4.9	4.7
1,2-Dichloropropane	10	101	5.0	4.9
Ethylbenzene	10	102	3.9	3.8
Hexachlorobutadiene	10	102	9.2	9.0
Methylene chloride	10	99	4.6	4.6
Naphthalene	10	114	12.0	10.5
Styrene	10	109	6.5	6.0
1,1,1,2-Tetrachloroethane	10	96	4.6	4.7
1,1,2,2-Tetrachloroethane	10	98	6.0	6.1
Tetrachloroethene	10	90	3.8	4.2

Table 5. (Continued)

Analyte	Conc. µg/L	Recovery[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Toluene	10	109	11.6	10.8
1,2,4-Trichlorobenzene	10	108	9.0	8.3
1,1,1-Trichloroethane	10	100	8.0	8.0
1,1,2-Trichloroethane	10	113	10.9	9.6
Trichloroethene	10	92	5.2	5.6
Trichlorofluoromethane	10	84	7.1	8.4
1,2,3-Trichloropropane	10	78	6.7	8.6
Vinyl chloride	10	93	8.3	8.9
o-Xylene	10	106	10.8	10.2
m-Xylene	10	96	4.6	4.8
p-Xylene	20	104	8.3	7.1

a. Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

b. Based on eight analyses.

Table 6. ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN POTW WATER DETERMINED WITH A WIDE BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Average Recovery[a] %	Percent Rel. Std. Dev.	Recovery Corrected for Background
Benzene	10	86	4.8	b
Bromodichloromethane	10	92	3.8	
Bromoform	10	83	4.2	
Bromomethane	10	77	11.8	
Carbon tetrachloride	10	87	6.9	
Chlorobenzene	10	89	3.5	88
Chloroethane	10	78	18.3	
Chloroform	10	101	4.8	85
Chloromethane	10	79	4.7	74
2-Chloronaphthalene	10	120	6.4	102
1,2-Dibromo-3-chloropropane	10	82	3.9	
Dibromochloromethane	10	86	3.7	85
1,2-Dibromoethane	10	82	4.0	
Dibromomethane	10	87	3.9	
1,2-Dichlorobenzene	10	131	4.1	78
1,3-Dichlorobenzene	10	106	9.8	82
1,4-Dichlorobenzene	20	116	4.0	81
1,2-Dichloroethane	10	88	4.4	
1,1-Dichloroethene	10	84	4.8	84
trans-1,2-Dichloroethene	10	92	5.2	
1,2-Dichloropropane	10	90	3.6	
cis-1,3-Dichloropropene	10	91	3.1	
trans-1,3-Dichloropropene	10	94	3.6	
Ethylbenzene	10	91	3.9	86
Hexachlorobutadiene	10	84	4.5	83
Hexachloroethane	10	92	4.0	
Methylene chloride	150	91	6.9	89
Naphthalene	10	91	4.2	87
Styrene	10	87	3.8	
1,2,4,5-Tetrachlorobenzene	10	101	4.5	88
1,1,1,2-Tetrachloroethane	10	85	4.4	
1,1,2,2-Tetrachloroethane	10	87	4.2	
Tetrachloroethene	10	87	5.2	86

Table 6. (Continued)

Analyte	Conc. µg/L	Average Recovery[a] %	Percent Rel. Std. Dev.	Recovery Corrected for Background
Toluene	10	90	4.0	80
1,2,4-Trichlorobenzene	10	263	3.7	57
1,1,1-Trichloroethane	10	88	6.1	88
1,1,2-Trichloroethane	10	86	3.7	
Trichloroethene	10	91	3.3	
1,2,3-Trichloropropane	10	87	5.1	
Vinyl chloride	10	87	5.4	87
o-Xylene	10	95	3.7	88
m-Xylene				
p-Xylene	20	94	3.6	85

a. Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

b. A blank value indicates the compound was not found in the blank and no correction was made.

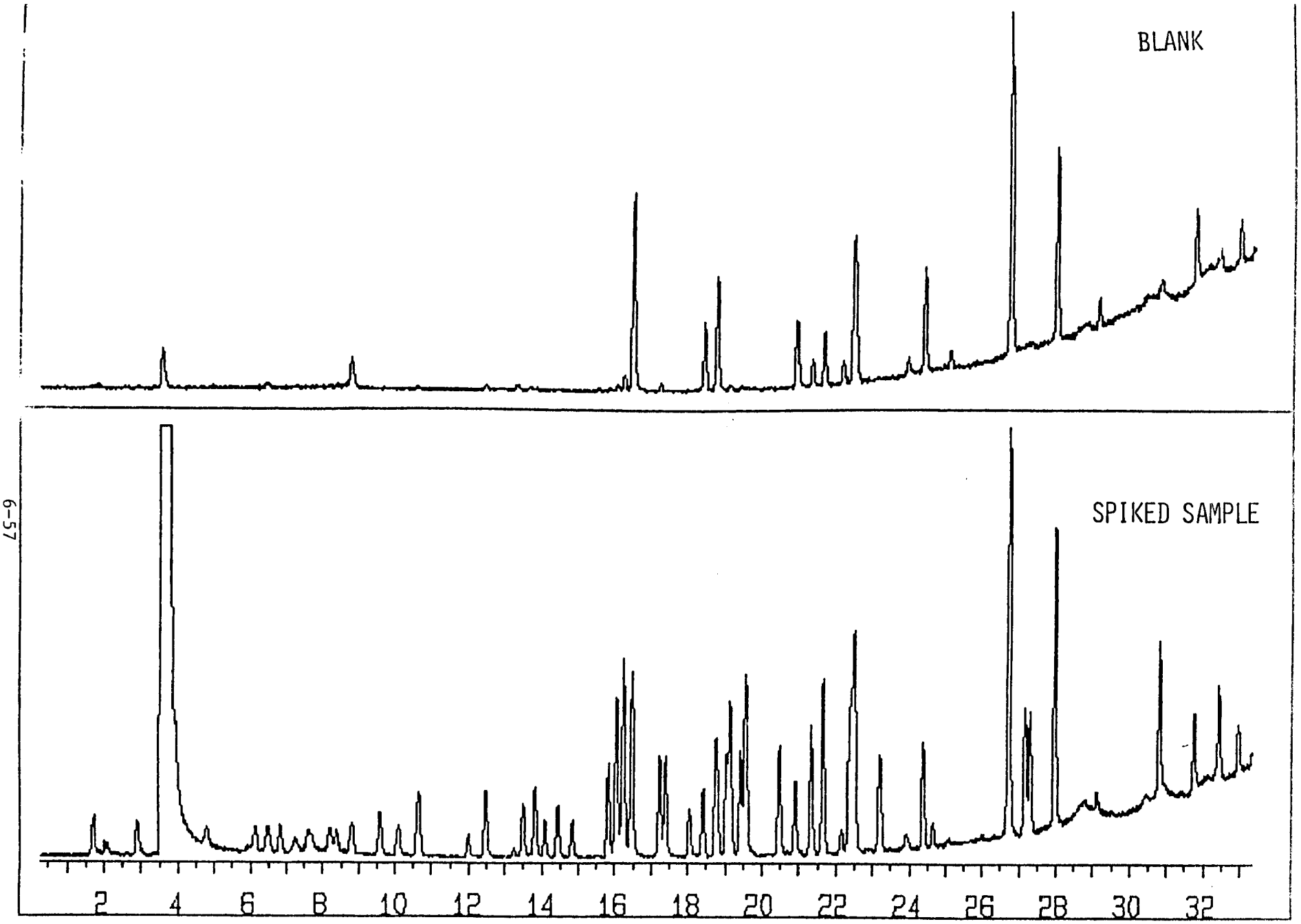

FIG. 1. CHROMATOGRAM OF VOLATILE COMPOUNDS IN POTW EFFLUENT

DETERMINATION OF FORMALDEHYDE IN SAMPLES OF ENVIRONMENTAL ORIGIN

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ABSTRACT

An analytical method was developed for the determination of formaldehyde in liquid samples and leachates of solid samples. After a review of the current literature, five candidate methods involving chemical derivatization were chosen for evaluation. Methods involving both liquid and gas chromatographic procedures was considered. The derivatization method which satisfied all performance criteria was reaction with 2,4-dinitrophyenylhydrazine (DNPH) at pH 5, followed by quantification using liquid chromatography with absorbance detection. Mildly acidic derivatization conditions were employed to avoid unwanted generation of formaldehyde from ubiquitous precursors. Optimized experimental procedures include a 30 minute reaction time, followed by extraction using methylene chloride or a solid sorbent method. The derivatization of formaldehyde proceeded in high yield with excellent reproducibility. Laboratory blank levels were in the 10 - 15 μg/L range. The method satisfied performance criteria over the range of 15 - 1400 μg/L. Several authentic sample matrices were used to evaluate the method. A study of the kinetics of formation of derivative indicated that the method was indeed measuring free formaldehyde in solution and was not generating formaldehyde from precursors. The method was subjected to a single laboratory validation protocol.

INTRODUCTION

The goal of this program was to develop and validate an analytical method for the determination of formaldehyde in samples of environmental origin. The potential application of the method to other carbonyl compounds was also of interest. Formaldehyde is of primary concern because of its potential environmental hazard and the fact that there are numerous sources for this chemical in the environment. These sources may be classified as direct, consisting of free formaldehyde in solution, or indirect, resulting from decomposition of various formaldehyde precursors.

The problem of formaldehyde generation from precursors is a well-documented phenomenon (1). Numerous chemical entities, both naturally occurring and synthetic, will release formaldehyde upon application of an appropriate pH change and/or heat. The desired

analytical method should be capable of measuring free formaldehyde as well as any formaldehyde generated under representative environmental conditions. These levels must be distinguished from formaldehyde which is generated only by unusual conditions used in the analysis. Although suitable analytical methods exist for the determination of formaldehyde in air, methods available for determination of formaldehyde in other environmental matrices are not suitable in terms of sensitivity, selectivity, pH and temperature. Analysis of real samples is complicated by the fact that existing literature procedures require high acid concentrations for demigration, which may result in unwanted generation of formaldehyde from precursors. The method development activities described here have been designed to avoid this problem.

PROCEDURE

Liquid samples are initially filtered using centrifugation and a glass fiber filter. A 100 mL aliquot of sample is adjusted to pH with 4 mL of 5 M acetate buffer. A 6 mL aliquot of a 1 mg/mL solution of 2, 4-dinitrophenylhydrazine (DNPH) in ethanol is added and the solution is placed on a wrist action shaker for 30 minutes at room temperature. After 30 minutes, a 10 mL aliquot of saturated NaCl is added and the formaldehyde-DNPH derivative is extracted from the reaction solution using either methylene chloride or a reverse phase solid sorbent. If the methylene chloride is used, the solvent is concentrated and a solvent exchange to methanol is performed. If a solid sorbent extraction method is used, the sorbent is eluted with ethanol. The final volume is 10 mL in each case. The ethanol or methanol solution is injected directly into a liquid chromatography system employing an absorbance detector. The principal chromatographic operating parameters are - injection volume: 20μL; column:4.6 x 250 mm Zorbax ODS; mobile phase: methanol/water (75/25); flow rate: 1.0 mL/min.; detector: 360 nm. Quantification is achieved from injection of independently synthesized formaldehyde-DNPH standards.

RESULTS AND DISCUSSION

Literature Search

A search of the existing literature was conducted using the Chemical Abstracts data base. Three main categories were searched: analytical method, reagent, and analyte. The purpose of this search was to assess the current status of methodologies for determination of formaldehyde and similar compounds and to identify candidate analytical methods for further study. The original search yielded a core list of references which was supplemented with individual references obtained by project personnel.

The analytical methods considered involved either liquid or gas chromatography. An initial survey of the citations resulted in identification of five derivatization reagents which appeared to satisfy method requirements in terms of sensitivity, selectivity, rate of reaction, and limited severity of reaction conditions. The five reagents were: 2,4-dinitrophenylhydrazine (DNPH), 2,4-pentanedione (acetylacetone), 3-methyl-2-benzothiazolinone hydrazone (MBTH), pentafluorophenylhydrazine (PFPH), and pentafluorobenzyloxyamine (PFBOA). A subsequent search of the data base was concerned with citations involving these reagents and carbonyl compounds. More than 60 citations were obtained. The citations are provided in Table 1 which is organized by reagent.

THE PH DEPENDENCE OF THE DNPH REACTION

Experiments designed to optimize the DNPH reaction at a pH above 3 were conducted. A method employing mild acid conditions was desired to minimize formation of formaldehyde from samples during the analysis itself. Additional method development work was necessary since existing literature procedures used high acid conditions (i.e., pH < 1).

Reaction conditions were adjusted to ensure an excess of both buffering acid and DNPH reagent. Analysis time was also held constant, as well as other analytical parameters such as extraction conditions. A 1 wg/mL solution of formaldehyde in reagent water was studied at solution pH values in the range from 1.7 to 7.0. A plot of recovery versus solution pH revealed a smooth curve over the entire range (Figure 1), with maximum recovery of approximately 90 percent occurring at pH 4. Little difference in recovery was observed over the pH range from three to five. Reactions performed at a pH of 5 were expected to minimize unwanted generation of formaldehyde from precursors. Derivatization at pH 5 using an acetate buffer also allowed dust evaluation of leachates from the Toxicity Characteristics Leaching Procedure (TCLP) (2).

EVALUATION OF CANDIDATE METHODS

The five analytical methods identified during the information gathering stage were subjected to a laboratory evaluation. The comparison of these methods was designed to minimize experimental variations between the procedures and allow a comparison of the efficacy of each individual reagent for the derivatization of formaldehyde and acetaldehyde. Formaldehyde was chosen as the primary analyte of interest. Acetaldehyde was included to indicate efficacy for homologs of formaldehyde. Each reaction was performed on a 250 mL sample of reagent water which was spiked at 1 mg/L levels with both formaldehyde and acetaldehyde. For each candidate method, the results were evaluated in terms of six performance criteria: reaction yield, reaction rate, chromatographic

TABLE 1. LITERATURE SEARCH RESULTS

REFNO	AUTHOR	REFERENCE	YEAR	REAGENT(s)
1	Beasley, Ronald K.; Hoffmann, Catherine E.; Rueppel, Melvin L.; Worley, Jim	Anal. Chem., 52(7), 1110-14	1980	DNPH/SILICA
2	Cant, P. A. E.; Walker, J. N.	J. Chromatogr., 130, 267-73	1977	DNPH
3	Chiavari, Giuseppe; Bergamini, Cecilia	J. Chromatogr., 318(2), 427-32	1985	DNPH
4	Deki, Mitsuo; Yoshimura, Minoru	Chem. Pharm. Bull., 23(6), 1374-6	1975	DNPH
5	Fung, Rochy; Grosjean, Daniel	Anal. Chem., 53(2), 168-71	1981	DNPH
6	Guenier, J. P.; Simon, P.; Delcourt, J.; Didierjean, M. F.; Lefevre, C.	MuChromatographia, 18(3), 137-44	1984	DNPH/SILICA GEL
7	Halvarson, Hans	J. Chromatogr., 57(3), 406-9	1971	DNPH
8	Honda, Susumu; Kakehi, Kazuaki	J. Chromatogr., 152(2), 405-11	1978	DNPH
9	Honda, Susumu; Kakehi, Kazuaki; Takiura, Kiyoshi	Anal. Chim. Acta, 77, 125-31	1975	DNPH
10	Hoshika, Yasuyuki; Takata, Yoshinori	J. Chromatogr., 120(2), 379-89	1976	DNPH
11	Jacobs, W. A.; Kissinger, P. T.	J. Liq. Chromatogr., 5(4), 669-76	1982	DNPH
12	Kallio, Heikki; Linko, Reino R.	J. Chromatogr., 766(1), 229-32	1973	DNPH
13	Kallio, Heikki; Linko, Reino R.; Kaitaranta, Jukka	J. Chromatogr., 65(2), 355-60	1972	DNPH
14	Kalo, Paavo	J. Chromatogr., 205(1), 39-47	1981	DNPH
15	Komarek, Karel; Novakova, Jarmila; Ventura, Karel; Churacek, Jaroslav	Collect. Czech. Chem. Commun., 47(8), 2121-7	1982	DNPH, NPH
16	Koroi, A.N.; Doubush, T.I.	Chem. Anal. (Warsaw), 27 (5-6), 449-57	1982	DNPH
17	Kuwata, Kazuhiro; Uebori, Michiko; Yamasaki, Yoshiaki	J. Chromatogr. Sci., 17(5), 264-8	1979	DNPH
18	Lawrence J. F.; Iyengar, J. R.	Int. J. Environ. Anal. Chem., 15(1), 47-52	1983	DNPH
19	Levin, Jan Olof; Andersson, Kurt; Lindahl, Roger; Nilsson, Carl Axel	Anal. Chem., 57(6), 1032-5	1985	DNPH/H3PO4/MECN
20	Liebezeit, G.	HRC CC, 5(4), 215-16	1982	DNPH
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22	Lynch, Catherine; Lim, C. K.; Thomas, Mervyn; Peters, Timothy J.	Clin. Chim. Acta, 130(1), 117-22	1983	DNPH
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25	Meng, Z.; Tanner, R. L.	Report, BNL-51725; Avail. NTIS 1984, 9(15), Abstr. No. 29197	1983	DNPH
26	Nichols, Troy; Svarnas, George; Thomas, Robert E.	Report, MERADCOM-2276; Avail. NTIS Index (U.S.) 1979, 79(24), 158	1979	DNPH
27	Papa, L. J.; Turner, L. P.	J. Chromatogr. Sci., 10(12), 744-7	1972	DNPH
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29	Pias, J. B.; Gasco, L.	Chromatographia, 8(6), 270-3	1975	DNPH
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31	Reindl, B.; Stan, H. J.	J. Chromatogr., 235(2), 481-8	1982	DNPH
32	Reineccius, G. A.; Anderson, H. C.; Felska, B. J.	J. Food Sci., 43(5), 1494-6	1978	DNPH
33	Ronkainen, Pentti; Brummer, Saara	J. Chromatogr., 28(2), 253-8	1967	DNPH
34	Selim, Sami	J. Chromatogr., 136(2), 271-7	1977	DNPH
35	Smith, R. A.; Drummond, I.	Analyst (London), 104(1242), 875-7	1979	DNPH

TABLE 1. (Continued)

REFNO	AUTHOR	REFERENCE	YEAR	REAGENT(a)
36	Steinberg, Spencer; Kaplan, I. R.	Int. J. Environ. Anal. Chem., 18(4), 253-66	1984	DNPH
37	Swarin, S.J.; Lipari, F	J. Liq. Chromatogr. 6(3), 425-44	1983	DNPH
38	Takami, Katsushige; Kuwata, Kazuhiro; Sugimae, Akiyoshi; Nakamoto, Masao	Anal. Chem., 57(1), 243-5	1985	DNPH
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48	Kobayashi, Keiko; Tanaka, Michiru; Kawai, Satoshi; Ohno, Takeo	J. Chromatogr., 176(1), 118-22	1979	PFPH
49	Hoshika, Yasuyuki; Muto, Gichi	J. Chromatogr., 152(1), 224-7	1978	PFPH(DNPH-AB)
50	Kobayashi, Keiko; Tanaka, Michiru; Kawai, Satoshi	J. Chromatogr., 187(2), 413-17	1980	PFBOA, PFPH
51	Stahovec, W.L.; Hopper, K.	J. Chromatogr., 298(3), 399-406	1986	CHD
52	Frei, R.W.; Lawrence, J.F.	J. Chromatogr., 83, 321-30	1973	DANSYL-CL+
53	Parsons, James S.; Mitzner, Stanley	Environ. Sci. Technol., 9(12), 1053-8	1975	DESORB
54	Chian, E.S.K.; Kuo, P.P.K.; Cooper, W.J.	Environ. Sci. Technol., 11(3), 282-5	1977	DISTILLATION
55	Carey, M. A.; Persinger, H. E.	J. Chromatogr. Sci., 10(9), 537-43	1972	DPNH
56	Boyce, Scott D.; Hornig, James F.	Water Res., 17(6), 685-97	1983	D.L.I.
57	Knuth, Michael L.; Hoglund, Marilynn D.	J. Chromatogr., 285(1), 153-60	1984	D.L.I.
58	Zlatkis, A.; Wang, F.S.; Shanfield, H.	Anal. Chem., 55(12), 1848-52	1983	D.L.I.
59		J. Chromatogr., 285(2), 385-8	1984	HCN
60	Metwally, Mohamed M. E.; Amundson, Clyde H.; Richardson, Thomas	J. Amer. Oil Chem. Soc., 48(4), 149-54	1971	HYDRAZ
61	Gil-Av, E.; Schurig, V.	Anal. Chem., 43(14), 2030-3	1971	METAL COMPLEX
62	Guebitz, G.; Winterstelger, R.; Frei, R.W.	J. Liq. Chromatogr., 7 (4), 839-54	1984	NBD-H
63	Sawicki, E.; Sawicki,C.R.	Academic Press, London	1978	REF.
64	Sawicki, E.; Sawicki, C.R.	Academic Press Longon	1975	REF.
65	[illegible]nkainen, Pentti; Brummer, Saara	J. Chromatogr., 28(2), 259-62	1967	HYDRAZ
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69	Uden, Peter C.; Bigley, Imogene E.; Walters, Frederick H.	Anal. Chim. Acta, 100, 555-61	1978	METAL COMP.

(a) See text for identification of pertinent acronyms.

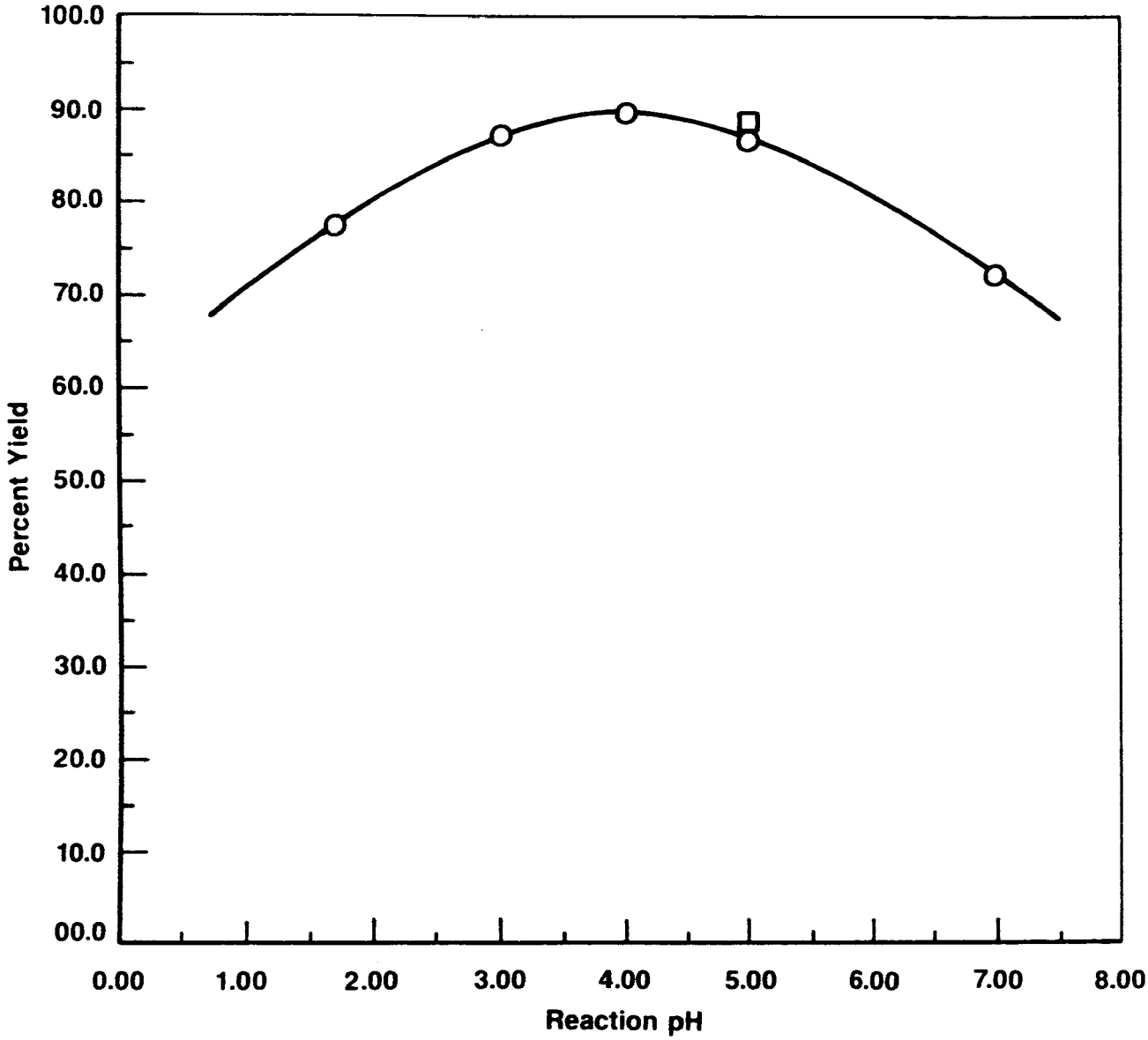


Figure 1. Effect of reaction pH on percent yield for derivatization of formaldehyde with DNPH. Circles: phosphate buffer; square: acetate buffer

separation, sensitivity, reproducibility, and chromatographic interferences.

The room temperature DNPH reaction was found to provide almost quantitative derivatization of formaldehyde in less than one hour. Recovery of the DNPH derivative was consistent at approximately 90 percent over a spike range from 50 to 1000 μg/L. Consistent laboratory blank levels were observed in the 10 to 15 μg/L range for formaldehyde and 100 to 120 μg/L for acetaldehyde. The source of the analytes appearing in the laboratory blanks was not determined but appeared to arise from multiple sources. Instrumental detection limits were estimated to be in the low μg/L range for this derivative. No chromatographic interferences were observed; excess reagent, formaldehyde derivative, and acetaldehyde derivative were readily separated using a simple isocratic mobile phase with absorbance detection at 360 nm.

The MBTH reaction provided high yield (i.e., 90 percent) of the formaldehyde derivative in less than one hour over a spike range from 100 to 2000 μg/L. Chromatographic separation of the derivatives was easily accomplished using the same system employed for the DNPH derivatives, except that the absorbance detector was operated at 310 nm. Estimated method detection limits were in the low μg/L range. However, the reagent eluted as a broad band in the same time window as the formaldehyde derivative, which made quantification more difficult at low analyte levels. These results indicate that this derivative may be useful for other analyses. Additional work is needed since liquid chromatographic separations with this derivative have not been reported previously in the literature.

The product of the reaction of acetylacetone, ammonia, and formaldehyde was monitored by liquid chromatography with fluorescence detection. The rate of derivatization was slow with derivative still being formed after six hours. Although fluorescence detection offered excellent detector sensitivity with no interferences, the method was considered inappropriate for the present analytical problem due to the slow kinetics of derivatization.

The PFPH derivative of formaldehyde could not be readily synthesized in large quantities, so quantification was not possible for this reaction. The chromatograms obtained using gas chromatography with electron capture detection showed a readily identified formaldehyde-PFPH derivative which could be confirmed by mass spectrometry. However, numerous small peaks were also present throughout the chromatogram, indicating impurities in the reagent or reaction side products. Chromatographic performance deteriorated after multiple injections which suggested the presence of nonvolatile material.

Similar problems were encountered with the PFBOA derivative. Fewer impurities were observed in the chromatogram but chromatographic performance deteriorated after multiple injections.

The DNPH reaction was chosen for additional study as a result of these experiments. The excellent recovery, reproducibility, sensitivity and freedom from interferences were primary factors in choosing this method over the other four candidates.

MATRIX STUDIES

The initial DNPH analytical method was evaluated further with five matrices to assess the need for any additional modifications. Five authentic environmental matrices, three liquid and two solid, were chosen in consultation with EPA technical personnel. One liquid matrix consisted of a groundwater sample removed from a well below a landfill site. Another liquid sample consisted of a final effluent. The third liquid sample was a landfill leachate. One solid sample was a dry solid sludge taken from a facility using phenol-formaldehyde glue. The second solid sample was wood dust collected from a wood product using urea-formaldehyde glues.

The solid samples were extracted according to the Toxicity Characteristics Leaching Procedures (TCLP) which used a pH 5 acetate buffer. This method produced leachate which was amenable to derivatization with the existing procedure. The liquid samples were derivatized as received, after centrifugation.

In an initial storage experiment the samples were stored at 4° C. Aliquots were removed at regular intervals and analyzed in triplicate with and without formaldehyde spikes. These experiments provided data on analytical reproducibiliity, spike recovery, and stability upon storage. The groundwater sample showed formaldehyde levels which were not statistically different from laboratory blanks. The analyzed levels remained constant over a two week storage period and spike recoveries were approximately 90 percent. The final effluent showed low levels of formaldehyde and was stable upon storage, but spike recoveries were erratic due to emulsion formation during extraction. Formaldehyde levels in the landfill leachate decreased steadily upon storage, indicating that the sample was still biologically active. Reproducibility and spike recoveries were also poor due to emulsion formation. The sludge's leachate was stable upon storage, providing good reproducibility and recovery of spikes. Formaldehyde levels were approximately 80 μg/g. Similar results were obtained for the wood dust extract, except that the formaldehyde levels were in excess of 700 μg/g and increased with time. Reproducibility and recovery for the two solids leachates were superior to the results obtained for the liquid samples because the solid extracts did not form emulsions upon extraction.

METHOD REFINEMENT

The DNPH derivatization procedure was further refined to ensure complete reaction of formaldehyde in solution and subsequent extraction of the derivative. The minor changes involved an increase in buffer and DNPH concentrations, and the addition of NaCl before extraction.

While the recovery obtained using the new procedure was not statistically different from that obtained using the original method, the new reaction conditions allowed the substitution of the methylene chloride extraction step with a reverse phase solid sorbent extraction procedure. Solid sorbents available from three different manufacturers were evaluated in this experiment. The results indicated that equivalent recovery of derivative, compared to solvent extraction, was obtained using a total of 1.5g of a C18 sorbent obtained form J.T. Baker Chemical Company. This alternative extraction procedure reduced the analysis time for each sample and avoided reproducibility problems caused by emulsion formation during methylene chloride extraction.

The modified reaction conditions and solid sorbent extraction procedure were used in all subsequent experiments. Representative chromatograms for standards and each matrix type are provided in Figures 2 through 6.

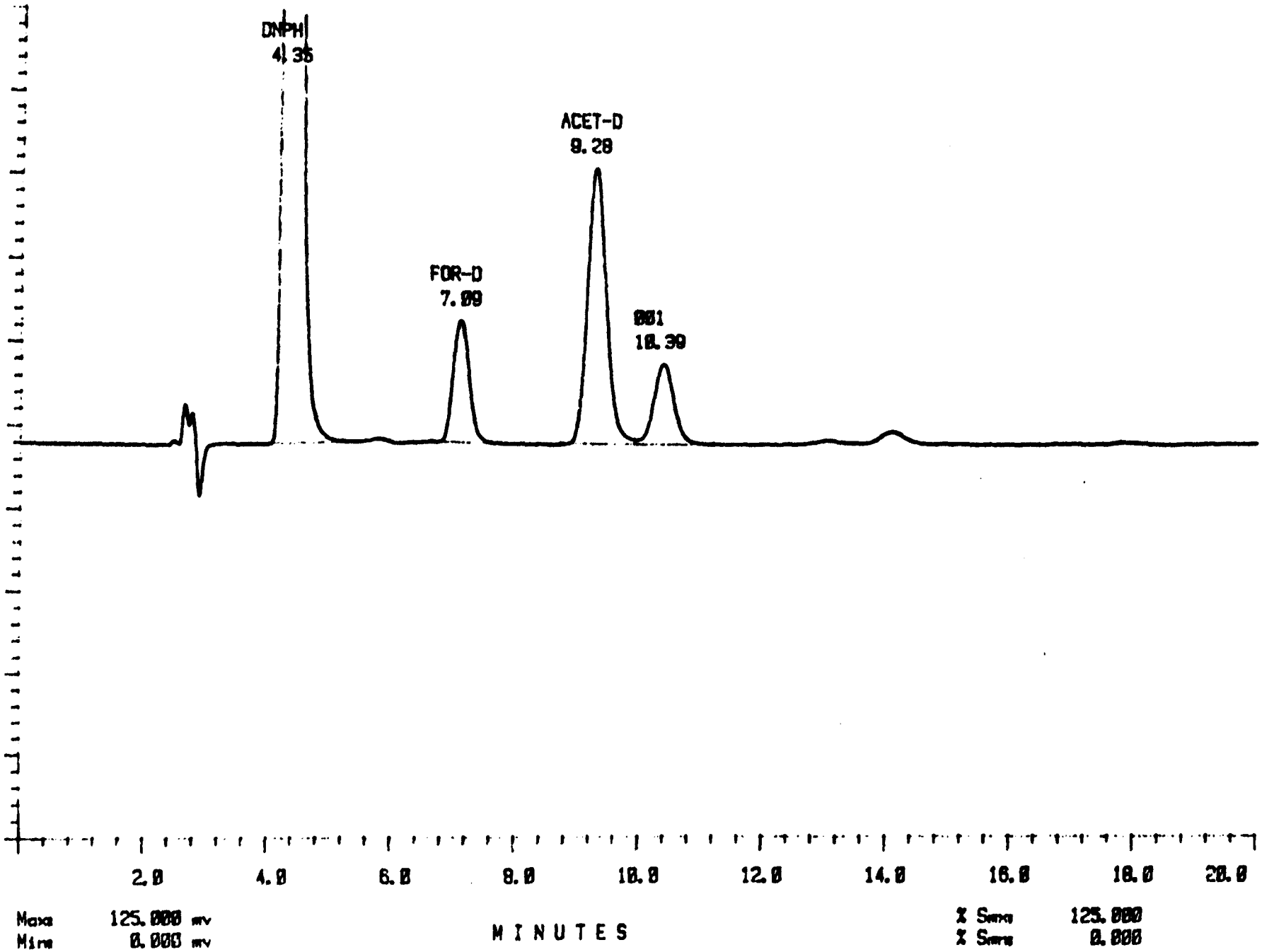
GENERAL APPLICATION OF THE DERIVATIZATION METHOD

Efficacy of the procedure for determination of other analytes of interest to EPA was assessed also. Potential interferences from paraformaldehyde, a polymer of formaldehyde, were examined by derivatizing a constant level of formaldehyde in the presence of varying levels of paraformaldehyde. These experiments demonstrated that a significant increase in analyzed formaldehyde levels only occurred when paraformaldehyde was present at higher levels than free formaldehyde.

Four other carbonyl compounds were also derivatized. Acrolein, chloroacetaldehyde, benzaldehyde, and cyclohexanone were derivatized using the procedure optimized for formaldehyde. Derivatives were tentatively identified in the chromatogram for each compound. The highest yields were obtained for acrolein and cyclohexanone. Since the reaction occurred to a measurable extent for each compound, acceptable yields could probably be obtained by adjusting appropriate experimental variables such as DNPH concentration, reaction time, and reaction temperature.

KINETICS OF FORMATION OF THE FORMALDEHYDE-DNPH DERIVATIVE

This study was undertaken to measure the rate at which the formaldehyde-DNPH derivative was formed under the reaction



89-9

Figure 2. Representative chromatogram from derivatization of a 50 ppb solution of formaldehyde using the optimized method. Abbreviations -- FOR-D: formaldehyde derivative; ACET-D: acetaldehyde derivative.

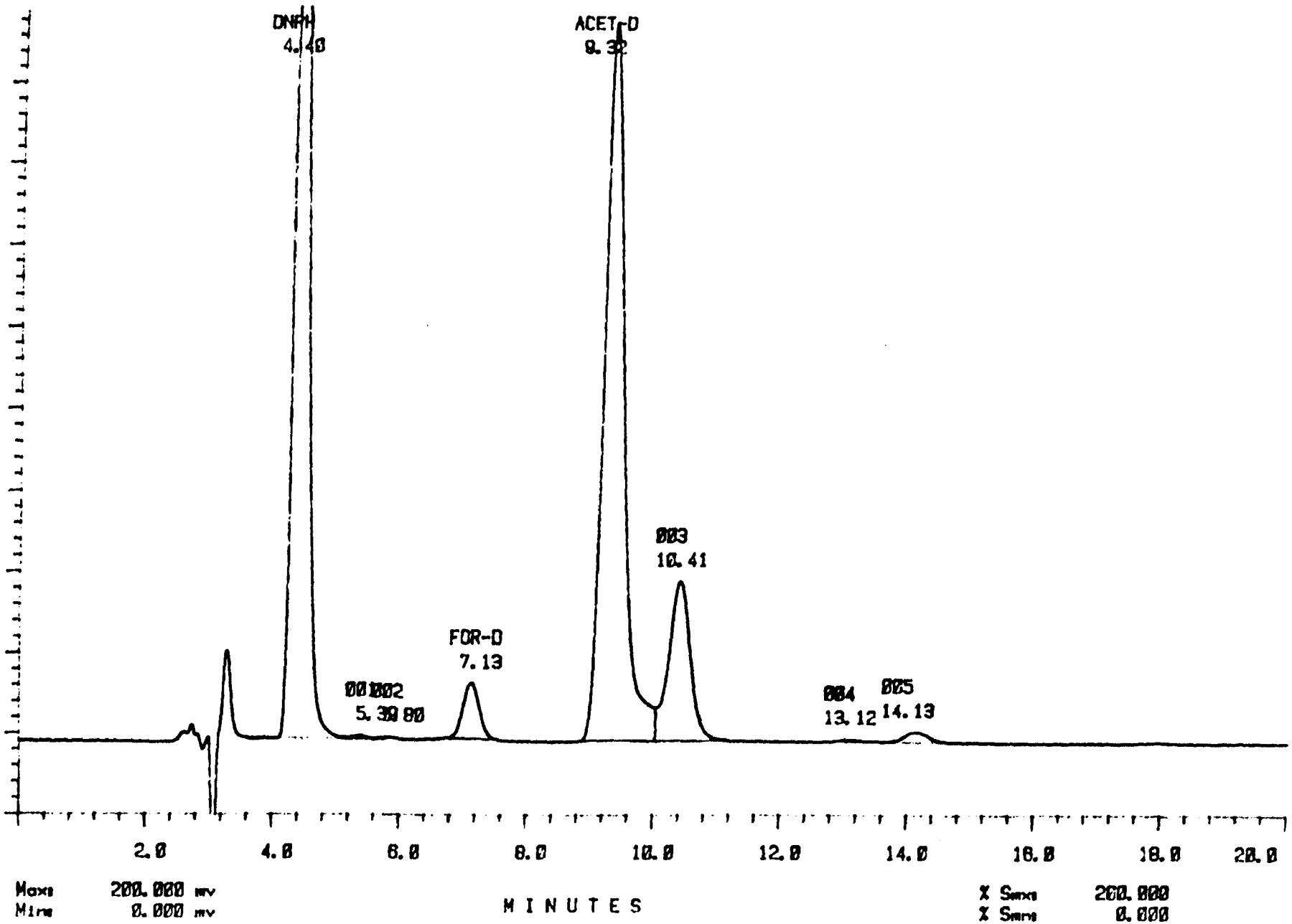


Figure 3. Representative chromatogram from derivatization of final effluent sample.

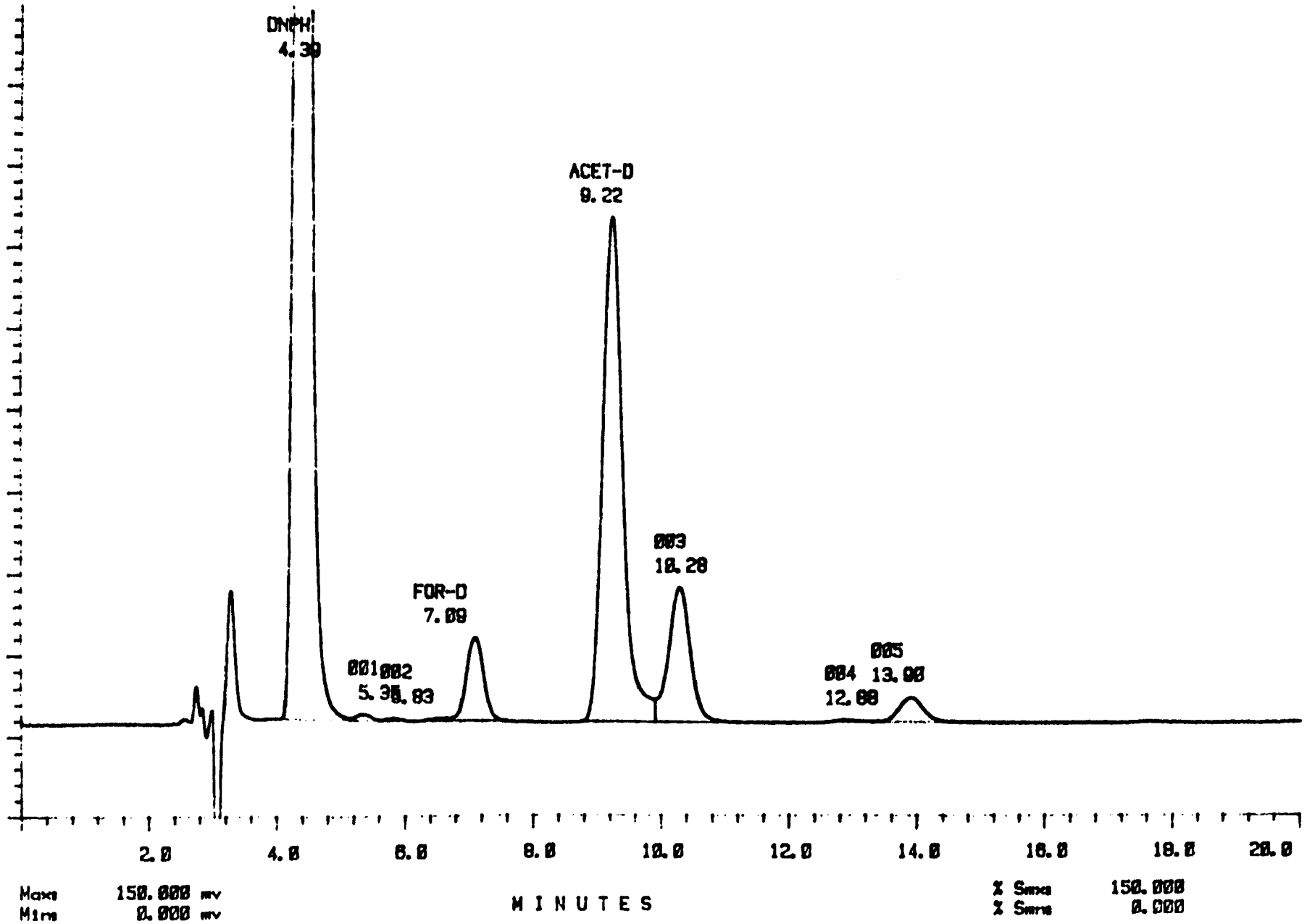


Figure 4. Representative chromatogram from derivatization of landfill leachate sample.

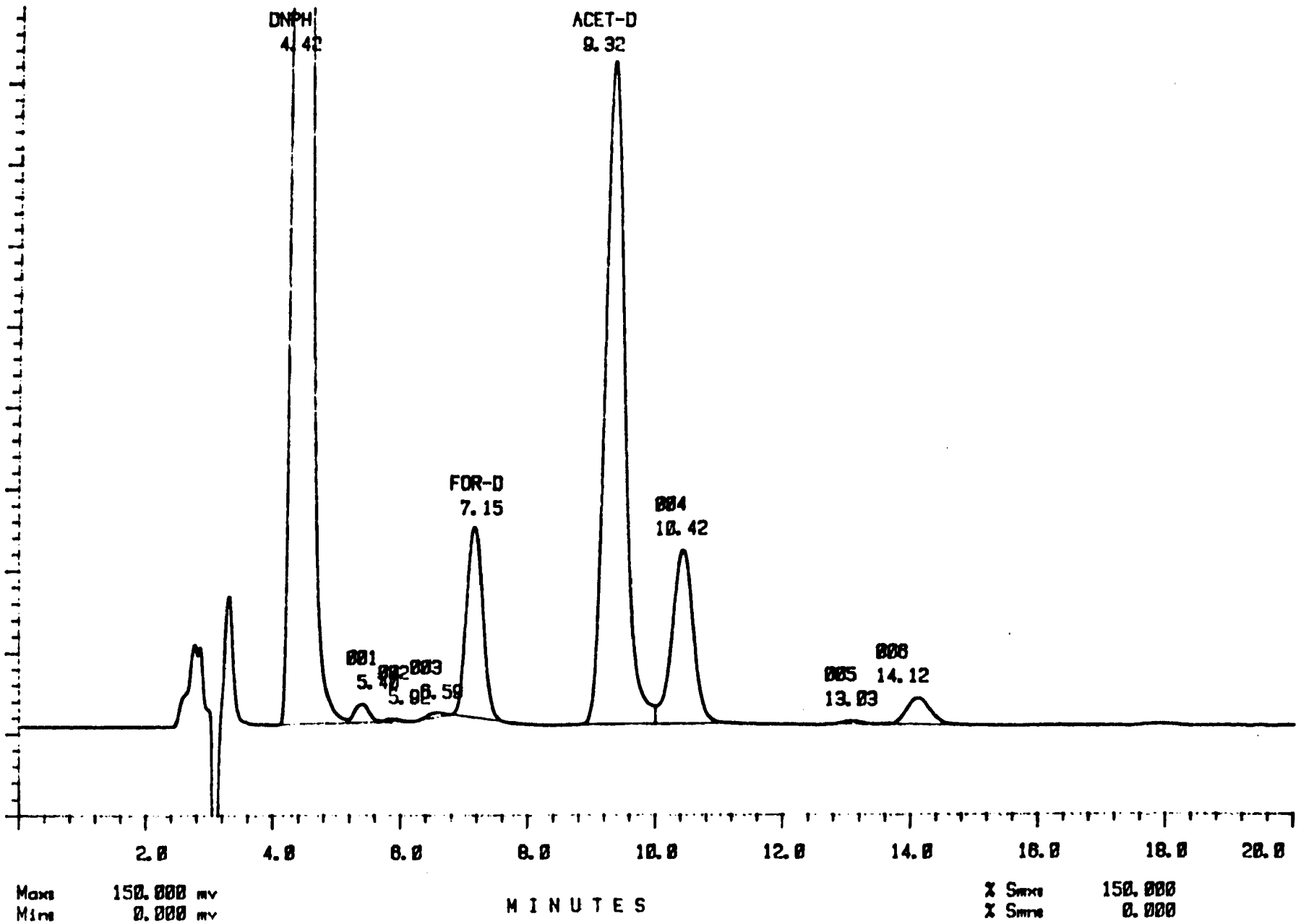


Figure 5. Representative chromatogram from derivatization of sludge extract.

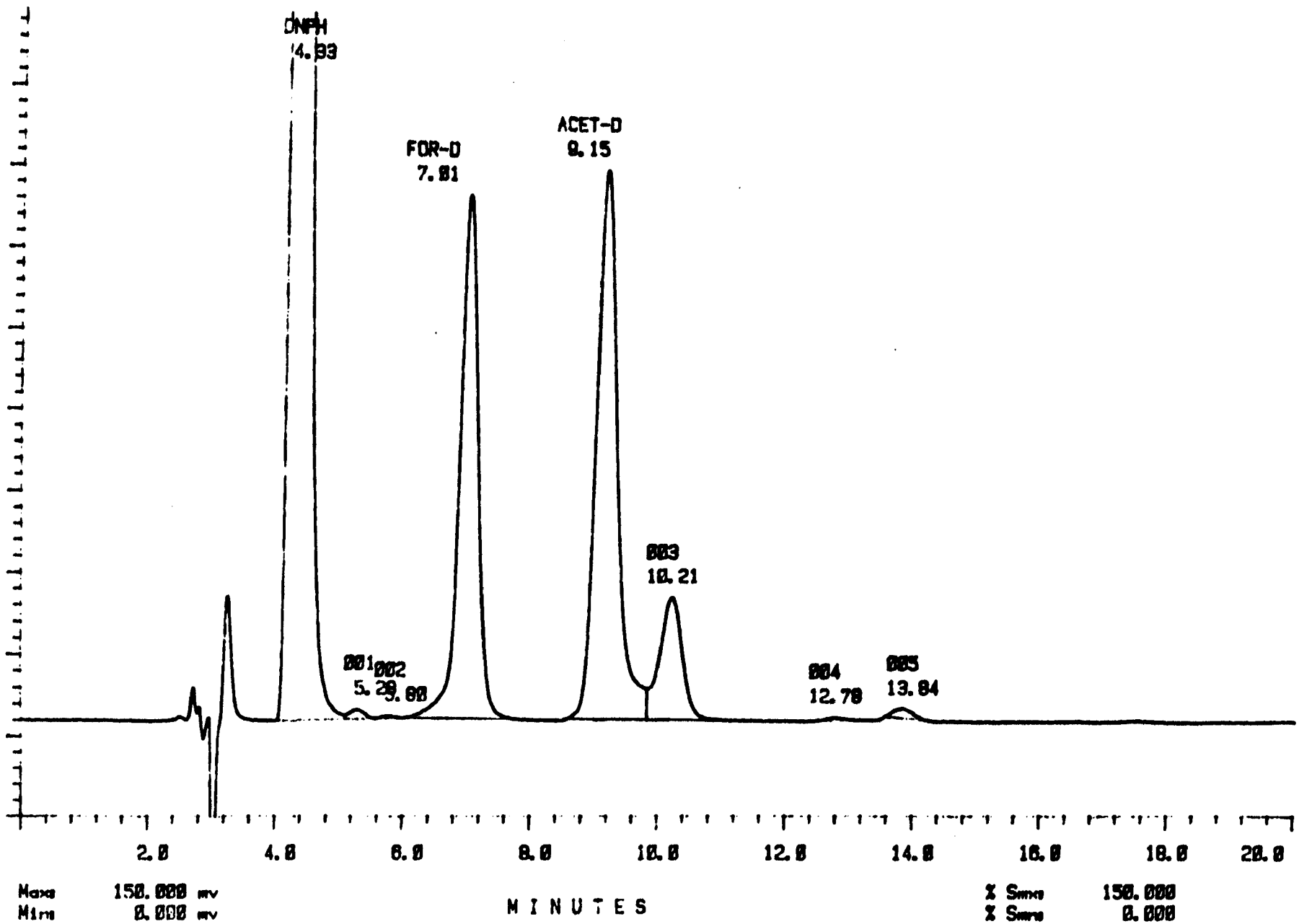


Figure 6. Representative chromatogram from derivatization of wood dust extract.

conditions employed. The reaction conditions assured an excess on all reagents, providing pseudo-first-order conditions for the reaction for formaldehyde, and first-order formation of the derivative. The purpose of these experiments was to determine the apparent rate constant, k, for the formation of the derivative using spiked reagent water, and compare this rate to the value obtained from derivatization of formaldehyde in sample matrices. The data would also allow a comparison of the form of the kinetic equation for each sample, as evidenced by the shape of the kinetic plots.

Linear first-order plots were obtained for formation of the formaldehyde-DNPH derivative matrices, indicating no complex kinetic relationships. In addition, the observed rate constants (Table 2) for the samples were not statistically different from the value obtained from standards. In other words, the derivatization proceeded at the same rate in all cases, and the analysis did not generate additional formaldehyde from precursors. These data suggest that the analytical results obtained using this derivatization procedure represent levels of free formaldehye in the samples.

SINGLE-LABORATORY VALIDATION OF THE METHOD FOR FORMALDEHYDE

A single-laboratory validation protocol was used to evaluate the final, optimized method for the determination of formaldehyde. The protocol consisted of six steps -- instrumentation range, preliminary method evaluation, ruggedness testing, method range and detection limit, referee validation, and matrix validation. All steps except the referee validation were performed.

The liquid chromatography system with absorbance detection was determined to be linear from 1.43 to 1430 wg/L formaldehyde. The preliminary method evaluation consisted of multiple replicates at a spike level of 75 wg/L. A mean percent recovery of 88 percent with a relative standard deviation of under four percent was obtained in these experiments (Table 3). Ruggedness testing was performed to demonstrate that reasonable variation in method parameters did not affect the analytical results. Four method variables (reaction time, reaction pH, volume of DNPH reagent, and number of sorbent cartridges) were chosen because they were considered most likely to be subject to variation in the course of an analysis. Relatively broad limits were selected for each variable. However, none of the experimental variables was found to significantly affect the analytical results, suggesting that the method was sufficiently rugged to be useful in other laboratories (Table 4). The method detection limit was calculated to be 7.2 wg/L (Table 5). Finally, the method was evaluated with two matrices (final effluent and sludge). Although some significant differences in recovery were observed between standards and spike matrices, the precision and recovery data for the matrix experiments easily satisfied the established method performance criteria (Table 6). Additional

TABLE 2. SUMMARY OF FIRST-ORDER RATE CONSTANTS FOR APPEARANCE OF FORMALDEHYDE DERIVATIVE

Matrix	Average k (s^{-1})	Standard Deviation
Standard (250 ppb)	1.83×10^{-3}	0.12×10^{-3}
Landfill Leachate	1.70×10^{-3}	0.50×10^{-3}
Final Effluent	1.98×10^{-3}	0.36×10^{-3}
Wood Dust	1.90×10^{-3}	0.34×10^{-3}
Sludge	1.97×10^{-3}	0.47×10^{-3}

TABLE 3. RESULTS OF PRELIMINARY METHOD EVALUATION

Spike Level (ppb)	75.0
Mean Response For Eight Replicates	65.8
Mean Percent Recovery	87.7
Lower Confidence Bound	85.2
Upper Confidence Bound	90.2
Percent Relative Standard Deviation	3.42

TABLE 4. RESULTS OF RUGGEDNESS TEST EXPERIMENTS

Parameter	Low Condition	High Condition	Parameter Effect[a]	Significance[b]
Reaction Time	25 min	40 min	-0.447	Not significant
Reaction pH	4.8	5.2	2.27	Not significant
DNPH Reagent	5 mL	7 mL	4.13	Not significant
Number of Cartridges	2	4	3.49	Not significant

(a) A measure of the effect of the parameter on the analytical results.

(b) Critical Effect Level = 6.92 for 7 degrees of freedom.

TABLE 5. RESULTS FOR METHOD RANGE AND METHOD DETECTION LIMIT EXPERIMENTS

Spike Level[a] (ppb)	Percent Recovery[a]	Confidence Bound for Recovery (Lower/Upper)	Percent Relative Standard Deviation	Confidence Bound For Percent Relative S.D. (Lower/Upper)	Method Detection Limit (ppb)	Number of Replicates
15.0	70.6	57.3/84.0	22.6	15.0/46.1	7.19	8
46.8	94.6	86.8/102	9.77	6.46/19.9		8
146	88.9	85.5/92.3	4.57	3.02/9.31		8
457	86.4	82.9/89.9	4.37	2.82/9.63		7
1,430	91.7	87.9/95.5	4.91	3.25/10.0		8

(a) All values are corrected for a laboratory blank value of 12.5 ug/L.

TABLE 6. SUMMARY OF MATRIX VALIDATION EXPERIMENTS

Spike Level ppb	Final Effluent 46.8	Final Effluent 1430	Sludge Extract 457	Sludge Extract 1430
Percent Recovery				
Test Matrix	99.1	80.5	106	82.2
Standard Matrix[a]	94.6	91.7	86.4	91.7
Relative Standard Deviation				
Test Matrix	6.84	4.57	3.24	1.98
Standard Matrix	9.77	4.91	4.37	4.91
Percent Recovery Difference	4.5	-11	20	-9.5
Confidence Bounds for Percent Recovery Difference (Lower/Upper)	-6.3/15	-16/-6	15/25	-14/-5
Significant Difference[b]	No	Yes	Yes	Yes
Test/Standard Standard Deviation Ratio	0.86	0.82	1.0	0.38
Confidence Bounds for Standard Deviation Ratio (Lower/Upper)	0.39/1.9	0.37/1.8	0.45/2.5	0.17/.85
Significant Difference[c]	No	No	No	Yes

(a) Data from Method Range experiments.

(b) Difference is not significant if confidence bound range includes zero.

(c) Difference is not significant if confidence bound range includes unity (1).

Table 7 provides a summary of single oeprator accuracy and precision.

TABLE 7. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Matrix Type	Average Percent Recovery	Standard Deviation (Percent)	Spike Range (µg/L)	Number of Analyses
Formaldehyde	Reagent Water	86	9.4	15.0-1430	39
	Final Effluent	90	11	46.8-1430	16
	Sludge	93	12	457-1430	15

matrix experiments may be necessary, but it can be concluded that the analytical results provided by this method accurately reflect the amount of formaldehyde in the samples.

CONCLUSIONS AND RECOMMENDATIONS

Quantification of formaldehyde at low wg/L levels is possible by employing DNPH derivatization at pH 5. The reaction solutions can be readily extracted using solid sorbent cartridges rather than solvent extraction. Under the conditions employed, the formation of the formaldehyde-DNPH derivative appears to follow first-order kinetics in all matrices studies. The results suggest that the procedure is indeed measuring free formaldehyde in solution and significant amounts of formaldehyde are not being formed from precursors during the derivatization. The single laboratory validation data indicate that the method is rugged and should perform well in other laboratories.

Additional work with this general derivatization approach should focus on application of the method to other matrix types. Derivatization of other carbonyl compounds may also be possible with minor modifications of the reaction conditions.

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HEATED PURGE-TRAP-DESORB ANALYSIS OF VOLATILE, WATER SOLUBLE COMPOUNDS

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ABSTRACT

In an on-going research program sponsored by the U. S. EPA, heated purge-trap-desorb (H-PTD) methodology has been investigated for its applicability to the analysis of high to moderate volatility organic pollutants which are too water soluble for conventional PTD analysis.

The 33 analytes selected for this study are Appendix VIII and Michigan List compounds. Some were selected due to an a priori expectation that they would require an H-PTD approach. Some were compounds which had failed prior SW-846 PTD method testing. Other volatile but highly polar compounds which had failed to elute in GC-MS suitability testing using the SP1000/Carbopack B packed GC column were also included. The analytes included 9 nitriles, 8 nitrogen bases, 5 alcohols, 6 carbonyl compounds, 3 thiols, and two others. Although most of the analytes displayed good GC behavior on the chosen GC column (30mm x 0.53mm ID fused silica; 1.0 micron Supelcowax 10), many were found to be hydrolytically unstable to the heated purge step, thermally unstable toward the trap desorption step, or non-recoverable by H-PTD for unknown reasons. H-PTD testing for method development was performed principally with acrolein, acetonitrile, propionitrile, acrylonitrile, methacrylonitrile, methyl ethyl ketone, isobutanol and dioxane.

Most of the recovery and reproducibility problems encountered in H-PTD analysis are associated with the large amount of water evaporated from the heated purge vessel. Three approaches were investigated in an attempt to control this water and prevent its condensation in the plumbing and trap of the H-PTD device: 1) A small condenser was used at the purge vessel outlet, 2) purge stream dilution with trapping at a temperature above the resultant dew point, and 3) chemically selective water removal. A fourth approach using a Nafion tube had already been shown to be impractical with highly polar analytes and, therefore, was not investigated. The first approach was the only water control method found practical. This approach was explored with regard to the breakthrough volumes of critical analytes, the use of more retentive traps, the temperature of the condenser, and the "salting out" effect of chlorides and sulfates of sodium and magnesium.

Results to date indicate that the developed method, which employs a standard 5-mL purge vessel is effective for hydrolytically stable analytes with water solubilities, vapor pressures and polarities similar to, or more favorable than, acetonitrile and isobutanol. Absolute H-PTD recoveries ranging from 75 to 100 percent with RSD's <10% (3 replicates) have been obtained at the 50 ug/L spiking level

using 5-mL samples and FID detection.

Future work expected to be completed before presentation to the symposium includes precision and accuracy studies with multiple replicates for all analytes of the original 33 for which the method provides some recovery. Results will be reported in terms of absolute H-PTD recovery (versus septum injection of the H-PTD sample), recovery (versus H-PTD calibration standards), precision (based on 6 to 8 replicates at high and low spiking levels), and estimated method detection limits for the tested analytes in reagent water.

EVALUATION OF EXTRACTION CONDITIONS FOR APPENDIX IX COMPOUNDS

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ABSTRACT

An analytical method utilizing gas chromatography/mass spectrometry (GC/MS) was selected as the mode of analysis for the extractable semi-volatile organic compounds comprising the Appendix IX list (Fed. Reg. Vol. 51, No. 142, Thursday, July 24, 1986). The chromatographic conditions specified in the Contract Laboratory Program (CLP) have been selected for analysis of the Appendix IX compounds, but the extraction conditions specified in the CLP, for the analysis of Appendix IX compounds are the subject of much criticism and variance. This is especially true when using the optional continuous extractors which supposedly remove the art form the extraction process, and enable the extraction of emulsion-forming water samples. The main criticism of the CLP extraction scheme seems to arise from the low recoveries of the more polar neutral and the acidic compounds by the base neutral extraction at elevated pH followed by acidification and extraction of the acidic compounds. These losses may be attributed to occlusion. Initial extraction under acidic conditions, however, eliminates many of these problems, but produces acid/neutral extracts that sometimes contain more interferences and other organic constituents. Subsequent pH elevation for the extraction of the basic constituents gives less precipitation and flocculation than when extracted initially at elevated pH.

In these studies, a set of experiments was set up to compare the recoveries of Appendix IX analytes from reagent water under various extraction conditions, all utilizing continuous extraction with methylene chloride. The following schemes were examined:

1. Acid/neutral extraction followed by basic extraction
2. Base/neutral extraction followed by acidic extraction
3. Neutral extraction followed by acidic extraction
4. Extraction at pH 4 only

Percent recovery data for the analytes under the various extraction schemes was presented with statistical evaluation.

INTRODUCTION

As mandated by Sections 304(h) and 501(a) of the Clean Water Act of 1977, The U.S. Environmental Protection Agency proposed fifteen test procedures for measuring the concentration of priority pollutants in

industrial wastewaters (1) which, after extensive public comment, laboratory testing and subsequent editorial revision, were promulgated as approved methods (2). Among the most ubiquitously applied of these procedures has been EPA Method 625, an omnibus method for measurement of trace, semivolatile, organic pollutants by gas chromatography/mass spectrometry (GC/MS following extraction of a water sample with methylene chloride using separatory funnel or continuous extractor and concentration of the extract by Kuderna-Danish (K-D) evaporation. The method was designed to recover basic, neutral and acidic compounds. Thus, water samples are first extracted under basic (pH 11) conditions, acidified to a pH 2 and reextracted. The two extracts are then analyzed independently under different chromatographic conditions. The basic and neutral compounds contained in the first extract are separated by a packed, 1.8 meter glass column with a stationary phase of 3% SP-2250 (or equivalent) while separation of acidic compounds is accomplished with a similar column packed with SP-1240DA (or equivalent). With the advancement in recent years of fused silica capillary column (FSCC) technology, however, separations adequate for mass selective detection of basic, neutral and acidic organic compounds have been achieved with a single, bonded-phase, silicone FSCC. Accordingly, the Superfund (CERCLA) Contract Laboratory Protocol (CLP) and the SW-846 (RCRA) program have adopted capillary column GC/MS procedures which analyze combined, base/neutral and acid extracts.

Since the inception of Method 625, it has been understood that while the base/neutral-acid extraction sequence provides acceptable analytical recoveries for a preponderance of priority pollutants, chlorinated hydrocarbon pesticides, such as a-BHC, -BHC (lindane), endosulfans I and II and endrin, displayed impaired recoveries due to decomposition under alkaline extraction conditions (3). Subsequently, a neutral (pH=7) - acid (pH 2) extraction procedure was shown to outperform Method 625 in the recovery of these compounds (4). Similar losses have also been demonstrated for certain phthalate esters which were attributed to hydrolysis under basic conditions (5).

The most strident criticism of the B/N-A extraction procedure regards the low recoveries of polar neutral and acidic compounds form groundwater and wastewater samples. These losses have been attributed to occlusion. The acid/neutral-base extraction sequence has found favor with many analysts because of its ability to mitigate the flocculation and precipitation which engenders occlusion of trace organic compounds in the sample. There is some concern, however, that an initial acidic condition may produce interferences or modification of constituents.

In an effort to arrive at some consensus on extraction methodology, EMSL-Cincinnati has designed an experiment to evaluate 4 candidate

extraction procedures when applied to approximately 200 representative compounds from the priority pollutants, RCRA Appendix VIII and IX and Hazardous Substance lists. The 4 procedures included base/neutral extraction at a pH 11 followed by acidic extraction at a pH 2(B/N-A), acid/neutral extraction at a ph 2 followed by basic extraction at a ph 11(A/N-B), neutral extraction at pH=7 followed by acidic extraction at pH 2(N-A) and, finally, a single extraction at a pH of 4 (pH4). This last procedure has been proposed as an option for the continuous extraction technique on the premise that a prolonged extraction period can compensate for less favorable partition coefficients. All extractions were accomplished using continuous, liquid-liquid extractors (method 3520). Continuous extraction was employed in favor of the separatory funnel technique (Method 3510) to simulate the extended extraction conditions which would be most conducive to analyte decomposition and for formation of interferences and to minimize random variance that would accompany numerous repetitions of the labor intensive manual procedure.

The initial phase of this study consisted of an investigation of analyte recoveries form spiked reagent water samples using the 4 extraction procedures. The 200 compounds were divided into 8 analysis groups. Extracts of five of these groups were measured by GC/MS analytical procedures for semivolatile, organic pollutants detailed in the CLP. The remaining three analysis groups comprised RCRA Appendix VIII compounds which for reason of involatility or thermal lability were deemed unsuitable for GC/MS analysis (6). Following the same extraction protocol, these compounds were analyzed by high performance liquid chromatography (HPLC) using SW-846 Methods which are currently in the late developmental phase here at EMSL-Cincinnati.

At the completion of the above experiment, spiked POTW samples will be analyzed by the same protocol in order to evaluate the matrix dependent characteristics of these extraction procedures.

DESIGN

Approximately two hundred compounds from the priority pollutant, RCRA Appendix VIII and Hazardous Substance Lists were grouped for analytical convenience into eight analysis sets. These compounds were obtained as standard concentrates from both commercial and EPA sources. Each analysis set was spiked into reagent water and processed by continuous extraction according to each of the following treatment procedures.

*A/N-B: Extraction at pH 2 followed by adjustment to pH 11 and reextraction.

*B/N-A: Extraction at ph 11 followed by acidification to ph 2 and reextraction.

*N-A: Extraction of neutral sample (pH=7) followed by reextraction at pH 2.

*pH4: Single extraction at pH=4.

Four replicate extractions were performed for spikes of each analysis set under each of the four extraction conditions itemized above. The resultant extracts were then concentrated by K-D techniques and analyzed by GC/MS or HPLC procedures. Percent recoveries achieved for the analytes under each extraction condition were then compared. Recovery differences were identified at p 0.01 significance level using ANOVA statistical processing. (Statistician's MACE, Matrix Calculating Engine, Inc., Madison, Wisconsin).

EXPERIMENTAL DETAIL

Apparatus and Chemicals:

The continuous, liquid-liquid extractor used in this study is described in Figure 1. The remaining glassware, the solvents and reagents, obtained from a variety of commercial suppliers, all conformed to specifications presented in Sections 2.3 and 2.4 of the CLP.

Analytes:

GC/MS analytes were acquired from commercial and EPA sources. Supelpreme - HC Standards (Supelco, Inc., Bellefonte, PA) served a source of priority pollutants and HSL compounds. The Quality Assurance Branch (QAB) of EMSL - Cincinnati provided spiking concentrates of RCRA Appendix IX compounds which were prepared by QAB for the interlaboratory validation study of SW-846 Method 8270. HPLC analytes were obtained for the Aldrich and Sigma Chemical Companies as neat materials and from the EPA Repository for Hazardous Materials as reference standards.

Spiking Solutions:

The 200 compounds were divided into 8 analysis sets. A spiking solution constituting each analysis set was prepared by dilution with either methanol, for the GC/MS spikes, or acetonitrile, for the HPLC spikes.

Set A: Priority Pollutants and HSL Compounds - This spiking solution was composed of the Supelpreme - HC mixes listed below. All mix constituents were at concentrations of 2000 ug/mL.

Base/neutral Mix 1 (4-8900)
Base/neutral Mix 2 (4-8901)
Pesticides (4-8903)

Phenols (4-8904)
Polynuclear Aromatic Hydrocarbons (4-8905)
Benzidines (4-8906)

One-half mL of phenol mix and 0.25 mL of each of the remaining mixes were diluted with methanol to 25.0 mL in a volumetric flask. To constitute the sample, 1.0 mL of the spiking solutions was pipetted into 2.0 L of reagent water.

Set B: Method 8270 MV Mix 1 - Six mL of Mix 1, Ampule 3 spiking concentrate was placed in a 50.0 mL volumetric flask and diluted to the mark with methanol. Two liters of reagent water were spiked with 2.0 mL of this solution. Parameters in Mix 1, Ampule 3 concentrate were at concentrations of either 200, 160, and 120 ug/mL.

Set C: Method 8270 MV Mix 2 - Compounds in Mix 2, Ampul 2 concentrate were uniformly at a concentration of 400 ug/mL. Three mL of this concentrate was diluted to 50.0 mL with methanol and spiked at a level of 2.0 mL per 2.0 L of reagent water.

Set D: Method 8270 MV Mix 3 - The Ampul 2 concentrate of this mix was diluted and spiked in a manner identical to Mix 2, above.

Sets F, G and H: Appendix VIII HPLC Compounds - Spiking solutions were prepared by dilution of neat materials and repository standards with acetonitrile. Spiking volume was 2.0 mL for 2 L volume of reagent water. The spike concentration of each analyte was such that a 100% recovery would yield a detector response equivalent to 20 x the EDL. Analyte set constituents are listed below:

Set F

Ethylene thiourea
1,2 - Diphenylhydrazine
Rotenone
N-Nitroso-N-ethylurea
Benomyl

Set G

Mitomycin C
Methomyl
1,2-Phenyldiamine
1,5-Napthalenediamine
Actinomycin D

Set H

Thiourea
1-Acetyl-2-thiourea
1,3-Phenyldiamine
1-(o-chlorophenyl)-2-thiourea
Diethylstilbestrol

Surrogate Standards

Each water sample was spiked with CLP, acid and base/neutral surrogate compounds. Spiking solutions consisted of methanolic dilutions of surrogate standard mixes supplied by Supelco, Inc.

Calibration Standards

Supelpreme-HC Standard Mixes and CLP Surrogate Mixes were also used to prepare GC/MS calibration standards for priority pollutants (Analysis Set A). Calibration standard concentrates for the RCRA Appendix IX compounds were provided by Quality Assurance Branch of EMSL-Cincinnati. Calibration curves were generated using three standards prepared by serial dilution of the standard mix concentrates with methylene chloride. HPLC calibration standards were made by dilution of neat materials and repository standards with acetonitrile.

Internal Standards

As per CLP a 10WL aliquot of internal standard solution was added to all calibration standards and sample extracts just prior to GC/MS analysis. The internal standard solution was supplied by Supelco, Inc.

Instrumentation

The instrument used for GC/MS analysis was a Hewlett Packard 5890 GC coupled with an HP 5970B Mass Selective Detector (MSD). Instrument output was processed using a HP-200 data system.

With HPLC, a Waters Associates modular system was used for all analyses. The system included a WISP autosampler (Model 710B), two solvent pumps (Model 510), a fixed wavelength UV detector (Model 440) and system controller (Model 721). An IBM PC/AT with Nelson Analytical software (Rev. 3.6) and a Nelson Analytical Interface 00odel 762B) collected and processed the chromatographic data.

Continuous Extraction

The continuous extractor was a 2-L capacity, all glass system fabricated by Paxton Woods Glass Ship, Cincinnati, Ohio. A diagram of the extractor is presented in Figure 1. The extractor was first loaded with 150 mL of methylene chloride after which 300 mL of methylene chloride was placed in the distilling flask. Two liters of spiked water sample were then poured gently into the extractor with the aid of a stirring rod. The stirrer-condenser assembly was attached and actuated, after which the methylene chloride reservoir (distilling flask) was warmed to 40°C with a heating mantle. The solvent volume cycled at a rate of approximately 0.6 hour^{-1}. Samples were extracted overnight for a period of 20 $\pm$ two hours.

Adjustment of the sample pH was accomplished just prior to initiating the extraction with the sample in the extractor. Sample pH was measured by a pH meter to the nearest tenth of a pH unit. To adjust acidity to pH 2 and basicity to pH 11, 6 N H_2SO_4(aq) and 6N

NaOH(aq) solutions were employed. Adjustments to pH=7 and pH=4 were performed using phosphate buffers.

Following the initial extraction, samples were readjusted to the second pH. Methylene chloride in the flask was collected for K-D concentration and replaced by fresh solvent. The sample was then reextracted in the manner described above. A second extraction was not required for the sample at pH4.

Extracts were dried with acidified sodium sulfate and concentrated to a volume of 1.0 mL by K-D techniques as prescribed in Method 8270. Concentrate pairs of the same sample were combined in 0.50 mL portions in 1.5 mL injector vial. Following the above procedures, extracts prepared for HPLC analyses required a solvent exchange step. One mL of combined extract was dosed with 2.0 mL of acetonitrile and reconcentrated to 1 mL.

GC/MS Analysis

Analyses of Sets A through E were accomplished using procedures for GC/MS quantitation of semivolatile extractables detailed in the CLP. Recommended chromatographic conditions were followed using a 30 m x 0.32 mm (I.D.), 1 um film thickness, DB-5 fused silica capillary column (J. & W. Scientific). Application was made of SW-846 Method 8270 (7) in selection of ion masses (m/z) for quantitation of RCRA IX compounds not included in the CLP.

HPLC Analysis

Sets F, G and H were measured by HPLC. These methods employed reverse phase separation with a 4.6 mm x 25 um, 10 um ODS analytical column (Resolvex C18, Fisher Scientific) in a mobile phase consisting of acetonitrile (MeCN) and water. Chromatographic separations were obtained using the following linear solvent gradients:

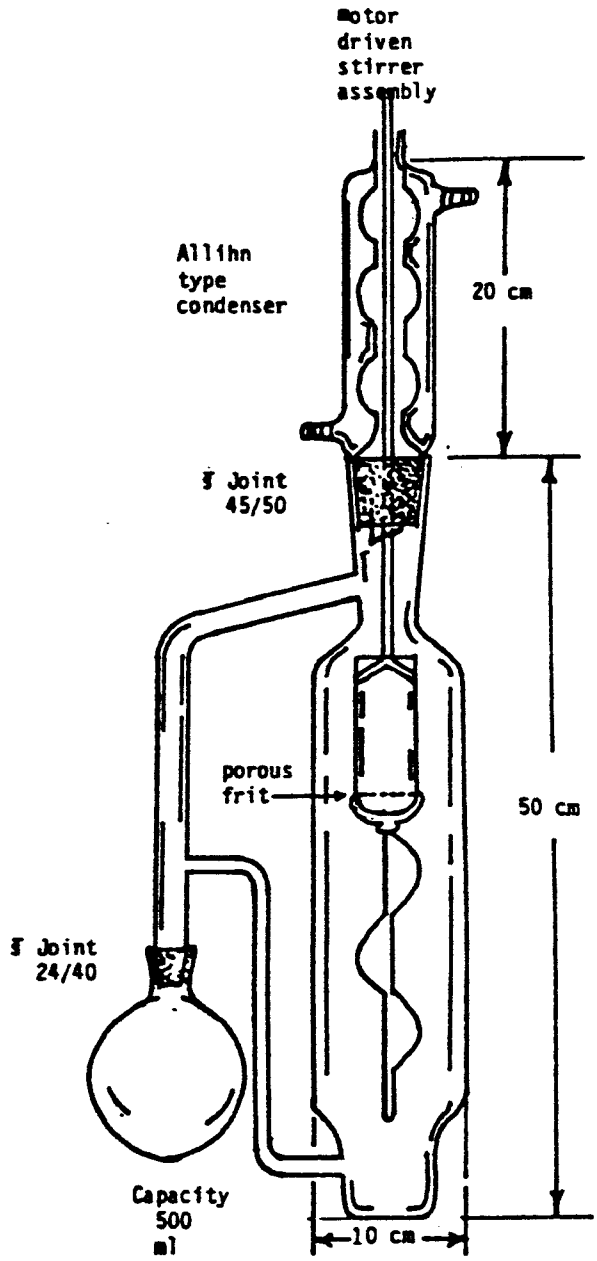
(1) 20% MeCN:80% H_2O to 100% MeCN (20 minutes)
(2) 100% H_2O (5 minutes), 100% H_2O to 100% MeCN (20 minutes)

Analytes were detected by UV at a wavelength of 254 nanometers.

RESULTS

At the time of this writing, we are able to report on recoveries of the priority pollutants and RCRA Appendix VIII, HPLC compounds. GC/MS analysis and data reduction for the RCRA Appendix IX compounds are still in progress. These results will be incorporated into this report for presentation at the Symposium For Solid Waste Testing and Quality Assurance, 13 - 17 July 87.

Figure 1. Liquid/liquid Continuous Extractor



Percent recovery data for priority pollutants and RCRA Appendix VIII, HPLC compounds are shown in Tables 1 and 2, respectively. Table 1 also includes results obtained for surrogate standards, which, for each of the four extraction methods tested, fell within the performance based limits set forth in Exhibit E, Section IV of the CLP. Percent recoveries were calculated as follows:

$$PR = \frac{Cexp}{Ct} \times 100\%$$

where, Cexp is the experimentally determined analyte concentration in the water sample and Ct is the nominal, true concentration. Analyte recoveries were not corrected (normalized) to responses obtained from a synthetic, reference solution of the spiking concentrate. Reference solutions were employed, however, for quality assurance purposes. Results were statistically processed using the ANOVA t-test to identify method dependent recovery differences with a null hypothesis significance of $p(t) \_ 0.01$. While all extraction method combinations were compared, this report focuses on comparisons of the CLP method (base/neutral-acid) with each of the other tested procedures. Table 3 lists priority pollutants which displayed significant recovery differences and Table 4 provides a similar listing of RCRA Appendix VIII, HPLC compounds.

Priority Pollutants

In comparing the B/N-A and the A/N-B extraction schemes, 18 out of 57 compounds presented improved recoveries under the A/N-B procedure while only 2 had significantly diminished recoveries. Thirty-three differences were found for B/N-A versus N-A with 15 cases of greater recovery and 18 cases of lesser under the N-A procedure. The pH4 extraction method fared worst in comparison with B/N-A where the latter outperformed the former for 27 out of 32 compounds presenting significant recovery differences.

The comparative performance of the pH4 extractions was a puzzlement. It was expected that this method would mimick A/N-B and N-A procedures in recovering neutral and weakly acidic compounds. However, the pH=4 extraction, with a few exceptions, yielded recoveries uniformly lower than A/N-B and N-A. The most obvious explanation for this discrepancy is the pH4 procedure was performed as a single 20-hour continuous extraction whereas the other processes consisted of 2 such extractions conducted sequentially on the same sample. Given the high partitioning efficiency of the continuous extractors, it seems unlikely that any molecular compounds would remain in the sample after a 20-hour extraction, thus rendering the above explanation as specious. It will be tested, nevertheless, by repeating the pH4 method employing a second extraction.

The most consistent and pronounced differences in extraction performance occurred with the alpha, delta and gamma isomers of BHC (1,2,3,4,5,6-hexachlorocyclohexane) and the phthalate esters (Table 3).

Decomposition of α-BHC and γ-BHC(lindane) under alkaline extraction conditions has been documented for EPA Method 625. Slayton and Trovato have noted diminished recoveries of lower molecular weight phthalate esters under the B/N-A regime. The latter findings were attributed to basic hydrolysis at the initial extraction pH which could be mitigated by sterical effects (5). Phthalate ester results reported in Table 1 suggest this hypothesis, as well. A compilation of pertinent phthalate ester data is given on the next page:

		Δ ((A/N-B)-(B/N-A))
phthalates -	methyl -	93.2
	ethyl -	82.3
	butyl-benzyl -	60.0
	di-N-butyl -	32.2
	bis(2-chloroethoxy) -	6.0
	bis(2-chloroethyl) -	3.0
	bis(2-chloroisopropyl) -	2.9
	di-N-octyl -	-5.0
	bis(2-ethylhexyl) -	-12.0

A majority of phenols demonstrated improved recoveries when not exposed to initial, basic extraction conditions as evidenced by the results of the B/N-A and N-A extraction schemes detailed in Table 5. As the table shows the significant increases were fairly modest (9% - 16%) and the B/N-A phenolic recoveries by themselves were quite acceptable.

TABLE 5
PERCENT RECOVERIES OF PHENOLS BY B/N-A, A/N-B AND N-A EXTRACTION SCHEMES

Compound	B/N-A	A/N-B	N-A
D-5 Phenol	79.5	93.3	87.8*
phenol	82.0	92.5	94.8
4-Chloro-3-methylphenol	92.8	101.0*	106.0
2-Chlorophenol	70.8	80.2*	68.8*
2,4,6-Tribromophenol	81.3	89.5	92.8
2,4-dichlorophenol	88.0	97.8	103.0
2-Nitrophenol	89.8	95.3*	104.0
2,4,6-Trichlorophenol	80.3	89.0	96.0
2-Fluorophenol	73.0	86.3	86.5
Pentachlorophenol	114.0*	116.0*	136.0*

*Not significantly different from B/N-A recovery at $p \geq 0.01$.

RCRA APPENDIX VIII, HPLC COMPOUNDS

The Appendix VIII, HPLC parameters are an assortment of approximately 50 compounds sharing the properties of low volatility and/or thermal lability, characteristics which make them inappropriate for inclusion in GC/MS protocols. This list comprises a fairly high percentage of therapeutic agents with characteristic suseptibility to decomposition or rearrangement at extremes of pH. The 19 compounds reported in Table 2 are those for which acceptable liquid chromatography has been developed thus far. Using B/N-A extraction, acceptable recoveries were achieved for only 8 of 19 compounds. The remaining methods each provided significant recovery increases for 8 or more compounds when compared to B/N-A (Table 4). In terms of the number of acceptable recoveries the methods rank as follows:

$$\text{ph4(16)} > \text{N-A(14)} > \text{A/N-B(13)} > \text{B/N-A(8)}.$$

As expected, a number of compounds demonstrated interesting extraction performances under the 4 procedures. Initial basic extraction conditions apparently caused N-nitroso-Nethylurea, 1-acetyl-2-thiourea, methomyl and actinomycin D to decompose, while even mildly acidic conditions elicited the same response from Mitomycin C. Three compounds, Rotenone, Benomyl and N-nitroso-N-ethylurea were found to achieve better recoveries under mildly acidic conditions than at the pH extremes.

CONCLUSIONS

Thus far in this experimentation, the acid/neutral-base extraction scheme has demonstrated significantly higher recoveries than the base/neutral-acid procedure for 18 priority pollutants and 10 RCRA Appendix VIII, HPLC compounds, most noteworthy of which are the BHC isomers and phthalate esters, supporting the previously reported findings of Slayton and Travato (5). Like A/N-B, the neutral acid and pH4 methods also achieved recovery improvements over B/N-A for many of the same compounds, but also presented a number of cases of diminished recovery. A/N-B, on the otherhand, was significantly out performed by B/N-A in only 5 cases, and one of these, 1,2,4-trichlorobenzene, may have been artifactual. The N-A and pH4 extractions yielded better overall recoveries for the RCRA VIII HPLC compounds alone. However, A/N-B recovery performance for these compounds was more than ample to make it feasible as a cost effective approach for an omnibus, GC/MS - LC/MS protocol where extract splitting would be employed.

EMSL - Cincinnati will continue its research on standard matrix recoveries of RCRA Appendix IX compounds employing continuous extraction and analysis methods described herein. Upon completion of the list of 200 compounds in the experimental design, the second phase of this experiment will investigate recoveries of the same compounds from municipal and industrial wastewaters.

Table 1. Average Percent Recoveries of Priority Pollutants Using Four, Methylene Chloride, Continuous Extraction Procedures

Compound	True Value (ug/L)	A/N - B		B/N - A		N - A		pH4	
		PR	SD	PR	SD	PR	SD	PR	SD
Anthracene	10	81.5	5.2	83.3	4.4	72.3	7.0	63.3	5.7
B-BHC	10	97.0	5.9	96.3	5.7	98.5	4.0	81.3	6.3
Benzo(a)anthracene	10	86.3	3.8	84.0	1.6	62.0	9.1	60.5	8.7
Benzo(a)pyrene	10	101	7.9	106	7.6	78.5	11.1	61.8	11.5
Benzo(b)fluoranthene	10	101	1.8	100	10.0	72.5	14.5	63.3	18.4
Bis(2-ethylhexyl)phthalate	10	104	11.4	116	16.7	86.7	13.1	60.2	8.8
Bis(2-chloroethoxy)phthalate	10	94.0	4.8	88.0	3.4	95.5	5.8	83.3	3.8
Bis(2-chloroethyl)phthalate	10	109	6.7	106	2.9	114	2.2	96.5	4.8
Bis(2-chloroisopropyl)phthalate	10	87.2	8.5	84.3	5.0	92.5	3.7	76.3	6.9
Butylbenzylphthalate	10	112	14.8	52.0	34.7	96.3	8.7	63.0	5.6
Chrysene	10	86.3	3.8	84.0	1.6	62.0	9.1	60.5	8.7
D-5 Nitrobenzene(S)	25	91.0	5.0	85.3	1.9	95.3	2.2	74.3	2.7
D-5 Phenol(S)	50	93.3	7.1	79.5	5.8	87.8	3.7	71.5	3.3
D-BHC	10	90.5	3.5	21.0	2.4	92.3	3.4	75.2	3.8
Di-N-butylphthalate	10	99.5	8.5	67.3	3.9	98.5	8.3	75.3	6.9
Di-N-octylphthalate	10	120	13.5	125	13.4	83.5	15.1	64.2	9.3
Dieldrin	10	98.2	10.2	98.5	3.9	72.0	10.6	69.3	8.1
Diethylphthalate	10	89.8	5.0	7.5	8.7	92.2	5.4	78.2	5.1
Dimethylphthalate	10	93.2	4.9	0	-	95.3	6.0	76.5	5.8
Endosulfansulfate	10	98.5	8.9	74.3	5.6	84.0	7.8	71.5	8.5
Fluoranthrene	10	96.3	7.4	94.0	4.2	73.7	9.1	62.3	6.8
Fluorene	10	84.8	4.4	77.8	6.3	77.0	4.7	64.3	3.9
Heptachlor	10	109	12.6	106	13.1	76.0	16.2	44.0	29.4
Heptachlor Epoxide	10	104	12.8	105	5.1	82.0	10.6	64.8	6.6
Hexachlorobenzene	10	82.8	2.7	81.7	5.3	60.3	9.5	49.5	8.9
Hexachlorobutadiene	10	31.5	3.7	27.8	4.6	26.5	3.0	25.3	1.0
Hexachloroethane	10	38.5	4.9	33.5	1.7	34.5	3.0	40.0	4.5
ɣ-BHC (Lindane)	10	93.5	5.7	0	-	92.3	3.8	76.5	5.2
N-nitroso-di-N-propylamine	10	117	8.3	111	7.7	116	5.7	95.0	7.1
N-nitrosodiphenylamine	10	64.5	11.4	88.5	4.4	95.5	1.7	72.3	2.2
Naphthalene	10	74.3	2.5	68.0	3.8	74.3	8.2	64.3	1.0
Nitrobenzene	10	99.0	5.4	94.3	5.0	101	1.3	92.3	3.9
Pentachlorophenol	20	116	7.7	114	15.2	136	9.5	84.8	6.9
Phenanthrene	10	84.5	5.8	81.0	6.5	71.5	3.9	60.5	5.3
Pyrene	10	95.0	6.3	92.0	5.0	70.5	8.2	60.3	8.5
Phenol	20	92.5	3.3	82.0	8.1	94.8	2.1	81.5	3.1
Terphenyl(S)	25	88.0	5.8	87.0	2.9	93.8	4.2	70.5	3.0
1,2,4-Trichlorobenzene	10	53.5	1.3	128	11.1	53.8	4.3	47.0	2.4
1,2-Dichlorobenzene	10	59.5	1.9	53.5	2.1	59.8	4.3	55.8	1.7

Table 1
Continued

Compound	True Value (ug/L)	A/N - B PR	A/N - B SD	B/N - A PR	B/N - A SD	N - A PR	N - A SD	pH4 PR	pH4 SD
1,3-Dichlorobenzene	10	55.5	3.9	48.5	2.4	53.3	4.3	52.5	3.3
2,4,6-Tribromophenol(S)	50	89.5	7.0	81.3	7.5	92.8	4.9	71.8	5.2
2,4,6-Trichlorophenol	20	89.0	2.2	80.3	11.6	96.0	5.2	70.0	2.6
2,4-Dichlorophenol	20	97.8	4.6	88.0	11.6	103	3.4	83.3	2.6
2,4-Dinitrotoluene	10	89.5	11.8	95.0	108	108	8.0	92.0	2.4
2-Chloronaphthylene	10	74.5	5.0	64.0	8.3	71.8	3.9	63.0	3.2
2-Chlorophenol	20	80.2	2.8	70.8	10.2	68.8	4.6	55.5	5.7
2-Chlorophenyl-phenylether	10	87.3	2.9	78.3	7.7	91.8	5.1	77.5	4.8
2-Fluorobiphenyl(S)	25	78.3	2.1	72.3	5.5	79.0	5.6	66.5	1.0
2-Fluorophenol(S)	50	86.3	8.8	73.0	7.4	86.5	5.7	75.8	4.3
2-Nitrophenol	20	95.3	5.6	89.8	10.0	104	5.8	86.8	5.1
4,4-DDD	10	105	8.8	106	5.4	79.3	13.8	65.5	8.3
4,4-DDE	10	92.5	5.4	93.5	4.8	70.0	9.7	59.0	6.1
4,4-DDT	10	99.0	11.1	94.3	9.2	70.5	14.3	59.3	7.9
4-Bromophenyl-phenylether	10	86.8	3.1	82.3	7.1	71.0	4.2	54.0	5.8
4-Chloro-3-methylphenol	20	101	7.4	92.8	6.8	106	7.4	88.5	1.0
A-BHC	10	89.3	6.8	15.3	10.2	86.3	3.3	70.5	2.6
Acenaphthene	10	81.2	4.6	71.3	8.7	75.3	3.5	63.3	3.5

(S) - Surrogate Standard

Table 2. Mean Percent Recoveries of RCRA Appendix VIII, HPLC Compounds Using Four, Methylene Chloride, Continuous Extraction Procedures

COMPOUND	TRUE VALUE (ug/L)	A/N - B PR	A/N - B SD	B/N - A PR	B/N - A SD	N - A PR	N - A SD	Ph=4 PR	Ph=4 SD
Ethylene Thiourea	40	31.2	87.1	46.2	9.5	20.6	50.5	13.8	72.5
1,2-Diphenylhydrazine	40	55.4	16.2	95.8	8.6	85.6	3.3	86.6	7.4
Rotenone	130	53.8	4.8	59.2	8.1	86.6	5.1	90.2	7.8
N-nitroso-N-ethylurea	30	48.8	13.9	0	-	26.8	14.2	61.4	5.2
Benomyl	190	67.6	6.5	51.2	18.0	80.2	2.5	85.4	9.6
5-Nitro-o-tuluidine	7	92.6	7.3	102.2	5.1	81.6	4.2	83.2	7.5
N-nitroso-N-methylurea	30	72.4	10.2	0	-	21.6	11.1	82.0	12.9
Crotonaldehyde	130	93.8	14.9	44.0	17.7	69.8	4.0	72.0	7.2
Mitomycin C	60	0	-	75.6	5.7	0	-	0	-
Methomyl	100	97.8	5.8	0	-	103.9	8.7	99.3	3.2
1,2-Phenyldiamine	80	103.1	7.6	102.4	2.1	111.7	7.1	103.5	2.0
1,5-Napthalenediamine	80	51.0	6.2	43.8	9.1	45.2	14.1	21.5	23.7
Actinomycin D	100	87.7	4.3	0	-	98.9	3.3	88.8	10.7
1-Acetyl-2-thiourea	87	86.7	1.6	0	-	91.3	6.0	81.5	4.0
1,3-Phenyldiamine	103	85.0	11.3	92.9	19.0	80.2	4.5	79.0	3.2
1-Phenylthiourea	113	96.5	1.9	87.1	9.8	92.5	4.5	84.3	2.4
1-(o-chlorophenyl)-2-thiourea	110	99.4	3.2	86.2	10.2	93.7	4.9	87.1	3.1
1-Naphthyl-2-thiourea	44	95.6	3.3	82.5	13.5	84.6	3.2	81.1	2.6
Diethylstilbestrol	127	75.4	1.4	93.9	8.5	102.6	4.9	95.3	3.5

Table 3. Priority pollutants presenting significant recovery differences; a comparison of CLP extraction method with acid/neutral-base, neutral-acid and pH=4 procedures.

	Average Percent Recovery		
COMPOUND	B/N - A	A/N - B	
N-Nitrosodiphenylamine	88.5	64.5	-24.0
Phenol	82.0	92.5	10.5
1,2,4-Trichlorobenzene	128.0	53.5	-74.5
1,2-Dichlorobenzene	53.5	59.5	6.0
1,3-Dichlorobenzene	48.5	55.5	7.0
2,4,6-Tribromophenol(s)	81.3	89.5	8.2
2,4,6-Trichlorophenol	80.3	89.0	8.7
2,4-Dichlorophenol	88.0	97.8	9.8
2-Chloronaphthalene	64.0	74.8	10.8
2-Fluorophenol(s)	73.0	86.3	13.3
Butylbenzylphthalate	52.0	112.0	60.0
D-5 Phenol(s)	79.5	93.3	13.8
d-BHC	21.0	90.5	69.5
Di-N-butylphthalate	67.3	99.5	32.2
Diethylphthalate	7.5	89.8	82.3
Dimethylphthalate	0.0	93.2	93.2
Endosulfansulfate	74.3	98.5	24.2
γ-BHC(Lindane)	0.0	93.5	93.5
α-BHC	15.3	89.3	74.0
Acenaphthene	71.3	81.2	9.9

	Average Percent Recovery		
COMPOUND	B/N - A	N - A	
Anthracene	83.3	72.3	-11.0
Benzo(a)anthracene	84.0	62.0	-22.0
Benzo(a)pyrene	106.0	78.5	-27.5
Benzo(b)fluoranthene	100.0	72.5	-27.5
Bis(2-ethylhexyl)phthalate	116.0	86.7	-29.3
Chrysene	84.0	62.0	-22.0
D-5 Nitrobenzene(s)	85.3	95.3	10.0
d-BHC	21.0	92.3	71.3
Di-N-butylphthalate	67.3	98.5	31.2
Di-N-octylphthalate	125.0	83.5	-41.5
Dieldrin	98.5	72.0	-26.5
Diethylphthalate	7.5	92.2	84.7
Dimethylphthalate	0.0	95.3	95.3
Endosulfansulfate	74.3	84.0	9.7
Fluoranthrene	94.0	73.7	-20.3
Heptachlor	106.0	76.0	-30.0
Heptachlor epoxide	105.0	82.0	-23.0
Hexachlorobenzene	81.7	60.3	-21.4
γ-BHC(Lindane)	0.0	92.3	92.3
Pyrene	92.0	70.5	-21.5
Phenol	82.0	94.8	12.8

Average Percent Recovery

COMPOUND	B/N - A	N - A	
1,2,4-Trichlorobenzene	128.0	53.8	-74.2
2,4,6-Trichlorophenol	80.3	96.0	15.7
2,4-Dichlorophenol	88.0	103.0	15.0
2-Chlorophenyl-phenylether	78.3	91.8	13.5
2-Fluorophenol	73.0	86.5	13.5
2-Nitrophenol	89.8	104.0	14.2
4,4-DDD	106.0	79.3	-26.7
4,4-DDE	93.5	70.0	-23.5
4,4-DDT	94.3	70.5	-23.8
4-Bromophenyl-phenylether	82.3	71.0	-11.3
4-chloro-3-methylphenol	92.8	106.0	13.2
a-BHC	15.3	86.3	71.0

Average Percent Recovery

COMPOUND	B/N - A	pH = 4	
Anthracene	83.3	63.3	-20.0
b-BHC	96.3	81.3	-15.0
Benzo(a)anthracene	84.0	60.5	-13.5
Benzo(a)pyrene	106.0	61.8	-44.2
Benzo(b)fluoranthrene	100.0	63.3	-36.7
Bis(2-ethylheryl)phthalate	116.0	60.2	-55.8
Chrysene	84.0	60.5	-23.5
D-5 Nitrobenzene(s)	85.3	74.3	-21.0
d-BHC	21.0	75.2	54.2
Di-N-octylphthalate	125.0	64.2	-60.8
Dieldrin	98.5	69.3	-29.2
Diethylphthalate	7.5	78.2	70.7
Dimethylphthalate	0.0	76.5	76.5
Fluorene	77.8	64.3	-13.5
Heptachlor	106.0	44.0	-62.0
Heptachlor epoxide	105.0	64.8	-40.2
Hexachlorobenzene	81.7	49.5	-32.3
γ-BHC(Lindane)	0.0	76.5	76.5
N-Nitrosodipropylamine	111.0	95.0	-16.0
N-Nitrosodiphenylamine	88.5	72.3	-16.2
Pentachlorophenol	114.0	84.8	-29.2
Phenanthrene	81.0	60.5	-20.5
Pyrene	92.0	60.3	-31.7
Terphenyl(s)	87.0	70.5	16.5
1,2,4-Trichlorobenzene	128.0	47.0	87.0
2-Chlorophenol	70.8	55.5	15.3
2-Methyl-4,6-dinitrophenol	109.0	81.0	28.0
4,4-DDD	106.0	65.5	40.5
4,4-DDE	93.5	59.0	34.5
4,4-DDT	94.3	59.3	35.0
4-Bromophenyl-phenylether	82.3	54.0	28.3
α-BHC	15.3	70.5	55.2

Table 4. RCRA Appendix VIII, HPLC compounds presenting significant recovery differences; a comparison of CLP extraction method with acid/neutral - base, neutral-acid and pH4 procedures.

Average Percent Recovery

Compound	B/N - A	A/N - B	
1,2-Diphenylhydrazine	95.8	55.4	-40.4
N-Nitroso-N-ethylurea	0.0	48.8	48.8
N-Nitroso-N-methylurea	0.0	72.4	72.4
Benomyl	51.2	67.6	16.4
Crotonaldehyde	44.0	93.8	49.8
1-Acetyl-2-thiourea	0.0	86.7	86.7
1-Phenylthiourea	87.1	96.5	9.4
1(o-Chlorophenyl)-2-thiourea	86.2	99.4	13.2
1-Naphthyl-2-thiourea	82.5	95.6	13.1
Diethylstibestrol	93.9	75.4	-18.5
Mitomycin C	75.6	0.0	-75.6
Methomyl	0.0	97.8	97.9
Actinomycin D	0.0	87.7	87.7

Average Percent Recovery

Compound	B/N - A	N - A	
Rotenone	59.2	86.6	27.4
N-Nitroso-N-ethylurea	0.0	26.8	26.8
N-Nitroso-N-methylurea	0.0	21.6	21.6
Benomyl	51.2	80.2	29.0
5-Nitro-o-toluidine	102.0	81.6	-20.4
Crotonaldehyde	44.0	69.8	25.8
1-Acetyl-2-thiourea	0.0	91.3	91.3
Mitomycin C	75.6	0.0	-75.6
Methomyl	0.0	104.0	104.0
Actinomycin D	0.0	98.9	98.9

Average Percent Recovery

Compound	B/N - A	pH = 4	
Ethylene thiourea	46.2	13.8	-32.4
Rotenone	59.2	90.2	31.0
N-Nitroso-N-ethylurea	0.0	61.4	61.4
N-Nitroso-N-methylurea	0.0	82.0	82.0
Benomyl	51.2	85.4	34.2
N-Nitro-o-toluidine	102.0	83.2	-18.8
Crotonaldehyde	44.0	72.0	28.0
1-Acetyl-2-thiourea	0.0	81.5	81.5
Mitomycin C	75.6	0.0	-75.6
Methomyl	0.0	99.3	99.3
1,5-Naphthalenediamine	43.8	21.5	-22.3
Actinomycin D	0.0	86.8	88.8

Table 5. Percent recoveries of phenols by B/N - A, A/N - B and N - A extraction schemes.

COMPOUND	B/N - A	A/N - B	N - A
D-5 Phenol	79.5	93.3	87.8*
phenol	82.0	92.5	94.8
4-Chloro-3-methylphenol	92.8	101.0*	106.0
2-Chlorophenol	70.8	80.2*	68.8*
2,4,6-Tribromophenol	81.3	89.5	92.8
2,4-dichlorophenol	88.0	97.8	103.0
2-Nitrophenol	89.8	95.3*	104.0
2,4,6-Trichlorophenol	80.3	89.0	96.0
2-Fluorophenol	73.0	86.3	86.5
Pentachlorophenol	114.0*	116.0*	136.0*

* Not significantly different from B/N - A recovery at $p < 0.01$.

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PRELIMINARY EVALUATION OF TEST METHOD FOR VOLATILE ORGANICS IN HAZARDOUS WASTE: BATCH STEAM STRIPPING/DISTILLATION

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ABSTRACT

A test method for determining the volatile emission potential of hazardous waste using batch steam stripping/distillation has been evaluated for predicting whether pretreatment of a waste is needed to remove volatile organics compounds prior to disposal. The procedure provides an estimate of the minimum amount of volatile organics that can be recovered in a full-scale steam stripping system and some indication of the potential emissions from the original waste and its residue.

The test method was evaluated by preparing synthetic wastes which approximated the chemical and physical properties of six different waste categories. The six waste types included mixed phase aqueous, aqueous waste plus sludge, dilute aqueous waste, organic waste plus sludge, dry solvent waste, and organic solvent waste. Each type of waste contained known amounts of methylene chloride, 2-butanone, 1-butanol, pyridine, toluene, phenol, and naphthalene. These seven compounds were chosen to represent a wide range of volatilities, polarities, and reactivities of compounds that may be contained in actual wastes. In addition, three real wastes were tested; two contained chlorinated organics in water and the third contained hydrocarbons in a refinery sludge matrix. All distillations were performed in basic and acidic conditions to see if pH effected recovery. The steam distillations of the wastes were performed by collecting 40 percent of the total volume of the waste in several liquid fractions. Volatile compounds that did not condense were collected on a cold trap or in a bag. The various fractions were analyzed by gas chromatography (GC) and the amount of each component was determined. The total amount of a compound in all the fractions was related to its respective total percent recovered.

The recoveries from the waste ranged from 70 to 140 percent for most compounds. This range of recovery compared favorably with recoveries by other methods. There was, however, some variation of recovery in the different waste matrices. The recovery of semi-volatile compounds such as phenol was improved by extending the distillation. The test method was duplicated for each waste and the results were found to be reproducible. GC injections were also duplicated and variance was found to be less than 20 percent. The manner in which the synthetic waste were prepared, screening of the wastes, apparatus involved, sample analysis, and data reductions will be presented.

PREPARATION OF RADIOACTIVE "MIXED" WASTE SAMPLES FOR MEASUREMENT OF RCRA ORGANIC COMPOUNDS

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ABSTRACT

A radioactive "mixed" waste typically contains alpha, beta-, and/or gamma-emitting radionuclides and varying quantities of semivolatile and/or volatile organics, some or all of which may be named specifically by the Resource Conservation and Recovery Act (RCRA). Because there are no acceptable procedures currently available for the disposal of "mixed" wastes, they are presently stored above-ground at great cost to the user. For this reason, analytical procedures which can identify the presence, or at least confirm the absence, of RCRA organics in radioactive waste are necessary for deciding the proper approaches for their disposal. An important aspect of this is the development of methods for preparing mixed waste samples which allow the RCRA organics in radioactive waste are necessary for deciding the proper approaches for their disposal. An important aspect of this is the development of methods for preparing mixed waste samples which allow the RCRA organics to be measured in conventional organic analytical laboratories.

Our general approach to characterizing organic compounds in "mixed" wastes is two-fold: First, organic species are removed from the sample in such a way that transfer of the active radionuclides is minimized. Analytical equipment and procedures listed in EPA-approved methods are used wherever possible. However, methods such as solid-phase extraction of semivolatiles, which minimize solvent volumes and operator exposure, have been investigated as reasonable alternatives. Secondly, the final determinations are performed on the nonradioactive concentrated sample in conventional laboratories using EPA analytical methods.

Decontamination factors (the ratio of the initial to the final[1] radioactivities of the samples) ranging between 1,000 and 10,000 are achieved for water samples contaminated with Co-60, Cs-137, or Sr-90, using either simple continuous liquid-liquid extraction with pentane or solid-phase extraction employing octadecyl reversed-phase columns. At the same time, recoveries of semivolatile organic compounds, such as polycyclic aromatic hydrocarbons and neutral pesticides, is quantitative at ppm or ppb concentrations. Soxhlet extraction of radioactive sludges (mixed with anhydrous sodium sulfate to remove excess water) with pentane or methylene chloride achieves similar

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decontamination factors while extracting organics in an EPA-approved fashion.

Our initial experiences with volatile organic species indicate that a modified, inexpensive purging vessel coupled to a Tenax-GC sorbent trap is capable of achieving both substantial decontamination factors and the quantitative recovery of target compounds. This methodology has already been tested on supernatants of "mixed" waste sludges. Both recovery data and decontamination factors will be presented.

INTRODUCTION

A radioactive "mixed" waste typically contains alpha-, beta-, or gamma-emitting radionuclides and varying quantities of semivolatile or volatile organic species, some or all of which may be named specifically by the Resource Conservation and Recovery Act (RCRA). Because there are no acceptable means available currently for disposing of these mixed wastes, they are presently stored above-ground in sealed drums. For this reason, analytical procedures which can determine RCRA organics in radioactive waste are necessary for deciding the proper approach for disposal. An important goal of this work is the development of methods for preparing mixed waste samples in a manner which allows the RCRA organics to be measured in conventional organic analysis laboratories without special precautions.

Analytical procedures developed for handling mixed waste samples must satisfy not only the usual constraints present in any trace-level organic chemical determination, but also those needed to insure the protection of the operator from radioactive contamination. Consequently, procedures should be designed to use the least amount of radioactive sample commensurate with achieving acceptable sensitivity with the RCRA analytical methods. Furthermore, the usual laboratory glassware which would normally be used should be replaced with disposable materials wherever possible, in order to reduce the "clean-up" time required, and thereby reduce the operator's exposure to radioactivity. Actual sample handling should be reduced to the absolute minimum. Finally, the final isolate must exhibit a surfficiently low level of alpha, beta, or gamma activity to permit detailed characterization in a conventional organic analysis laboratory.

Clearly, not all traditional or EPA-approved sample preparation procedures will prove satisfactory for mixed waste samples, given these additional restrictions. This paper describes our experiences in analyzing mixed waste aqueous and solid samples using a variety of conventional and supplemental procedures. In general, it is entirely feasible to prepare isolates from radioactive samples which are enriched in either semivolatile or volatile species, yet which are essentially decontaminated, and are therefore suitable for analysis in conventional organic analysis laboratories.

EXPERIMENTAL

Samples

The radioactive sludge materials tested were provided by the Operations Division of the Oak Ridge National Laboratory, Oak Ridge, TN.

Reagents, Solvents, and Radioactive Tracers

All solvents used in this work were purchased in "Distilled in Glass" purity from American Burdick & Jackson (Muskegon, MI), and were used as received.

Standard mixtures of the EPA priority polycyclic aromatic hydrocarbons (PAH), phenols, and organochlorine pesticides were purchased from Supelco, Inc. (Bellefonte, PA).

Acidic solutions with a known activity of the radionuclides Co-60 and Cs-137 were supplied by the Radiochamical and Activation Analysis Group, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The pH 4.9 leaching solution used is that described in EPA Method 1310, Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test (1). 64.3 mL of 1 N sodium hydroxide and 4.7 mL of glacial acetic acid were made to exactly 1 L with distilled water.

Equipment

Liquid-liquid extraction of aqueous samples with solvents of lesser specific gravity than water (e.g., pentane) were performed using a glass apparatus similar, but not identical, to Kontes Part No. K-584000 Continuous Extraction Apparatus (Vineland, NJ). Liquid-liquid extraction of aqueous samples with solvents of greater specific gravity than water (e.g., methylene chloride, were performed using Kontes Part No. K-584100, Continuous Extraction Apparatus.

All high-pressure liquid chromatographic separation and measurements were performed with a Beckman Model 334 Gradient Liquid Chromatograph (Berkeley, GA). This instrument was equipped with UV detector (254 nm), a Spectra/Glo Filter Fluorometer (excitation filter, 280 nm; emission filter, "blue from fluorescamine") purchased from Gilson Medical Electronics (Middleton, WI), an HP 3390 integrator, and a stripchart recorder. The analytical column was protected by a 0.5 u porosity high-pressure inline filter (Scientific Systems, Inc., State College, PA, part nos. 05-0149 and 05-1055) and a guard column packed with Perisorb RP-18 (Upchurch Scientific, Inc., Oak Harbor, WA) connected in series. A Vydac No. 201 TP 5415 octadecyl column (The Sep/A/Ra/Tions Group, Hesperia, CA), 15 cm x 4.6 mm o.d., 5 u silica, was used for both PAH and phenol separations. The column was maintained at 30 degrees C using a Model 7931 column heater purchased from Jones Chromatography (Littleton, CO). The methanol and water reservoirs, as well as the detectors, operated at room temperature. A

10 uL sample volume was introduced onto the column during each determination.

The solid phase extraction columns, manifold, pump, and pressure controllers were purchased from J. T. Baker, Inc. (Phillipsburg, NJ). Two manifolds and pressure controllers were used, such that the same one was always used for collecting organic analytes from radioactive aqueous samples, while the other was always used for eluting these analytes from loaded columns which had been essentially washed free of radioactivity.

The organochlorine pesticides were separated and quantitated according to EPA Method 608 using a Perkin Elmer Sigma 300 Capillary Gas Chromatograph (Norwalk, CT) equipped with a Model AS-300 autosampler (Perkin Elmer) and an SE-54 fused silica capillary column (0.25 u film thickness, 0.25 mm I.D., 30 m) purchased from Supelco, Inc. (Bellefonte, PA). The injector and electron capture detector temperatures were both 300°C. The column temperature was programmed from 140°C to 180°C at 4°C/min, and from 180°C to 250°C at 2°C/min. The oven temperature was held at 250°C for 5 min before returning to the starting temperature. A 3 uL injection was employed. The carrier gas was 90/10 (v/v) argon/methane, flowing at 5 uL/min. Data were collected, displayed, and analyzed using a Model 3000 Chromatography Data System (Nelson Analytical, Inc., Cupertino, CA) and an IBM PC/XT personal computer.

The collection of volatiles was performed using equipment custom-made at the Oak Ridge National Laboratory. A special Teflon sampling head equipped with a Teflon-faced silicon rubber septum screwed snugly onto a 40 mL EPA VOA sampling vial. The head provided a 10/32 screw port for a reusable "Fingertight" fitting, manufactured by Upchurch Scientific (Oak Harbor, WA). A length of capillary Teflon (1/16" o.d. x 0.3 mm i.d.) passed through the fitting into the VOA vial. The other end of the Teflon tubing was attached to a nitrogen cylinder with a flow controller. The head provided an additional port for a 1/8"-to-1/4" Swagelok reducing union; the 1/8" side was screwed into the collection head. The other end of the Swagelok union was connected to a 25 cm x 4.6 mm o.d. stainless steel column dry-packed with Tenax GC 35/60 mesh, which was purchased from Allteck Associates (Deerfield, IL). A simple calibrated rotameter was connected to the free end of the Tenax trap with a piece of rubber tubing.

The volatiles were analyzed using a procedure based on EPA Method 8240; however, modifications were introduced to allow the volatile analytes to be desorbed directly from a stainless steel trap packed with Tenax GC. A Model LSC-2 Tekmar Liquid Sample Concentrator (Tekmar Co., Cincinnati, OH) was used to desorb the organics of interest. The existing 1/8" o.d. trapping column and corresponding column heater in the oven were both removed and replaced with the 1/4" o.d. sample trap and corresponding heater. Exactly 250 ng each of bromochloromethane, 1-chloro-2-bromo- propane, and 1,4-dichlorobutane from a Purgeables Internal Standard Mix-624 (Supelco, Inc., Bellefonte, PA) was sparged onto the Tenax sample trap using an 11 min wet purge and a 4 min dry purge. The internal standards and analytes

present on the trap were desorbed at 180°C for 3 min using helium carrier gas. The components were swept onto the head of a 6.6' x 1/4" o.d. glass column packed with Carbopack B coated with a 1% SP-1000 (Supelco) located in a Hewlett-Packard 5995 GC/MS. The oven temperature was programmed from 45°C (hold for 3 min) to 180°C (hold for 45 min) at a rate of 8°C/min. The analytes were detected by the mass spectrometer, which operated at 70 eV ionization potential, mass range of 35-260 amu, and a scan time of 0.24 scan/sec.

All measurements of gamma activity were performed using a proportional scintillation counter. Two sodium iodide crystal well counters heavily shielded with lead were coupled to an EG & G Ortec (Oak Ridge, TN) system consisting of two Model 776 Counter/Timer boards, two Model 478 0-2 keV bias supply boards, and a Model 779 Interface/Controller board. The counter exhibits a typical efficiency of ca. 35% for Cs-137.

All measurements of beta activity were performed using a beta RIDL Proportional Counter consisting of a Model 40-9B voltage module (operating at 2300 V), a Model 30-19 sensitivity module, and a Model 49-25 timing and readout module. The lead sample chamber was continuously sparged with 10% methane/90% argon during each measurement. The counter typically exhibits 8% counting efficiency for Sr-90.

Procedures

Soxhlet Extraction of Sludges. Approximately 10 g sludge were mixed with 20 g anhydrous sodium sulfate, then transferred to a pre-extracted cellulose Soxhlet thimble. The sludge was then extracted overnight with methylene chloride or pentane. The extract was concentrated to exactly 1 mL; portions were taken for gross beta and gross gamma counting (see below).

Leaching of Sludges. Approximately 10 g of sludge and 200 mL of the pH 4.9 acetic acid/sodium acetate solution were stirred briskly overnight using an overhead electric stirrer.

Extraction of pH 4.9 Leachate. Exactly 100 mL of the pH 4.9 leachate described above were extracted continuously with pentane or methylene chloride overnight. The pentane extract was then concentrated using a Kuderna-Danish concentrator to exactly 1 mL. Aliquots were taken for gross beta and gross gamma counting (see below).

Solid Phase Extraction of EPA Priority Pollutant PAH from 4.9 Buffer. Three Baker-10 SPE 3 mL OCTADECYL columns were conditioned with methanol followed by 15% (v/v) isopropanol in water. An 18 mL portion of isopropanol was added to 100 mL water which had been spiked at 40-400 ppb with each PAH and 47,000 cpm (ca. 2200 Bq) Co-60. The resulting solution was passed through the OCTADECYL column using the "radioactive" manifold. The column was rinsed with a few mL of 15% (v/v) isopropanol in water. The PAH were eluted with exactly 1 mL of methylene chloride using the "clean" manifold (2). The final organic fraction was screened for gross gamma activity before performing the

final quantitation by HPLC.

Solid Phase Extraction of EPA Organochlorine Pesticides from Water. Three Baker-10 SPE 3 mL or 6 mL OCTADECYL columns were conditioned with methanol and water adjusted to pH 2 with HCl. A 100 mL volume of water was spiked with 120 ug of each priority pollutant phenol and 5.5 E+6 cpm (ca. 2.6 E+5 Bq) Cs-137. The solution was adjusted to pH 2 with HCl, and the phenols were "salted out" by adding 25 g of NaCl. The test solution was then passed through the column, which was later rinsed with 0.01 M HCl and permitted to air-dry briefly using the "radioactive" manifold. The phenols were eluted with 5 mL of methanol using the "clean" manifold (4). The final organic fraction was screened for gross gamma activity before performing the final quantification by HPLC.

HPLC Separation and Quantitation of EPA Priority Pollutant PAH. PAH were eluted from the HPLC column using a gradient which changed linearly from 70% methanol/water (hold for 10 min) to 99% methanol/water (hold for 10 min) over 15 min. Quantitation was performed using the integrator, which monitored the flurometer signal.

HPLC Separation and Quantitation of EPA Priority Pollutant Phenols. The phenols were eluted using a gradient program which changed linearly from 30% methanol/1% (v/v) acetic acid in water to 95% methanol/1% (v/v) acetic acid in water over 20 min. Quantitation was performed using the integrator, which monitored the UV detector signal (254 nm).

Collection of EPA Priority Volatiles from Water. Three 5 mL aqueous solutions containing 50 ppb each of the EPA volatiles and the purgeables surrogate standard were prepared in 40 mL EPA VOA vials. The Teflon sampling head was screwed onto the top of each vial, and a Tenax GC stainless trap was connected to the reducing union. The solutions were sparged with nitrogen at 90 mL/min for 15 min. The trap was then sealed and analyzed for volatiles, as described above. In separate experiments, 5 mL of unspiked water served as the blank, and 5 mL of water spiked with E+5 Bq Co-60 served as the test for transfer of radiation. In the latter, a Tenax column was unpacked, and the front end of the column was removed and tested for gross gamma emission.

Determination of Gross Gamma Radioactivity. A known volume (usually 1 mL) of organic isolate was placed into a 10 x 75 mm glass test tube, which was then stoppered and placed into the well counter. Gross gamma activity was typically counted to Bq, but only assuming that the gamma emitter had the same efficiency as Cs-137 (standard available).

Determination of Gross Beta Radioactivity. Exactly 200 uL of organic isolate was placed onto a 25 mm o.d. watch glass, and the solvent was allowed to evaporate. The watch glass was then placed in a cardboard mount featuring a mylar film window. The mount was placed into the lead sample chamber, and gross beta activity was measured for 10 min. The activity is reported in Bq.

RESULTS AND DISCUSSION

The barrel sludge and filter cake samples studied, which were obtained from a process water treatment clarifier, exhibited a nominal beta activity of 20,000 Bq/g (mostly as Sr-90). Historically, similar samples exhibit not more than twice that value. The remaining solid is an impoundment pond sediment in which Sr-90 is also the principal radionuclide, but at a nominal activity of 2000 Bq/g.

The usual conditions employed for leaching a solid as described in EPA Method 1310 (1) were deemed unsuitable for these radioactive solids. The practice of tumbling 100 g of solid and 2 L of leaching solution for at least 18 hours in a glass jar presented a significant risk of seepage or radioactive spill. Thus, a substitution was made for Method 1310 in which (a) both the mass of sample and volume of liquid were scaled down by a factor of ten, and (b) brisk stirring of the sample and leach solution using an overhead electric laboratory stirrer was substituted for the tumbler. In this manner, the spirit of Method 1310 -- intimate contact of the solid and leach solution -- was maintained, while minimizing the likelihood of a radioactive spill.

The subsequent liquid-liquid extraction of the radioactive leachate also was modified. EPA Method 3510 (1), Separatory Funnel Liquid-Liquid Extraction, similarly was deemed unsuitable for radioactive liquids. EPA Method 3520 (1), Continuous Liquid-Liquid Extraction, was substituted. In this procedure, the radioactive aqueous sample remains essentially undisturbed in a glass vessel, while the organic extraction solvent moves slowly through it. Continuous liquid-liquid extractors are available for solvents which have densities greater than water (e.g., methylene chloride) and less than water (e.g., pentane). In practice, the use of pentane yielded recoveries of test organic compounds comparable to those obtained with methylene chloride. Hence, a subsequent filtration step could be avoided. While many potential RCRA organic compounds are indeed less soluble in pentane than in methylene chloride, this deficiency may be readily overcome by simply extracting for a longer period of time than that used for methylene chloride. Furthermore, the RCRA compounds are frequently present at trace or ultratrace levels -- concentrations where the analyte would be reasonably soluble in pentane.

Table 1 follows the reduction in beta activity (due primarily to Sr-90) during the leaching of three test radioactive solids and the subsequent acid/base continuous extractions with pentane. Leaching with pH 4.9 sodium acetate/acetic acid solution reduced the activity by an order of magnitude. The acid/base extractions of the leachate using either methylene chloride or pentane yielded a further reduction to near-background levels, thereby suitable for analysis in a conventional organic laboratory. Thus, traditional extraction procedures are capable of providing a concentrated organic extract containing the extractable organics without carrying over a significant quantity of beta activity from Sr-90, an alkaline-earth radionuclide. A cursory HPLC examination of these concentrates revealed no UV-absorbing organic compounds present in these samples at

part-per-billion levels.

Sludge samples similar to those described above are also readily decontaminated when Soxhlet extracted with organic solvents such as methylene chloride. In a typical experiment, in which the final organic extract is concentrated to 1 mL, the total radioactivity present is <0.5 Bq/mL gross beta and <1 Bq/mL gross gamma (referenced to Cs-137) radiation over background — an activity level entirely compatible with conventional organic analysis laboratories.

The potential advantages of solid phase extraction (SPE) warranted careful evaluation of the technique applied to simulated aqueous samples near-quantitative recovery (>95%) of the EPA priority polycyclic aromatic hydrocarbons and the EPA organochlorine pesticides (both representing neutral compounds) at simulated environmental levels (40-400 ppb and 5 ppb, respectively) while simultaneously reducing the gamma activity present from a starting level of 20,000 or 40,000 cpm (ca. 1,000 or 2,000 Bq) to background or near-background levels (within instrumental uncertainty). The decontamination factors were ca. 2,000 for these samples. Note that in SPE, the sample preparation is complete in less than a half hour, more than one sample (up to ten) may be processed simultaneously, there is minimal cleanup required (columns are disposable), and the operator's exposure to the radioactive sample is minimized. It is assumed (but not confirmed) that most water-soluble radionuclides would behave similarly to Cs-137 and Co-60, and can be removed almost completely from the final organic extract.

Solid phase extraction did not prove as successful in recovering the EPA priority pollutant phenols from a test mixture, even though the gamma activity was reduced from a starting value of 5.5 E+6 cpm (ca. 2.6 E+5 Bq) to background levels (within instrumental uncertainty). A variety of columns, including OCTADECYL (two sizes), OCTYL, and PHENYL, were tested; however, the OCTADECYL columns yielded the best recoveries, as shown in Table 4. Clearly, the columns tested did not recover either phenol or 4-nitrophenol quantitatively at the test level of ca. 1 ppm, although they did recover most of the other phenols at or somewhat below the 95% level. These data indicate that while SPE certainly does have advantages in the analysis of phenols in mixed waste aqueous samples, the OCTADECYL columns should not be considered optimal. Columns packed with resins or porous polymers might give better recoveries of phenols; however, it must be demonstrated that these columns will also yield a final extract with a near-background level of radiation.

The determination of volatile constituents in radioactive aqueous samples was simplified greatly using the custom-made sampling head and VOA vial containers. The recovery of many EPA priority volatile materials using the sampling head and a dry-packed Tenax GC trap was quite reasonable at the 50 ppb level, as shown in Table 5, while maintaining a very low level of activity in the Tenax trap itself. During one of the trials using only Co-60 tracer as the "volatile" analyte, the Tenax from the front 3-5 cm of the trap was removed after sparging and subjecting to gross gamma counting. No gamma activity

was detected. Reducing the sparge gas flow rate from 90 mL/min to 25-40 mL/min and the sparge time from 15 min to 11 min would have probably led to an improved recovery of volatiles without adding additional activity to the trap. Furthermore, if the liquid sample is sparged gently, the sampling head itself should remain noncontaminated despite repeated use. The only part of the sampler which would become contaminated, therefore, would be the capillary Teflon tubing which is in contact with the sample. Even here, contamination is minimized because the Teflon tubing is not wetted with water, and should absorb very little radioactive solution. Hence, it is quite feasible to sparge volatiles from a radioactive aqueous sample onto a Tenax trap, and take the trap into a conventional organic analysis laboratory for detailed characterization because the trap is itself noncontaminated.

In general, then, our preliminary experiences in preparing low-level radioactive samples for analysis suggest that concentrates not contaminated by the gamma- or beta-emitting alkaline or alkaline earth metals may be prepared readily without expensive and exotic equipment. In addition, several of the major pollutant compound classes, such as the PAH, organochlorine pesticides, and phenols, may be readily concentrated using simple solid phase sorbent technology.

Our experiences have not addressed the effect of these sample preparation procedures on several important classes of radionuclides. These include common low-energy beta emitters such as tritium, volatile beta/gamma emitters such as iodine-131, and transuranic radionuclides such as americium-241. Furthermore, samples contaminated with alpha emitters such as Pu-239 require special handling techniques, such as glove boxes and inert atmospheres, regardless of the activity level present. Nevertheless, the procedures described here should be considered a reasonable starting point for preparing suitable isolates of RCRA organic compounds. These procedures may also be entirely proper for preparing such isolates from alpha-contaminated samples provided that all manipulations are performed in a contained environment.

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3. "Rapid Extraction of Organochlorine Pesticides from Potable Water with 'BAKER'-10 SPE Disposable Column OCTYL (C8), 6mL", in 'Baker'-10 SPE Applications Guide, Vol. I, Phillipsburg, NJ, J.T. Baker Chamical Co., 1982, p. 12.

4. "Rapid Extraction of Phenols from Water for HPLC with 'BAKER'-10 SPE Disposable Column OCTYL (C8), 6 mL, in 'Baker'-10 SPE Applications Guide, Vol. I, Phillipsburg, NJ, J.T. Baker Chemical Co., 1982, p. 26.

Table 1

SUMMARY OF EXTRACTION AND LEACHING ACTIVITY DATA FOR THREE SOLIDS

Treatment		Pond Sludge 3513-A6, 30 g	Barrel 11 Sludge, 20 g	Filter Cake 20 g
Initial beta activity, Bq		62,400	316,000	426,000
Activity present after pH 5 leaching, Bq	(1)	1,200	34,000	39,200
	(2)	3,200	31,200	37,200
Activity present after acid/base extraction of the leachate with pentane, Bq	(1)	<22	< 4	0
	(2)	<26	<38	34
Activity present after acid/base extraction of the leachate with methylene chloride, Bq	(1)	< 1	120	53
	(2)	100	103	73

Table 2

Recovery of Priority PAH from 100 mL pH 4.9 Buffer

Compound	Spike Level 40-400 ppb Trial 1	Trial 2	Trial 3	Mean % rec.
Naphthalene	83	83	73	80
Acenaphthene	90	83	80	84
Phenanthrene	100	95	90	95
Anthracene	93	70	68	77
Fluoranthene	89	85	81	85
Pyrene	100	100	100	100
BaA	98	98	95	97
Chrysene	98	95	98	97
B(b)fluoran	90	94	90	91
B(k)fluoran	93	95	93	94
BaP	93	95	93	94
Dibenz(a,h)anth	96	99	95	97
Benzo(ghi)peryl	96	91	90	92
Indeno[1,2,3-cd]pyrene	91	93	90	91

Samples spiked with 47,000 cpm (ca. 2200 Bq) Co-60. Final activity <10 cpm (ca. <0.5 Bq), with measurement limited by instrumental uncertainty. Decontamination factor ca. 2000.

Samples prepared using solid phase extraction, as described in text.

Table 3

Recovery of EPA Organochlorine Pesticides at Test Level of 5 ppb

	Recovery, % at 5 ppb	
	Lindane	Endrin
Hexane -1	89	88
Hexane -2	100	100
Hexane -3	98	100
Average Recovery, %	96	96

All samples spiked with 18,000 cpm (ca. 900 Bq) Cs-137. Final activity < 10 cpm (ca. <0.5 Bq). Estimated decontamination factor >2000.

Samples prepared by solid phase extraction, as described in text.

Table 5

Test of Sparger for Purgeables in Radioactive Aqueous Samples at 50 ppb

Compound	Recovery in ppb Trial 1	Trial 2	Trial 3	Avg % Rec.
Methylene chloride	28	240	23	194
Acetone	87	140	73	200
Carbon disulfide	14	10	10	23
1,1-Dichloroethene	20	16	15	34
1,1-Dichloroethane	27	24	22	49
1,2-Dichloroethene	25	22	20	45
Chloroform	14	34	30	52
1,2-Dichloroethane	32	28	26	57
2-Butanone	97	105	92	196
1,1,1-Trichloroethane	23	24	22	46
Carbon tetrachloride	25	25	25	50
Vinyl acetate	32	30	27	59
Bromodichloromethane	26	27	27	53
1,2-Dichloropropane	28	28	27	55
cis-1,3-Dichloropropene	21	30	27	52
Trichloroethene	29	29	27	57
Dibromochloromethane	18	32	30	53
1,1,2-Trichloroethane	24	33	31	59
Benzene	30	44	26	67
trans-1,3-Dichloropropene	20	23	21	43
Bromoform	6	31	28	43
4-Methyl-2-pentanone	37	51	46	89
2-Hexanone	22	55	51	85
Tetrachloroethene	9	33	32	49
1,1,2,2-Tetrachloroethane	21	21	22	43
Toluene	21	35	22	52
Chlorobenzene	10	22	21	35
Ethylbenzene	9	21	21	34
Styrene	5	17	16	25
Xylenes	7	26	18	34

Radioactive spike added: 5.0 E+6 Bq Cs-137.
Final activity: background (within instrumental uncertainty)
Estimated decontamination factor >1 E+6

ENVIRONMENTAL APPLICATIONS OF MAGIC LC/MS

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ABSTRACT

MAGIC LC/MS (Monodispersed Aerosol Generation Interface Combining Liquid Chromatography and Mass Spectroscopy) is a technique for generating electron Impact spectra from analytes separated by High Performance Liquid Chromatography. The technique, developed by Browner et al.(1) consists of an aerosol generator, a desolvation chamber and a two stage momentum separator. The HPLC effluent is first nebulized by the aerosol generator. The resulting droplets are then desolvated at atmospheric pressure yielding a mixture of analyte particles and solvent vapor. In the momentum separator, the solvent vapor is pumped away and the analyte particles are allowed to enter the MS source where they are flashed vaporized and ionized by electron impact.

The technique requires very little modification of either the HPLC methodology or the MS operation. Typical LC flow rates range from 0.2 to 1.0 ml/min. A wide range of solvents can be used; the primary restriction being the mandatory use of volatile buffers. The Mass spectrometer can be used in either electron impact or chemical ionization modes.

The current work examines the application of MAGIC LC/MS to the analysis of pollutants in environmental samples. Specifically, the analysis of a group of compounds cited in the EPA Appendix VIII(2,3) which are not easily amenable to analysis by GC/MS, including thiourea, ethylene thiourea, naphthyl thiourea, maleic hydrazide, warfarin, benzindine, thiram, reserpine and others. Although these compounds have been analyzed by Thermospray LC/MS(4), this technique, while versatile is limited in its information content. MAGIC LC/MS generates standard EI spectra which can be computer-searched in standard libraries.

Additionally, data concerning basic performance specifications and optimization of the operational parameters will be discussed.

INTRODUCTION

Monodispersed Aerosol Generation Interface Combining Liquid Chromatography and Mass Spectrometry (MAGIC LC/MS), introduced by Browner et al. is a technique which allows Electron Impact (EI) spectra to be obtained from compounds which are not amenable to gas chromatographic (GC) separation due to low volatility or thermal lability. As such, MAGIC LC/MS offers an attractive complement, rich in structural information, to Thermospray LC/MS which

typically produces simple spectra consisting primarily of pseudo-molecular ions.

This approach offers some distinct advantages in applications in which the samples cannot be separated by GC on in which HPLC is the separation method of choice and in which structural data of unknowns or confirmatory data for target compounds is needed.

EXPERIMENTAL

Liquid Chromatography

The HPLC consisted of a Hewlett-Packard Model 1090 HPLC equipped with a DR-5 ternary pumping system, autosampler and a filter photometric detector. All HPLC columns were 100x2.1mm i.d.. The following column systems were used; Brownlee 5cm RP-18 and RP-8 (Brownlee Labs, Santa Clara, Ca) or Phase Separation 3 um RP-18 (Phase Separations, Norwalk, CT.).

Mass Spectrometry

All mass spectral measurements were performed on a standard, unmodified HP 5988 differentially pumped quadrapole mass spectrometer with high mass (2000 amu) option. In order to accept the MAGIC interface 0.5 inch probe, a standard DIP vacuum port was mounted on the left side of the source manifold. The standard GC/MS interface occupies the port on the right side.

Typical operating conditions are as follows: tuning using autotune routine; source temperature @ 330°C; source manifold pressure @ $7x10^{-6}$torr; Electron multiplier @ 2500-3000 V. For data acquisition in the scan mode: 50-500 amu sec^{-1}.

MAGIC LC/MS

The experimental MAGIC interface hardware is shown schematically in Figure 1. The interface consists of four main sections; aerosol generator, desolvation chamber, momentum separator and 0.5 inch transfer probe.

MAGIC LC/MS operates in the following manner: initially an aerosol is generated which consists of droplets within a narrow range of diameters. As the droplets travel through a desolvation chamber which is maintained at near ambient pressure and temperature, the volatile solvent is evaporated leaving a particle of non-volatile material (including analyte) behind. This mixture of solvent vapor and analyte particles enters a two stage momentum separator in which the vapor is pumped away while the relatively massive (and consequently high momentum) particles pass into the source of the mass spectrometer in a narrow particle beam. The particles impact

the heated source wall and are flash vaporized. Analyte molecules are then ionized by electron impact and mass analyzed in the standard manner.

The aerosol generator is shown schematically in Figure 2. The HPLC effluent enters vertically through a short piece of 25 cm fused silica capillary, forming a liquid jet which breaks up into a stream of droplets due to instabilities in the jet[3]. These droplets are dispersed by a jet of helium gas which enters at right angles to the liquid jet through a short length of 24 gauge hypodermic needle. The helium flow rate is approximately 1 L min^{-1}. The hypodermic needle tubing through which the helium enters is mounted on an x-y positioner to allow precise control of the intersection point with the droplet stream.

The desolvation chamber consists of a glass tube with formed details to accommodate the aerosol generator and pressure and temperature sensors. The chamber is wrapped with a heating tape, the power to which is generated by a feed back control system.

The momentum separator is constructed from stainless steel and consists of a cylindrical nozzle and two conical skimmers. The First stage is pumbed by a Balzers (Hudson, NH) Uno016B mechanical pump while the second stage is evacuated by a Balzers Duo016B mechanical pump. Since these pumps run relatively hot, it has not been found necessary to use a cold trap to isolate the HPLC mobile phase vapor.

Typical pressures in the system are as follows: desolvation chamber 200 torr; momentum separator (first stage) 2-5 torr; momentum separator (second stage) 0.1-0.5 torr; source manifold $7x10^{-6}$-$3x10^{-5}$torr.

Chemicals

Solvents were HPLC grade purchased from EM Science (Cherry Hill, NJ.).

Environmental standards were obtained courtesy of the EPA depository (Las Vegas, NV).

RESULTS AND DISCUSSION

Optimization

During the investigation and development of a viable experimental MAGIC system, it was necessary to evaluate those control factors which play a major role in performance. The most critical operational parameters were found to be: helium gas flow rate; desolvation chamber temperature and pressure; and the mass

spectrometer source temperature. These factors were evaluated under a range of conditions to determine optimal settings.

The helium gas flow rate and the position of the helium gas jet relative to the liquid jet depend on the characteristics of the HPLC mobile phase composition and flow rate. Referring to figure 2, at a certain point above the 25 cm fusio silica the liquid column breaks up into a stream of droplets due to instability inherent to the system.[3] The helium dispersion gas must enter the system slightly above this point with sufficient velocity to disperse the droplets at 90° relative to the initial liquid jet. As long as the dispersion point is above the droplet formation point, maximum signal is obtained. For a given flow rate, in a mobile phase consisting of mixture of either acetonitrile or methanol and water, the position of the droplet formation point varies over a 2mm range. The gas dispersion point, then is set optimally slightly above the highest position. For a typical mobile phase flow rate of 0.4mL/min, the helium gas flow rate is approximately 1 L/min. It is possible, however to operate the system with mobile phase flow rates between 0.1 and 1.2 mL/min by adjusting the gas flow rate accordingly.

The main purpose of thermostatting the desolvation chamber is to replace the heat which is absorbed by the desolvation process. As such, the temperature is optimally held a slightly above ambient temperature ($\approx$ 35-40°c). This temperature does vary towards slightly higher temperatures as the aqueous content of the mobile phase increases, reflecting the relatively larger amount of heat required to vaporize water. The effects of mobile phase and desolvation chamber temperature on the signal produced by 1 L injections of 10 ng of caffeine are shown in figure 3. Note that at approximately 35°c, the optimum response can be obtained for all mobile phase conditions.

The desolvation chamber pressure also plays an important role. In principle, the higher the pressure in the desolvation chamber, the more efficient the heat transfer and desolvation process. However, this does not take into account the pressure characteristics of the supersonic nozzle-skimmer system in the momentum separator. At sufficiently high pressures, the divergence of the nozzle jet becomes too large and transfer efficiency decreases through the system[6]. Due to the interplay of these two factors, there is an optimum desolvation chamber pressure around 200 torr.

The third important factor in the operation of the system has been found to be the mass spectrometer source temperature. Somewhat surprisingly, best performance was obtained with a relatively hot source (330°c). Our initial expectations were that thermal decomposition and decreased signal would result from high source temperatures. As shown in figure 4, however, this proved not to be

the case. For a range of compounds examined, signal intensity increased to a maximum at 330°c, while the normalized spectrum is essentially constant over this range. The compounds examined do show variations in their temperature dependence. Comparing for example, caffeine and reserpine (see figure 4), caffeine produces a nearly constant signal, while reserpine shows a significant increase in signal intensity (but not in spectral character). There are exceptional cases, however, where temperature shows a major effect on the spectrum. In particularly, cholesterol (MW=386) undergoes an increased loss of water, producing the fragment at m/z=368, as a function of temperature. This is shown graphically in figure 5 where the ration of the intensities of fragments 368 and 386 are plotted against source temperature. In our experience, it must be noted, this kind of temperature dependency is an exception rather than the rule.

PERFORMANCE

The quantitative performance was evaluated using caffeine as a probe and is shown in figures 6 and 7. In scan mode (50-300 amu/sec) the minimum detectable quantity (S/N=5) (fig. 6) was found to be 5 ng. In SIM mode (fig. 7.), monitoring m/z=194, MDQ was found to be 50pg. In both cases the r^2 value for the regression was 0.998 (0.5-500ng SIM: 5-1000ng Scan)(fig. 8). Note that for the SIM experiment, the signal obtained for the 1 ug injection saturates the detector and shows a loss in linearity. It should be noted that our experience has been that caffeine is neither the most sensitive nor the least sensitive compound examined and MDQ's may vary by a factor of 10 either up or down.

Qualitative performance was evaluated by examining a wide range of compounds (listed in table 1) in a flow injection mode. These compounds were injected at a 100ng level to generate reference spectra. Of these compounds, the majority can be found in the NBS/EPA/NIH spectral library. The spectra represent classical EI spectra. The advantage of this is that the data can generally be interpreted by computer library searches, and in those cases where the spectra are not found in the library, the interpretation can be performed according to well known rules. It is interesting to note that a large number of spectra that are in the library are not easily analyzed by GC.

APPLICATIONS

Several applications have been evaluated to demonstrate the potential of the technique. The applications examined are environmentally oriented, but the sample handling capabilities of HPLC due to precolumn technology suggest a wide variety of applicable matrices.

Figure 9 shows the separation of 12 triazine pesticides in full scan mode (50-400amu) at the 100ng level. Due to the excellent signal to noise demonstrated by this trace, average MDQ for these compounds is approximately 1 ng. The use of multiple ion monitoring generates useful detection and identification data at the 50pg levels. Although triazine pesticides can, in fact, be separated by GC/MS, this is an excellent example of a situation in which HPLC is the separation method of choice due to the ability to handle direct injection of relatively large volumes of aqueous samples. Mass spectrometry shows one of its particularly attractive features as a chromatographic detector in its ability to separate nearly coeluting compounds due to spectral differences.

Figure 10 shows the separation of 12 phenylurea herbicides in full scan mode (50-400amu) at 100ng level. Although there is an evident variation in the response factors of these compounds, it can be clearly seen that the detection limits are similar to those stated above. In selected ion monitoring, the detection limits in this application can be reduced slightly to an average of 20 pg, due to the fact that each of the compounds generates one of 4 fragments (61, 72, 91 or 114).

Finally, figure 11 shows the separation of 11 compounds listed on the EPA appendix IX list.[5] These compounds cannot easily be run using GC/MS. As above the date shown is for full scan mode (50-400 amu) at the 100ng levels, indicating similar detection limits. This application provides a rapid straight forward technique to separate, identify and quantitative these compounds.

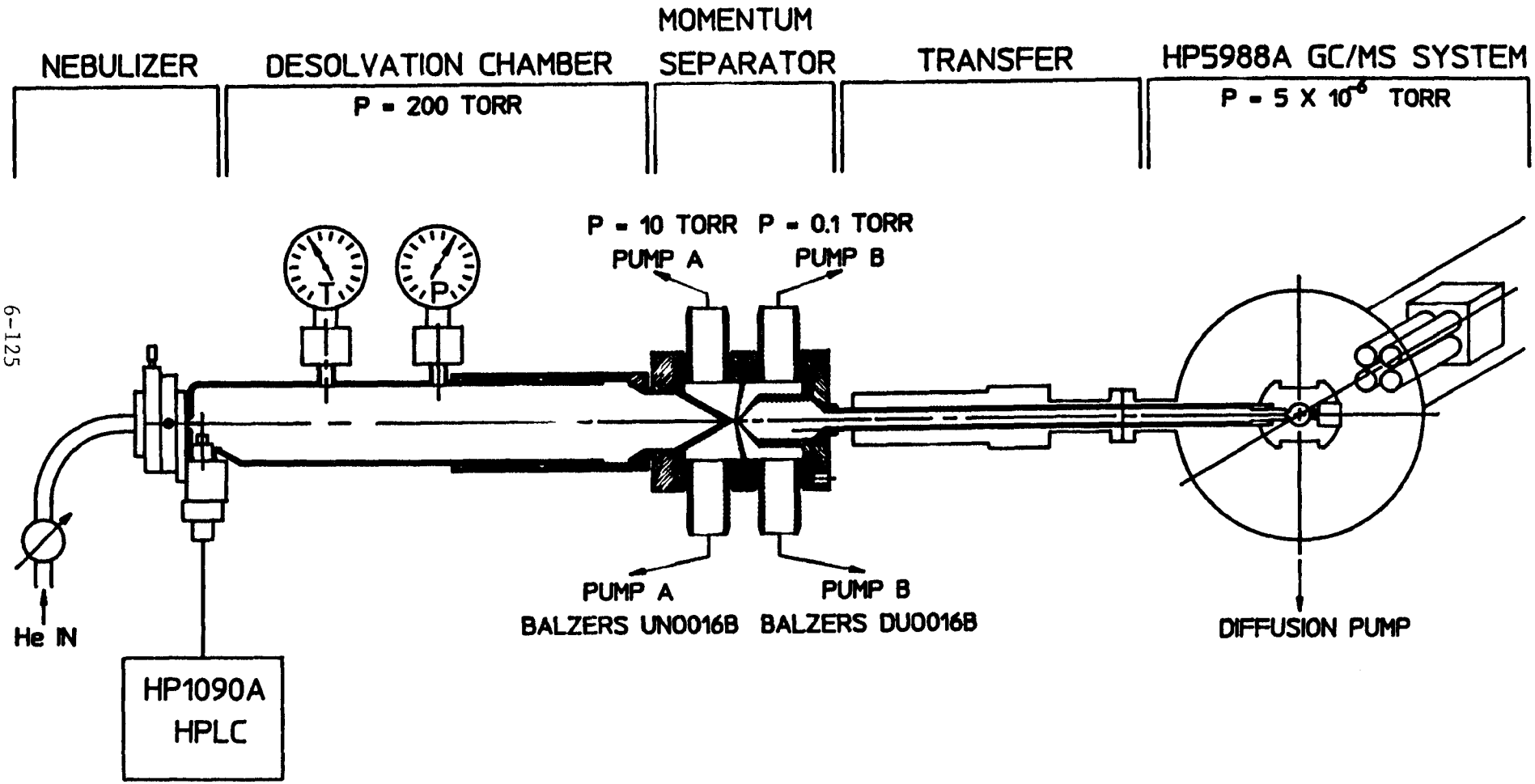
Conclusions

Recent advances in MAGIC LC/MS have lead to significant improvements in sensitivity and ease of use which make the technique a viable approach to LC/MS coupling in the analytical laboratory. The technique generates EI spectra from compounds separated by HPLC, which are difficult or impossible to separate by GC.

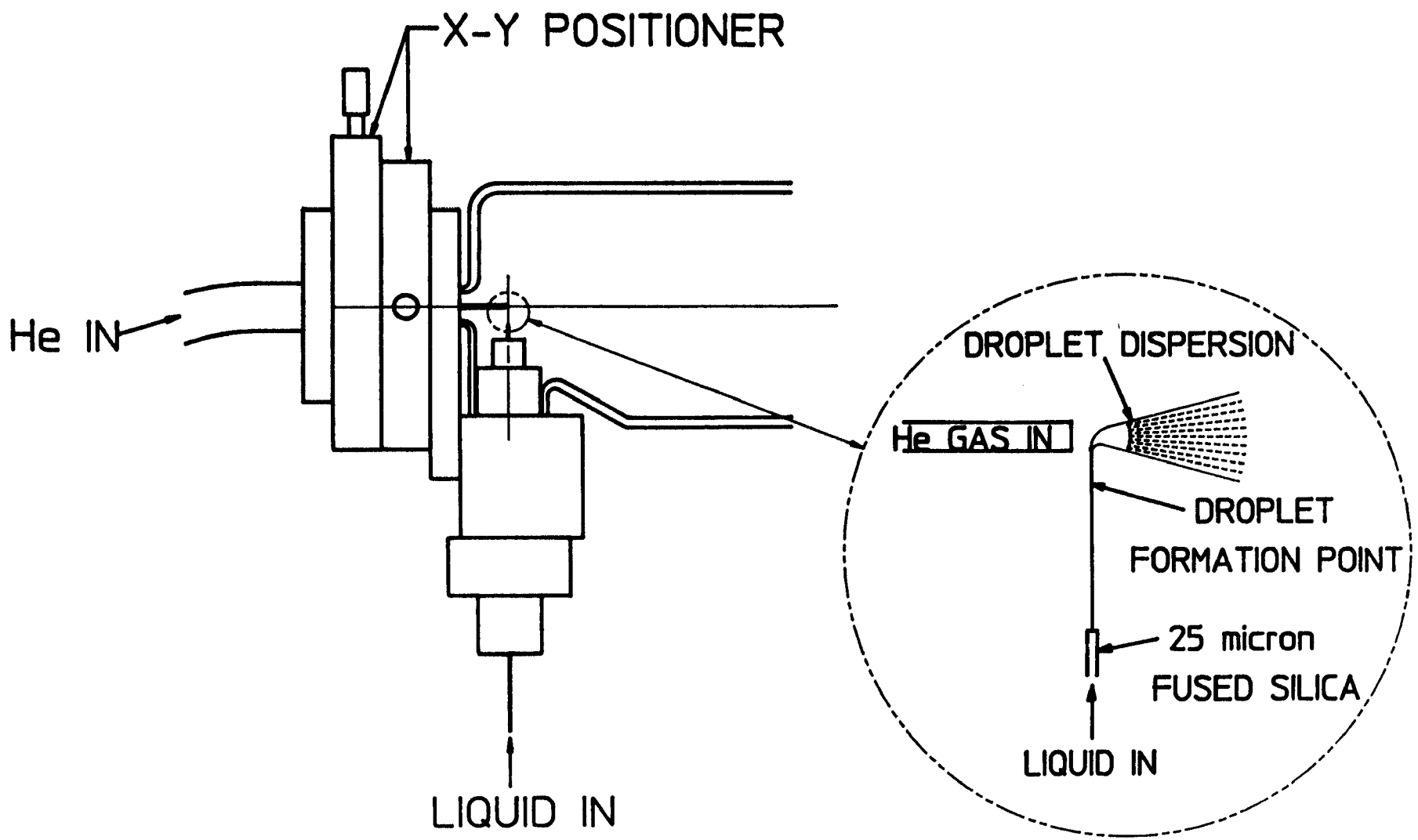
In its current stage of development, MAGIC LC/MS offers a useful complement of Thermospray LC/MS. Whereas Thermospray LC/MS has been found to be particularly useful for molecular weight information, MAGIC LC/MS generates EI spectra which are familiar, library searchable and easily interpreted. Where Thermospray LC/MS has been found very useful for relatively large molecular weight peptides and proteins, we have found MAGIC LC/MS to be most useful (but not limited to) for relatively low (<1000 amu) molecular weight compounds in which electron impact leads to a small number of identifiable fragments.

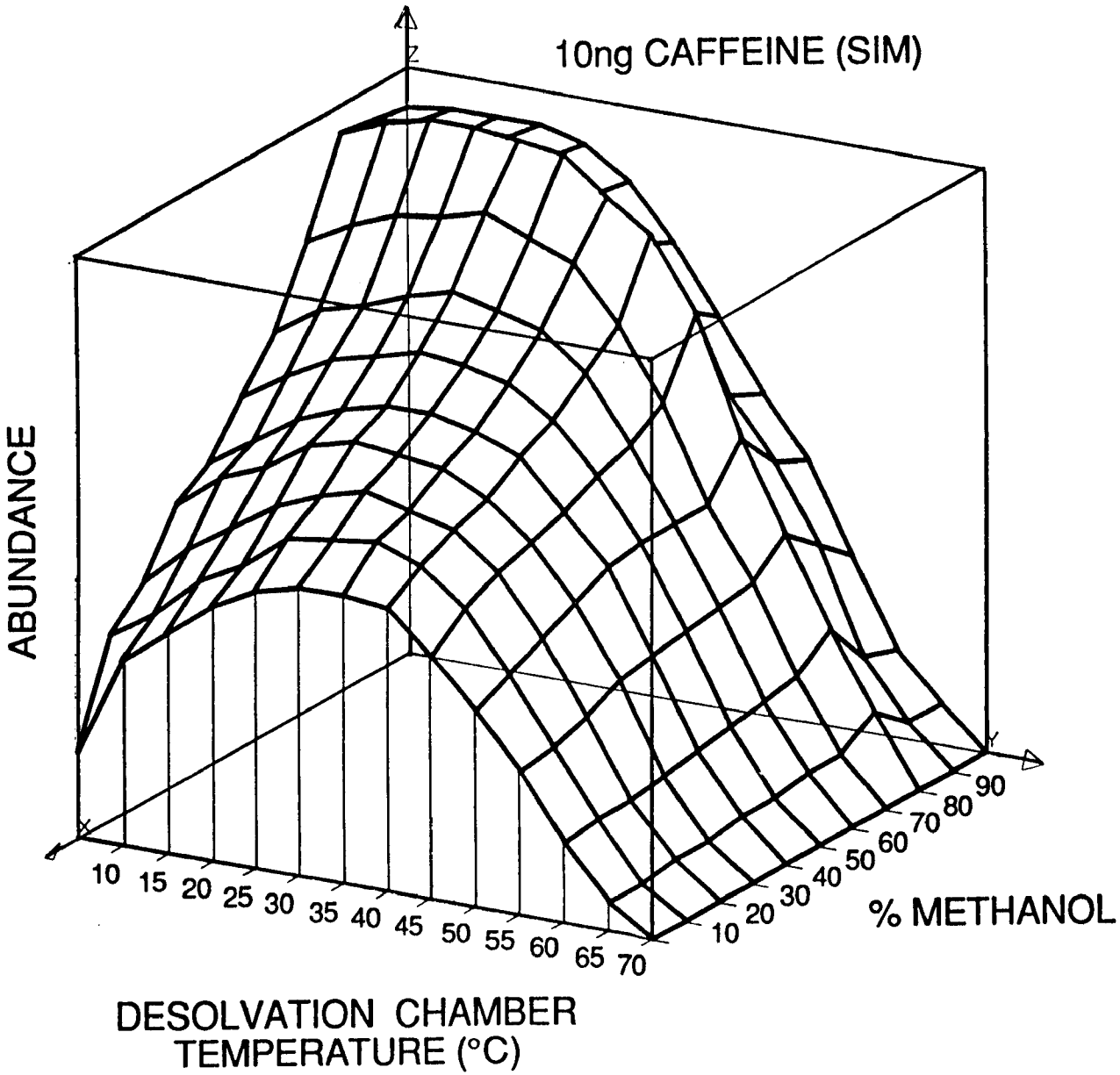
Our investigations indicate, however, that MAGIC LC/MS offers a

MAGIC LC/MS SYSTEM SCHEMATIC



MONODISPERSED AEROSOL GENERATOR




10ng CAFFEINE (SIM)
Z
ABUNDANCE
X
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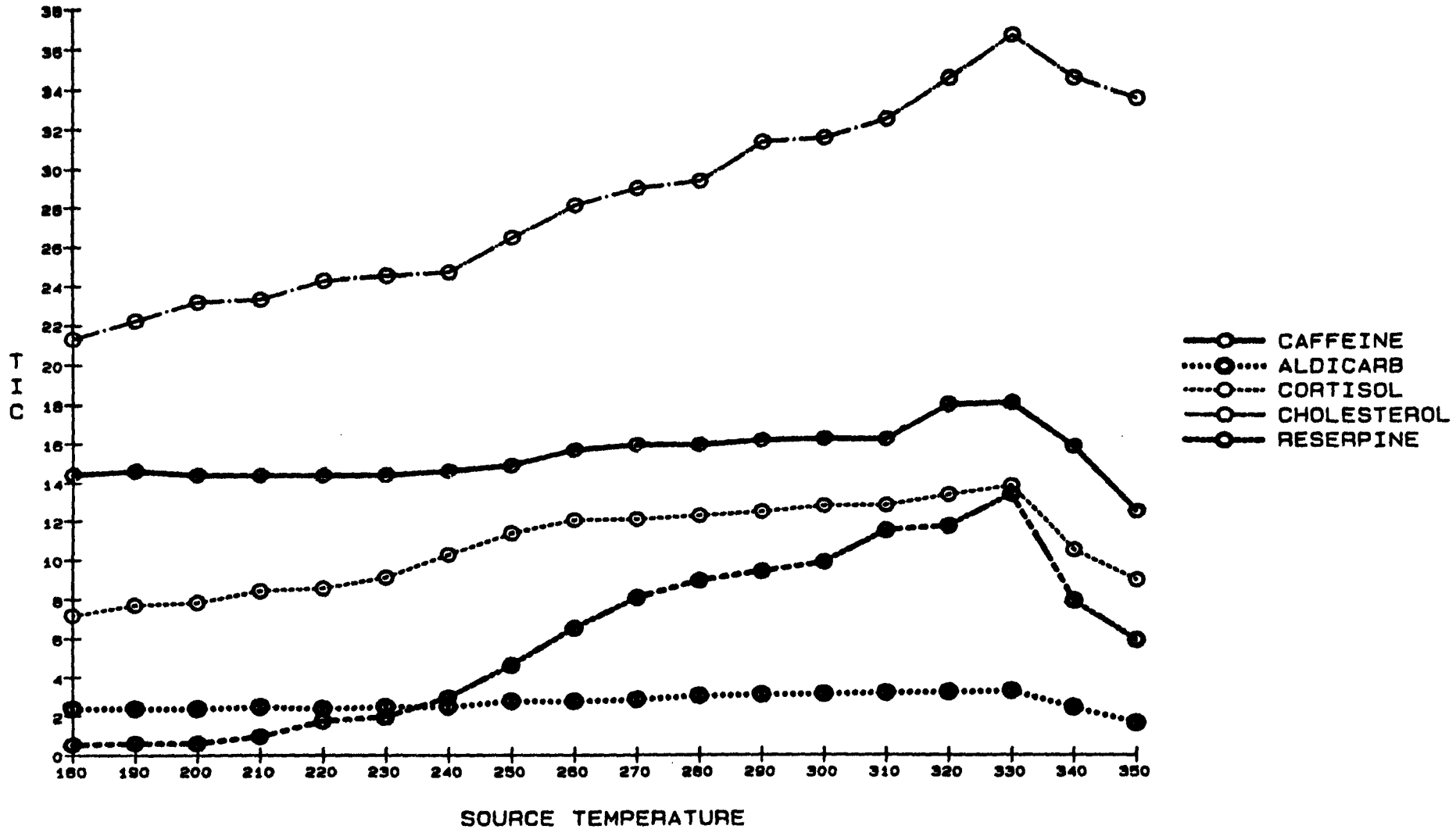
DESOLVATION CHAMBER
TEMPERATURE (°C)
Y
10 20 30 40 50 60 70 80 90
% METHANOL


TIC
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2
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6
8
10
12
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16
18
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28
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34
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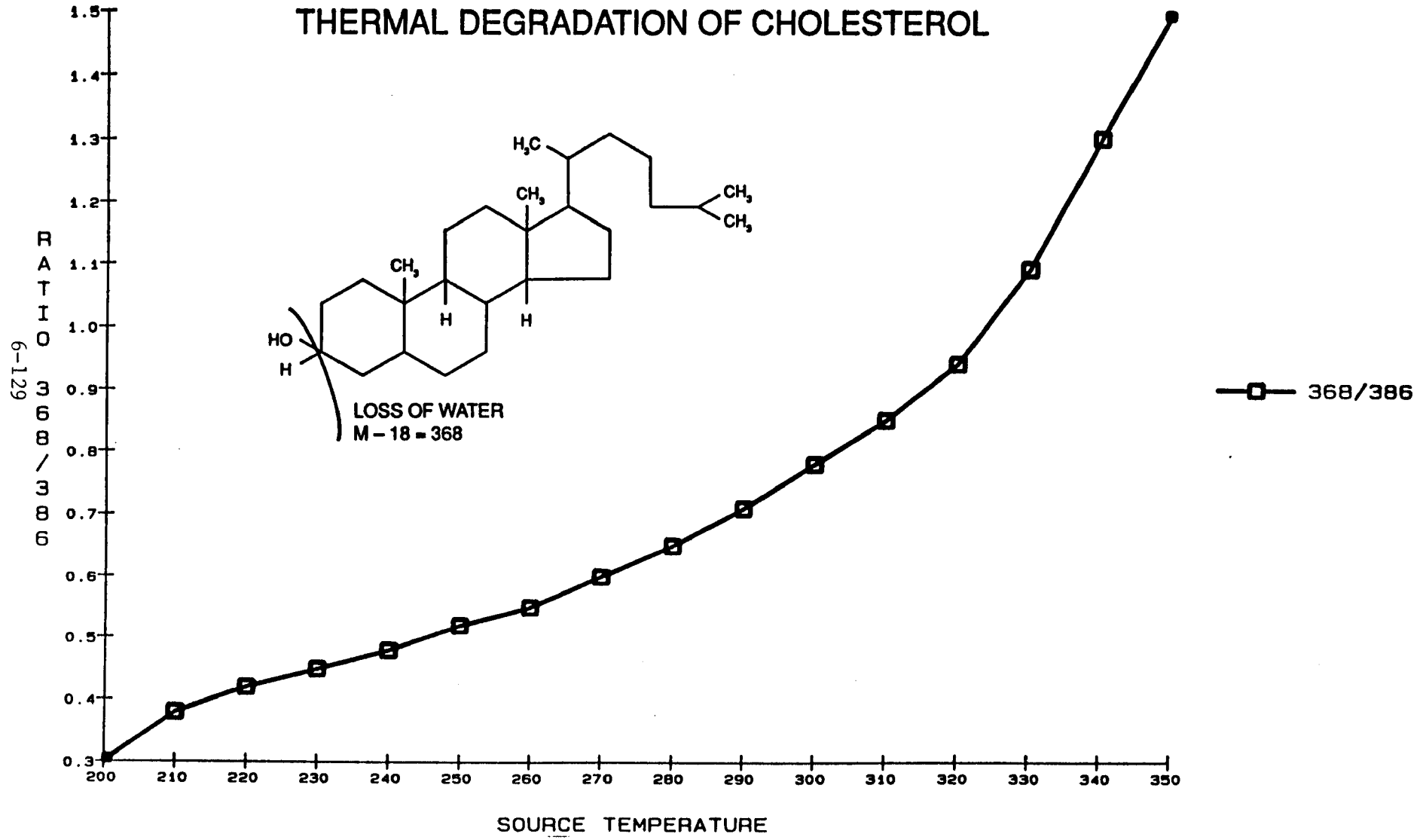
38
180
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
SOURCE TEMPERATURE
CAFFEINE
ALDICARB
CORTISOL
CHOLESTEROL
RESERPINE


THERMAL DEGRADATION OF CHOLESTEROL
RATIO 368/386
SOURCE TEMPERATURE
368/386
LOSS OF WATER
M – 18 = 368
HO
H
H
H
CH3
CH3
CH3
CH3
H3C
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
200
210
220
230
240
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260
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280
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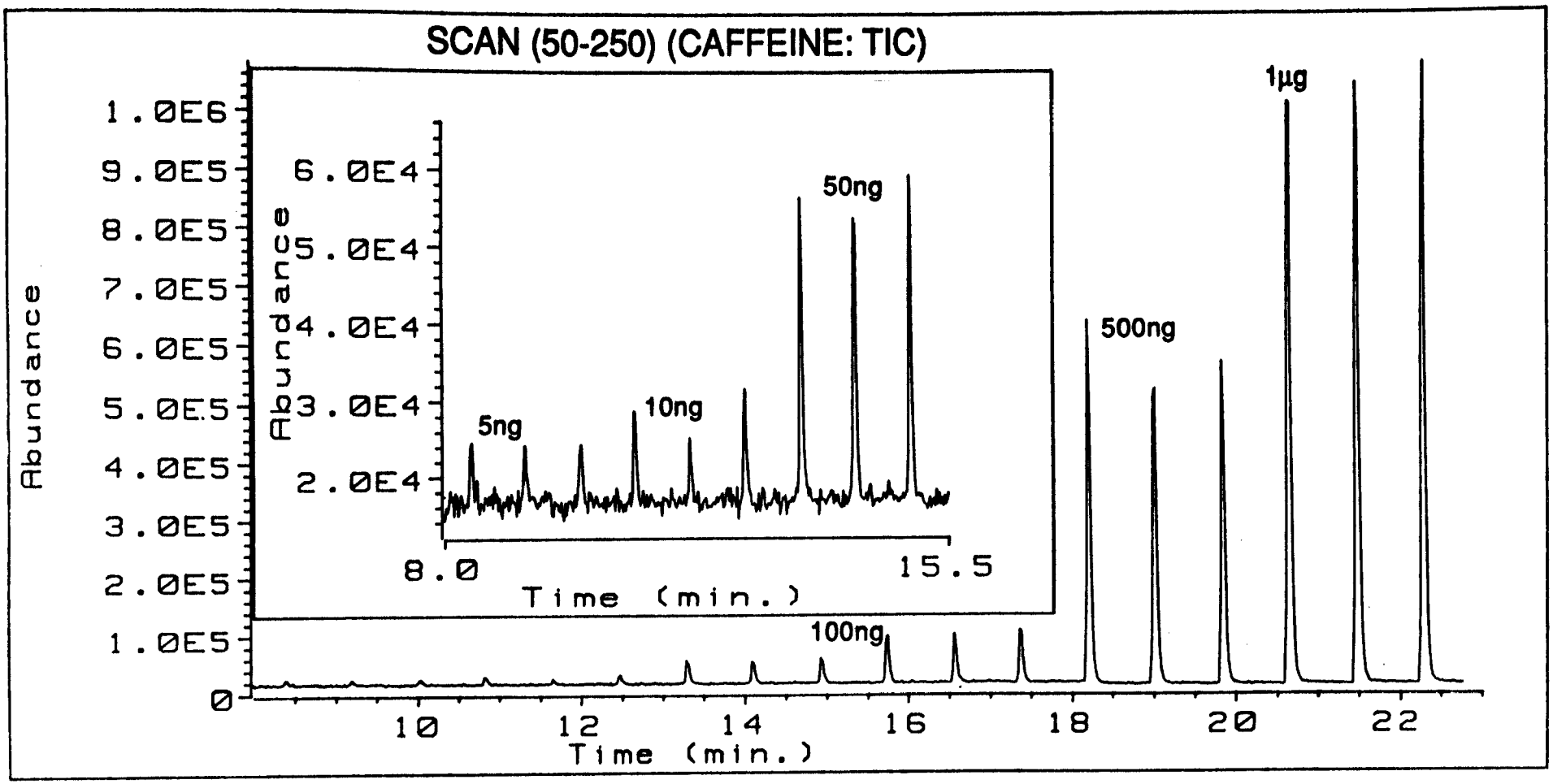
300
310
320
330
340
350


SCAN (50-250) (CAFFEINE: TIC)
Abundance
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9.0E5
8.0E5
7.0E5
6.0E5
5.0E5
4.0E5
3.0E5
2.0E5
1.0E5
0
10
12
14
16
18
20
22
Time (min.)
1µg
500ng
100ng
50ng
10ng
5ng
6.0E4
5.0E4
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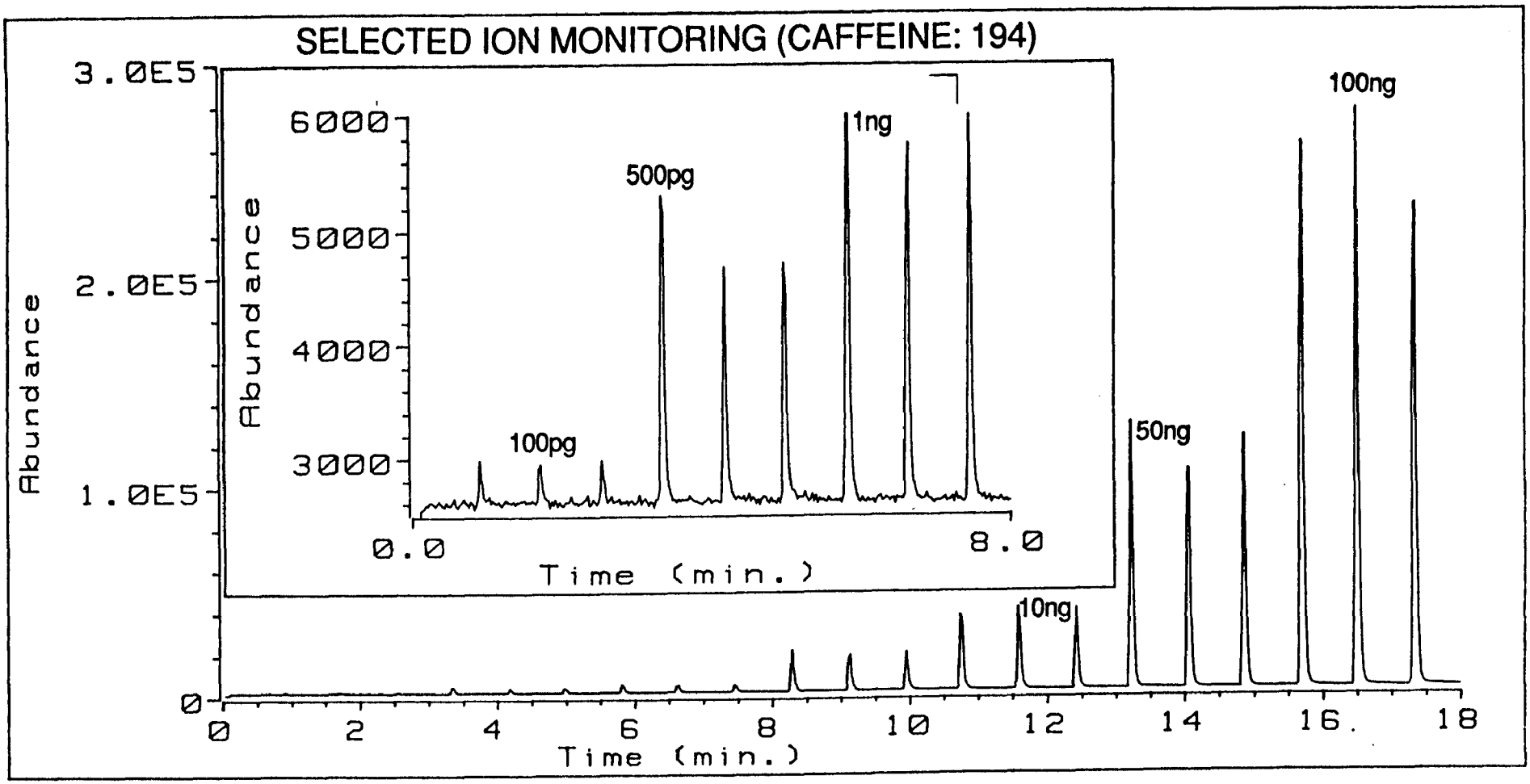
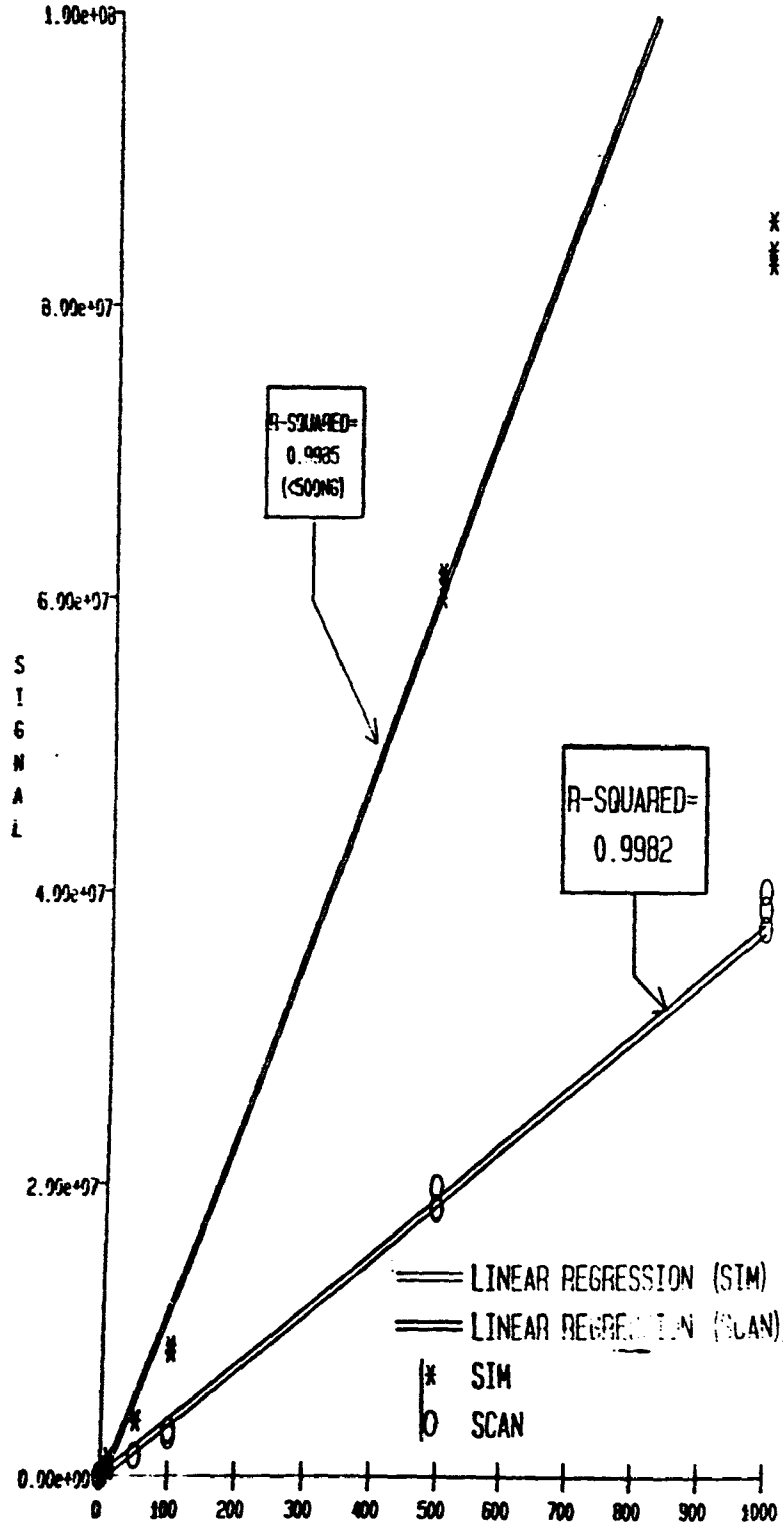
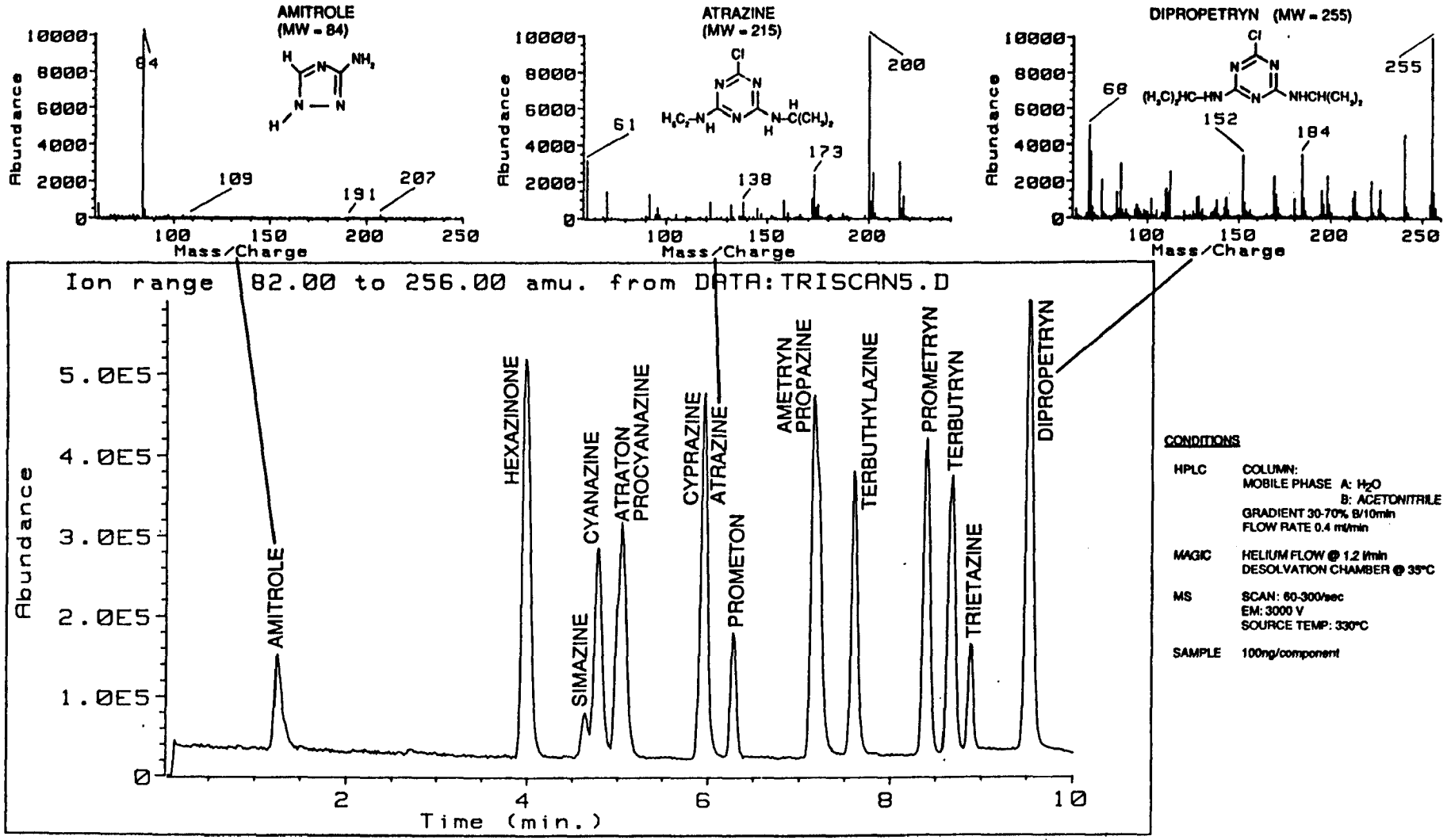
2.0E4
8.0
15.5

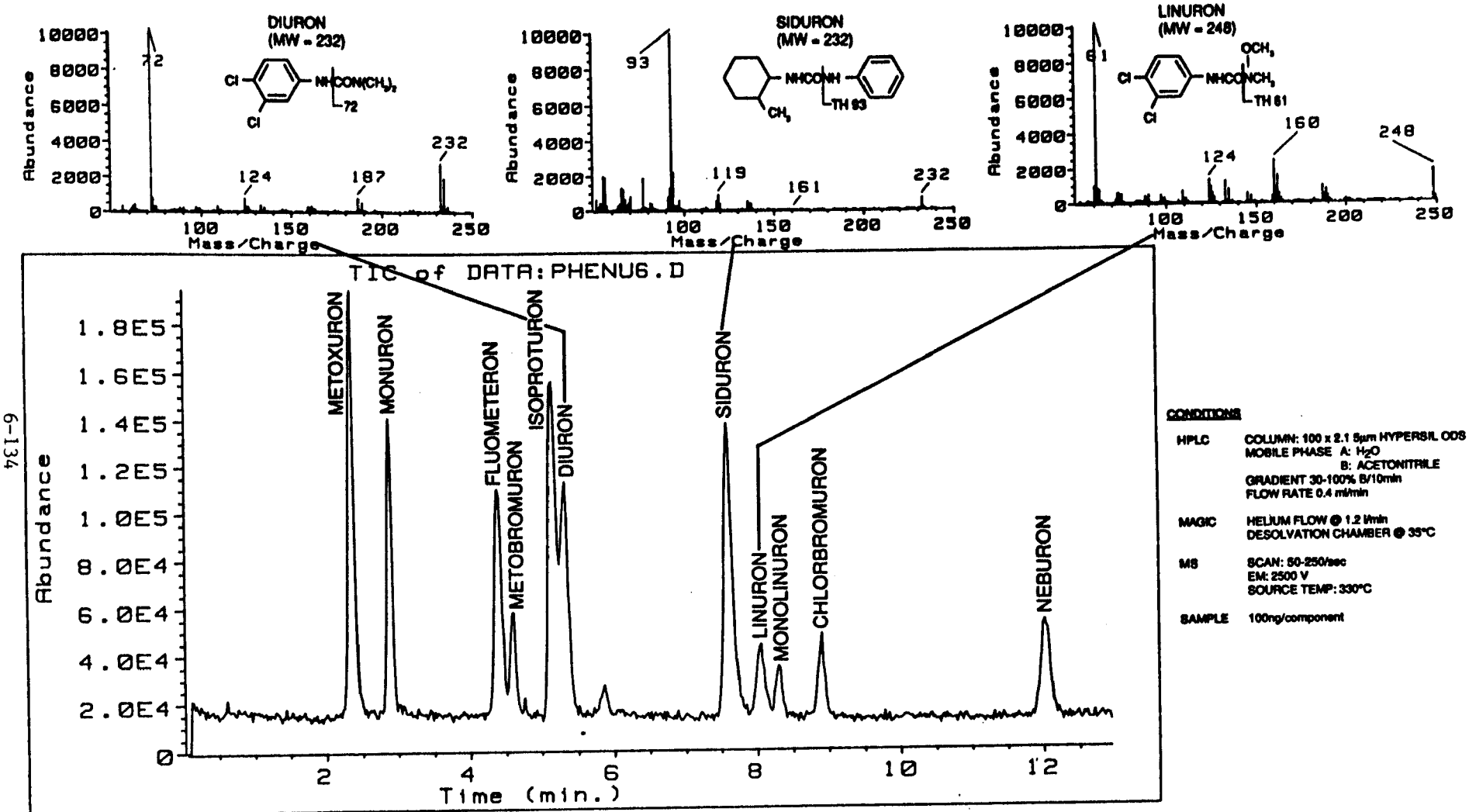

SELECTED ION MONITORING (CAFFEINE: 194)
Abundance
3.0E5
2.0E5
1.0E5
0
0
2
4
6
8
10
12
14
16
18
Time (min.)
100pg
500pg
1ng
10ng
50ng
100ng
Abundance
6000
5000
4000
3000
0.0
8.0
Time (min.)

MAGIC LINEARITY

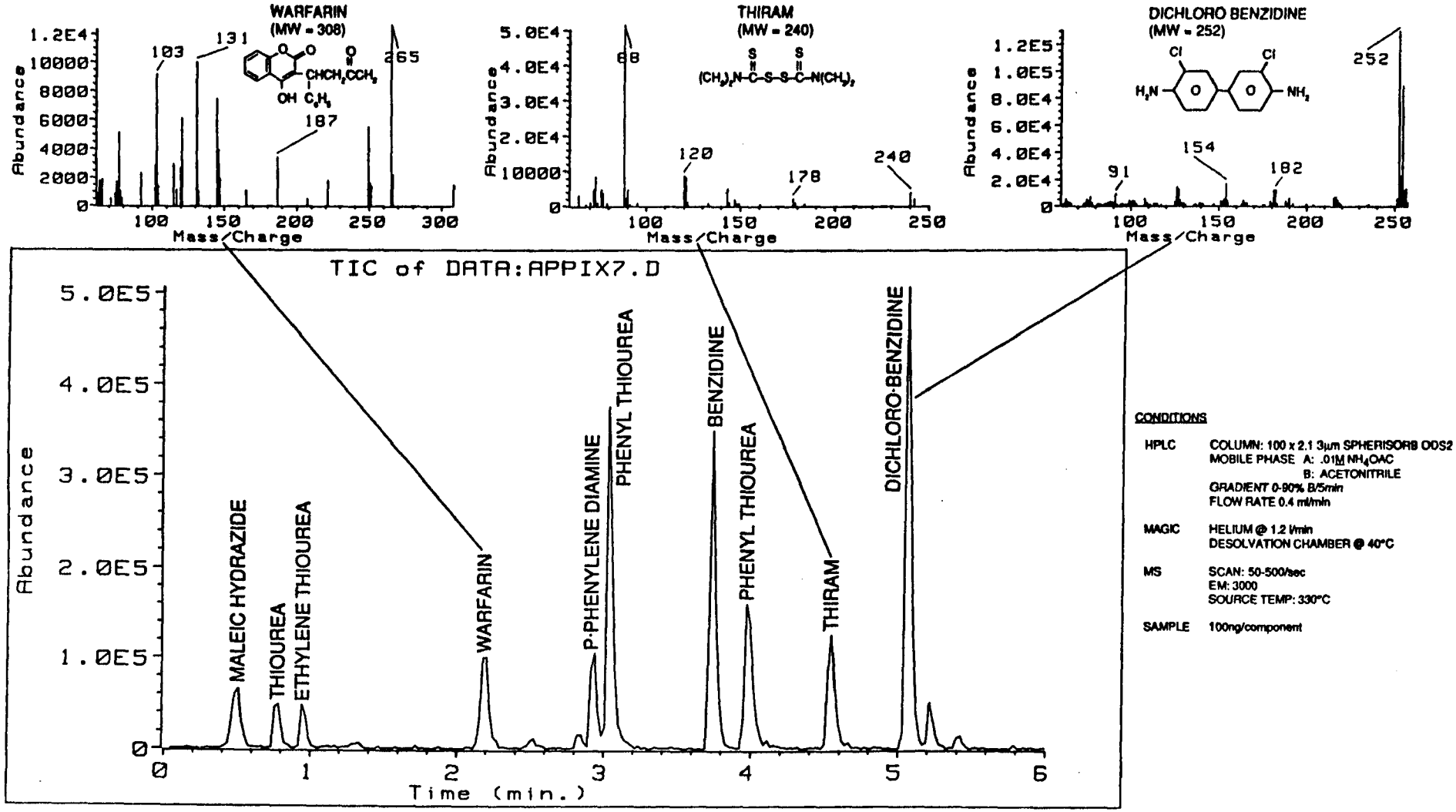




TRIAZINE PESTICIDES



PHENYLUREA HERBICIDES



EPA APPENDIX IX COMPOUNDS

number of further areas of development which could, in principle, significantly expand its areas of applicability. In particular, the use of alternative ionization modes show promise for ionizing compound which can be introduced to the mass spectrometer by MAGIC, but which do not undergo electron impact ionization. Initial experiments have generated chemical ionization (CI) spectra, and further investigation is underway.

FOOTNOTES

[1]Willoughby, R.C. and Browner, R.F., Anal. Chem. 56 (1984) 2626

[2]Federal Register 45, 99, May 19, 1980, p. 33132-3

[3]Federal Register 49, 191, October 1, 1984, p. 38797-8

[4]Thermospray LC/MS of EPA Appendix VIII Compounds. Goodley, P.C. and Thorp, J., Hewlett-Packard LC/MS Applications Note AN176-41

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Browner, R.F., Winkler, P.C., Perkins, D.D. and Abbey, L.E., Submitted for publication, Microchemical Journal.

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Israel, G.W. and Friedlander, J., J.Col.Int.Sci 1967 (24) 330.

Federal Register 45, 99, May 19, 1980, 33132-3.

COMPARISON OF CAPILLARY COLUMN AND PACKED COLUMN ANALYSIS FOR VOLATILE ORGANICS

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INTRODUCTION

The EPA GC/MS methods for volatile organic analysis in water, wastewater, and hazardous waste matrices (EPA methods 524, 624 and 8240) have always stipulated the use of packed columns. Only recently has EPA proposed the use of capillary column GC/MS analysis by printing Method 524.2 which covers volatile analysis in raw and finished drinking water for SDWA analyses. EPA is expected to issue formal capillary GC/MS methods for wastewater and hazardous waste matrices in the near future.

Capillary columns are superior to packed columns in peak resolution and sensitivity, thereby leading to better identification and quantification of compounds present in the samples. This is especially true for samples containing complex matrices. This also results in shorter runtimes, with increased productivity in the laboratory and reduced analytical costs. Capillary column use was not originally permitted because they were never part of the original ruggedness testing and method validation studies performed by EPA. Consequently, few environmental laboratories have had much experience with the use of capillary column GC/MS on a routine basis for analysis of volatiles.

Montgomery Laboratories has routinely used capillary columns for volatile organic analysis of water, wastewater, and solid waste matrices for over eight years. We were one of the few laboratories nationwide to be granted a formal EPA variance for using capillary columns in volatile organic analyses by GCMS. We will present our experience in working with the QA requirements described in the published volatile methods (524.1, 524.2, 624, and 8240). We have undertaken a comparison of the capillary column method versus the packed column method using both the Finnigan 5100 and Hewlett Packard MSD.

EQUIPMENT

The packed column analyses were performed on a Hewlett Packard 59980C Mass selective detector (MSD). The MSD was installed with a Tekmar LSC-2 Purge and trap device, a packed column injection port, a capillary column injection port, and a jet separator. Our original intention was to compare the packed and capillary columns on the MSD alone. However due to problems with the design of the MSD we were unable to consistently use it with a capillary column for volatile analysis. The packed column used was a 2 meter x 2 mm

ID glass column packed with Carbopack B (60-80) mesh coated with 1% SP-1000 The capillary column used was a 30 meter x 0.25 mm ID DB-5 FSCC with 0.25 um film thickness. Cryogenic focusing was performed by immersing a loop of the capillary column in a cup of liquid nitrogen. The capillary column was inserted directly into the source.

METHODS

The methods used were the EPA published methods 624, 524.2 and 8240. Method 524.2 was modified to use a loop of the capillary column for cryogenic focusing rather than the unit specified in the method.

COMPARISON OF THE PUBLISHED METHODS

EPA methods 524.1, 524.2, 624 and 8240 were all developed for the analysis of volatile organics in water. However, each method specifies different compounds, procedures and quality assurance procedures. Table 1 lists many of these differences. Method 524.1 is not included because it is the same as method 542.2 with the exception that 524.1 requires the use of packed columns.

Methods 624 and 8240 both specify only packed columns for analysis. Method 524.2 specifies either narrow or wide bore capillary columns. Method 524.1 is an equivalent packed column method. Each method also contains a different list of compounds which can be analyzed by the method.

The quality control requirements of the three methods differ substantially. Methods 524.2 and 8240 require that a five point initial calibration be performed, while method 624 requires only three. Method 524.2 requires that the percent RSD (relative standard deviation) of the response factors determined for initial calibration be within 10 percent in order to be called linear. If the percent RSD is higher, then a curve must be used. Method 624 allows a 35 percent RSD to be called linear, no curves allowed. Both methods 524.2 and 624 require BFB tuning and continuing calibration check to be performed "daily" while method 8240 specifies every 12 hours. The methods also have differing requirements for the frequency of analysis of duplicates, spikes and external standards.

Method 624 has a large list of compounds which can be used as internal and surrogate standards. Method 8240 has a smaller list, while the list for method 524.2 is even smaller. One of the surrogate standards to use for methods 624 and 8240 is a compound specified as an analyte in method 524.2.

TABLE 1

Comparison QC requirements for Several EPA Methods for GCMS Analysis of Volatiles

	524.2	624	8240
Column type	Capillary Wide bore Cap	Packed	Packed
Number of Compounds	58	30	34
Sample size	25 ml	5 ml	5 ml
Initial Calibration	5 point	3 point	5 point
% RSD for Standards	10% linear Curve otherwise	35% linear Curve OK	30% for certain compounds - linear
Cont. Cal. Frequency	"Daily"	"Daily"	12 hours
Cont. Cal. Criteria	20% difference	Varies with compound	25% for certain compounds
Tuning Frequency	"Daily"	"Daily"	12 hours
Duplicate Frequency	Not specified	Not specified	Matrix spike dups
Spike Frequency	Not specified	5%	5%
External Std	10% frequency All compounds 60-140% recov.	5% frequency All compounds Table of criteria	"daily" 6 Compounds Min RF=0.300
Surrogate and Internal Standards	Fluorobenzene D4-1,2-DCB BFB	Large table of acceptable compounds	D8-Toluene BFB D4-1,2-DCA BrChMethane 1,4-DFB D5-ChBenzene

DETECTION LIMITS

The detection limits published by the EPA in their methods differ greatly. Table 2 lists the published Method Detection Limits (MDLs) for a selected group of compounds in water. MDLs are defined as the minimum concentration of an analyte which must be present in a sample to be 99 percent confident that the measured signal comes from the analyte and not background noise. Note that the limits published for method 8240 (SW846 3rd edition) are not MDLs but rather PQLs (practical limits of quantitation). Both methods 624 and 524.1 are packed column methods, however the MDLs for 524.1 are much lower than those for 624. One reason for this is the larger volume of sample purged using method 524.1 (25 ml vs. 5 ml). Method 8240 is also a packed column method, however the PQL listed is approximately 5 ug/l. PQLs are defined as an estimate of "the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions." Therefore the PQLs listed for 8240 are more practical when considering environmental samples.

The method detection limits listed for the capillary column method (524.2) are all in the 0.02 to 0.2 ug/l range. Some of the numbers published originally were actually below the instrument detection limit (IDL) for the particular compound. These are now undergoing revision.

Table 3 shows the results of MDLs determined in our laboratory using method 624 for the packed column and method 524.2 for the capillary column. Note that the MDL on the capillary column was determined at two different concentrations. These MDLs were determined under routine working conditions, rather than under optimum conditions.

The MDLs determined on the packed column at 5 ug/l are similar to or slightly better than those presented for method 624. However, they are higher than those presented for method 524.1. The MDLs determined by the EPA for method 524.1 were spiked at approximately 1.5 ug/l. Since the MDL is determined at approximately three times the standard deviation of a set of seven replicates, a lower MDL can be obtained by spiking the replicates at a lower value. However at some low concentration the precision becomes poor and the MDL values do not become smaller. In addition the lower limit of the MDL is a function of the absolute instrument sensitivity. The sensitivity (IDL) of the MSD used to determine the MDLs was such that we could not spike at a lower value and obtain a smaller MDL for all compounds and spiking was therefore restricted to 5 ug/l.

The MDL for the capillary column was determined at a spiked value of 5 and 1 ug/l. At 5 ug/l the MDL determined was about the same for both the packed and capillary columns, which indicates that the precision of both methods is approximately the same. However, due

TABLE 2

Detection Limits for Published EPA Methods. (ug/l in Water)

Compound	EPA METHOD NUMBER 524.1	524.2	624	8240
Benzene	0.10	0.03	4.4	5
Bromoform	0.66	0.20	4.7	5
Bromomethane	--	0.06	--	10
Carbon Tetrachloride	0.28	0.02	2.8	5
Chlorobenzene	0.14	0.03	6.0	5
Chloroethane	--	0.21	--	10
2-Chloroethylvinylether	--	--	--	10
Chloroform	0.24	0.04	1.6	5
Chloromethane	--	0.05	--	10
Dibromochloromethane	0.30	0.07	3.1	5
Dichlorobromomethane	0.28	0.03	2.2	5
1,1-Dichloroethane	0.17	0.03	4.7	5
1,2-Dichloroethane	0.22	--	2.8	5
1,1-Dichloroethene	0.19	0.05	2.8	5
t-1,2-Dichloroethene	0.19	0.03	1.6	5
1,2-Dichloropropane	--	0.02	6.0	5
c-1,3-Dichloropropene	--	--	5.0	5
t-1,3-Dichloropropene	--	--	--	5
Ethylbenzene	--	0.03	7.2	5
Methylene chloride	0.13	0.09	2.8	5
1,1,2,2-Tetrachloroethane	0.41	0.20	6.9	5
Tetrachloroethene	0.29	0.05	4.1	5
Toluene	0.12	0.08	6.0	5
1,1,1-Trichloroethane	0.26	0.04	3.8	5
1,1,2-Trichloroethane	--	0.08	5.0	5
Trichloroethene	0.36	0.02	1.9	5
Trichlorofluoromethane	0.21	0.07	--	5
Vinyl chloride	0.31	0.04	--	10

Note: EPA methods 524.1, 624 and 8240 are packed column methods while method 524.2 is a capillary column method.

Detection limits listed for method 8240 are really PQLs.

Table 3

Determined MDL values
(ug/l in Water)

Compound	PACKED 5 ug/l	CAPILLARY 5 ug/l	CAPILLARY 1 ug/l
Benzene	0.74	1.1	0.15
Bromoform	0.94	0.68	0.31
Bromomethane	1.6	1.4	0.12
Carbon Tetrachloride	0.60	0.68	0.17
Chlorobenzene	0.54	0.91	0.14
Chloroethane	2.6	6.3	0.27
2-Chloroethylvinylether	--	0.63	0.15
Chloroform	0.60	0.90	0.15
Chloromethane	--	5.14	0.15
Dibromochloromethane	1.0	0.65	0.10
Dichlorobromomethane	0.64	6.3	0.48
1,1-Dichloroethane	0.50	0.80	0.26
1,2-Dichloroethane	0.5	1.2	0.23
1,1-Dichloroethene	1.2	1.1	0.20
t-1,2-Dichloroethene	1.1	0.93	0.33
1,2-Dichloropropane	0.81	1.8	0.33
c-1,3-Dichloropropene	--	0.62	0.21
t-1,3-Dichloropropene	--	0.80	0.25
Ethylbenzene	2.1	0.78	0.14
Methylene chloride	1.2	1.06	0.09
1,1,2,2-Tetrachloroethane	0.60	0.68	0.21
Tetrachloroethene	0.77	1.1	0.16
Toluene	0.40	0.64	0.11
1,1,1-Trichloroethane	0.57	0.69	0.17
1,1,2-Trichloroethane	1.1	0.69	0.08
Trichloroethene	0.91	1.1	0.36
Trichlorofluoromethane	1.2	0.99	0.23
Vinyl chloride	2.2	3.6	0.33

Note: The packed column data was obtained using laboratory water spiked a 5.0 ug/l. The capillary column data was obtained using laboratory water spiked at both 5.0 and 1.0 ug/l.

to the sensitivity of the capillary column, we were able to determine an MDL at a spike level of 1 ug/l. Spiking at the lower concentration of 1 ug/l gave lower MDL values. However, our determined values are much higher than those presented for method 524.2. The MDLs published for method 524.2 were spiked at 0.1 to 0.5 ug/l. If we were to determine our MDLs at a lower spike concentration we might expect to approach the published values (Table 2). However, as the EPA has noted, some of the values in Table 2 are below the IDL and are therefore unrealistic.

Table 4 lists the MDLs obtained in our laboratory using both packed and capillary columns compared to the value published in EPA method 8240 for soils. The replicates for both the packed and capillary column MDL determinations were spiked at 0.25mg/Kg and used 1 gram of soil diluted to 10mls (a 10 fold dilution) compared to method 8240 which uses 5 grams of soil in 5 ml of water (no dilution). MDL values in Table 4 assume no dilution factor. We feel that the MDL values for the capillary column could be pushed lower by spiking at 0.024 mg/Kg or lower.

CHROMATOGRAMS

The superiority of capillary columns over packed columns becomes most apparent when chromatograms are examined. Figure 1 is an example chromatogram of a 5 ug/l standard run by packed column on the MSD. Figure 2 is a chromatogram of a 2 ug/l standard run also run on the MSD using a capillary column. The packed column run shows that the 5 ug/l standard has a low signal to noise ratio. The capillary run, which was run at a lower concentration, has a much better signal to noise ratio. This is due to the capillary column being directly inserted into the MS source allowing all of the sample to be detected, rather than being split in the jet separator as with packed columns. The capillary peaks are also much sharper, because of the higher signal to noise ratio.

Figure 3 is a chromatogram of a 1 ug/l standard run on the 5100. Note that this chromatogram shows a lot less noise than the capillary run on the MSD. The 5100 is a more sensitive instrument, in part due to the 3KV conversion dynodes.

Figures 4 and 5 are chromatograms of jet fuel (JP-4) on both the packed and capillary columns. Both samples were run at 1.0 mg/l. JP-4 on the packed column does not show many of the lighter hydrocarbon which are present at the beginning of the chromatographic run using the capillary column. This may be impart due to discrimination of the jet separator. The capillary column chromatogram also shows many more heavy hydrocarbons than does the packed column chromatogram.

Table 4

Determined MDL values
(mg/Kg in soil)

Compound	PACKED 0.25 mg/Kg	CAPILLARY 0.25 mg/Kg	EPA METHOD 8240
Benzene	0.0097	0.0066	0.005
Bromoform	0.0054	0.0072	0.005
Bromomethane	0.011	0.0081	0.01
Carbon Tetrachloride	0.014	0.0063	0.005
Chlorobenzene	0.012	0.0071	0.005
Chloroethane	--	0.0220	0.01
2-Chloroethylvinylether	--	0.0063	0.01
Chloroform	0.011	0.0068	0.005
Chloromethane	--	0.0169	0.01
Dibromochloromethane	0.012	0.0068	0.005
Dichlorobromomethane	0.0086	0.0067	0.005
1,1-Dichloroethane	0.0095	0.0067	0.005
1,2-Dichloroethane	0.0070	0.0063	0.005
1,1-Dichloroethene	0.011	0.0066	0.005
t-1,2-Dichloroethene	--	0.0068	0.005
1,2-Dichloropropane	0.011	0.0068	0.005
c-1,3-Dichloropropene	0.0092	0.0070	0.005
t-1,3-Dichloropropene	--	0.0070	0.005
Ethylbenzene	0.0094	0.0075	0.005
Methylene chloride	0.0071	0.0072	0.005
1,1,2,2-Tetrachloroethane	0.011	0.0079	0.005
Tetrachloroethene	0.011	0.0074	0.005
Toluene	0.011	0.0081	0.005
1,1,1-Trichloroethane	0.012	0.0064	0.005
1,1,2-Trichloroethane	0.0082	0.0052	0.005
Trichloroethene	0.011	0.0071	0.005
Trichlorofluoromethane	0.011	--	--
Vinyl chloride	0.014	0.0256	0.01

Note: The packed and capillary column data was obtained by spiking a soil sample at 0.25 mg/Kg and was corrected for dilution as explained in the text.

Detection limits listed for method 8240 are really PQLs.

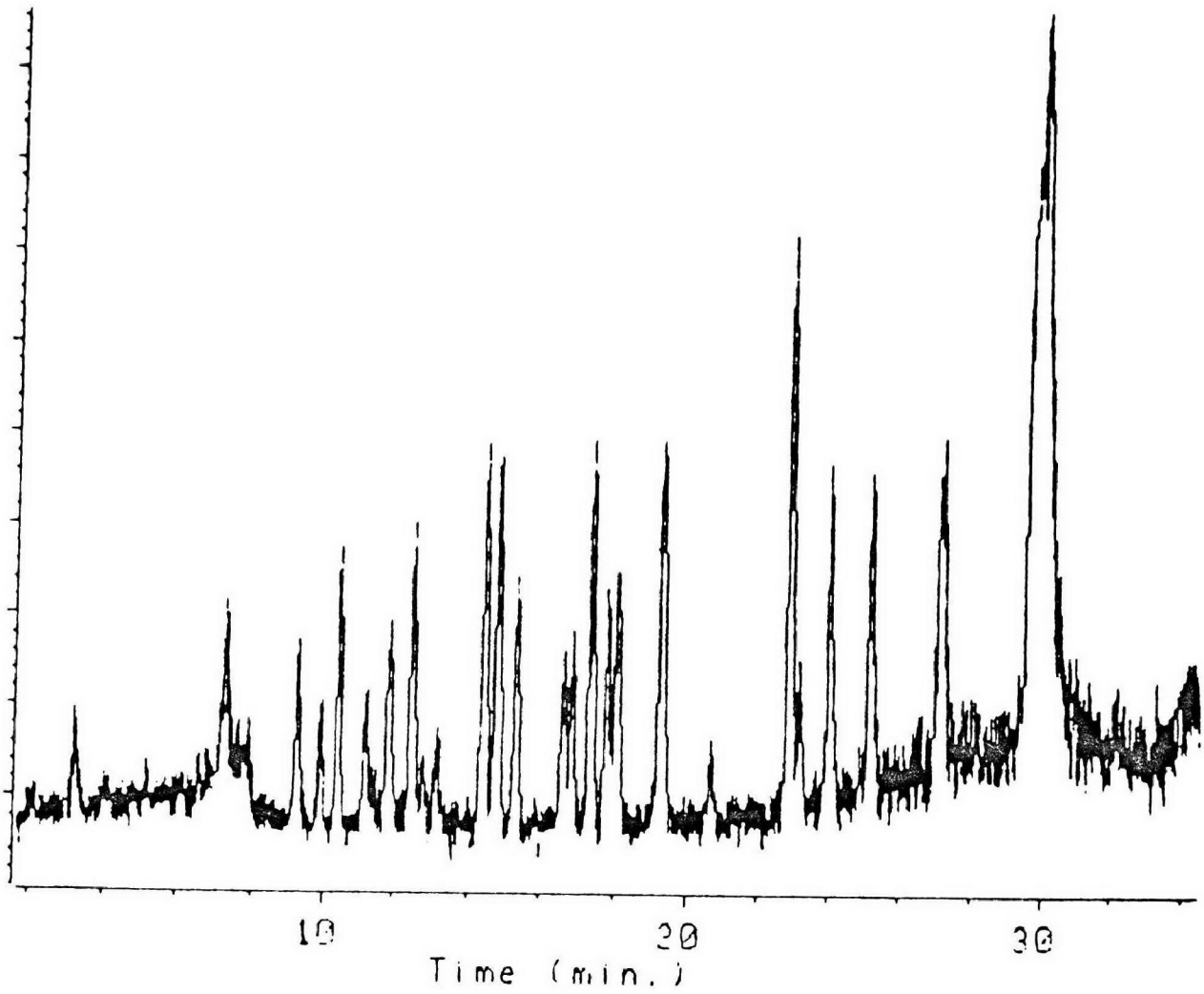

FIGURE 1

5 ug/l STANDARD PACKED COLUMN (MSD)

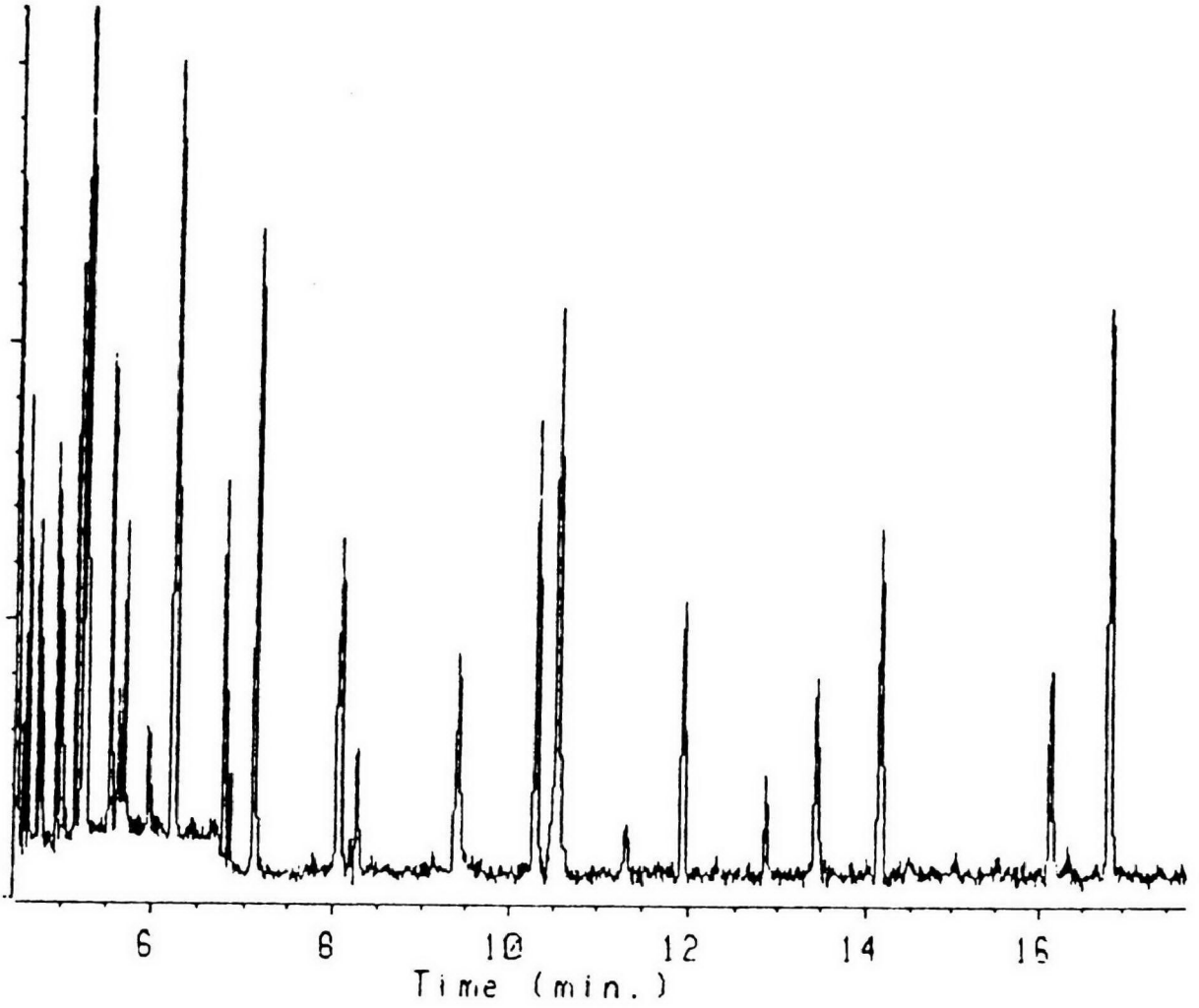

FIGURE 2

2 ug/l STANDARD CAPILLARY COLUMN
(MSD)

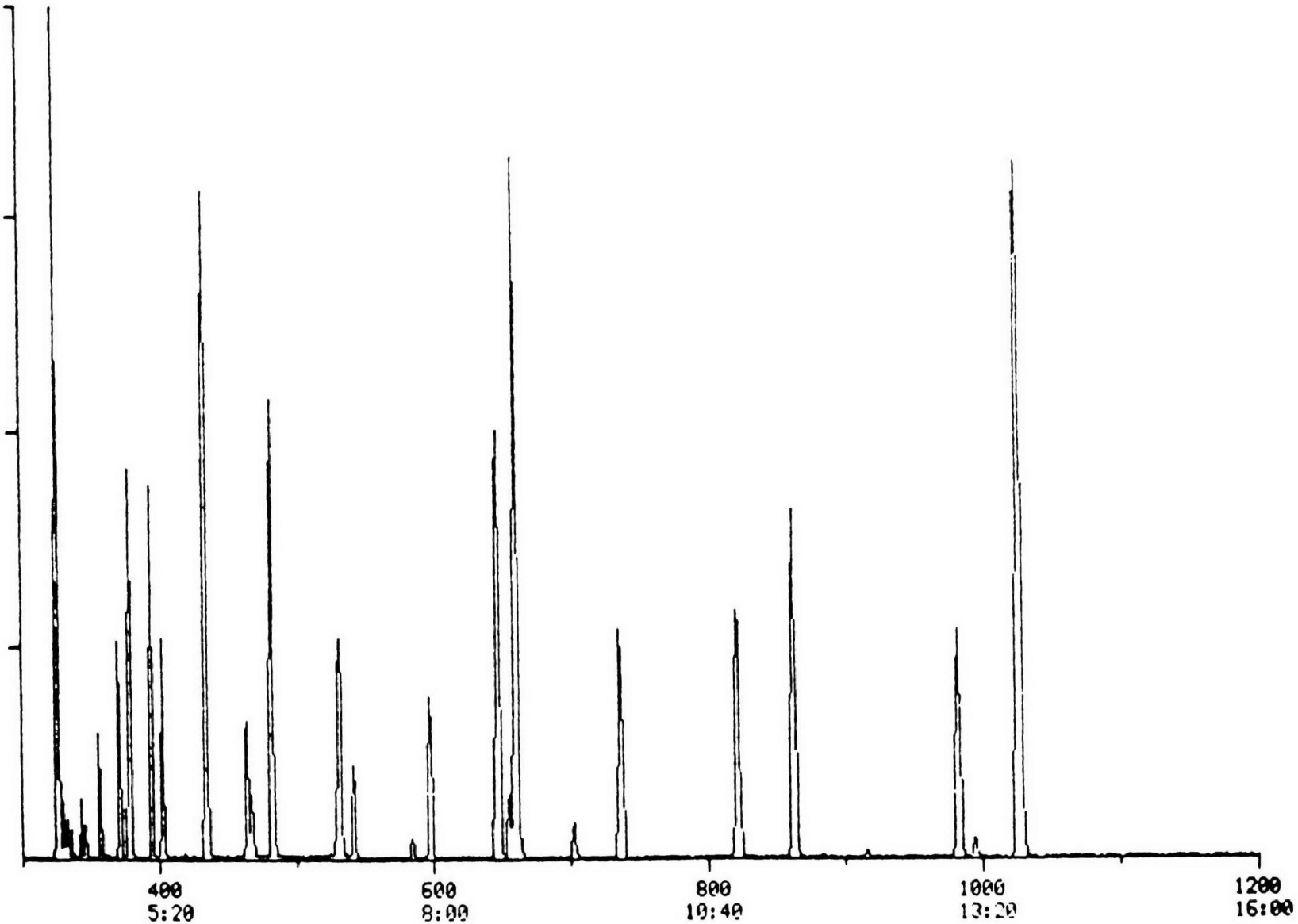

FIGURE 3

1 ug/l STANDARD CAPILLARY COLUMN
(5100)

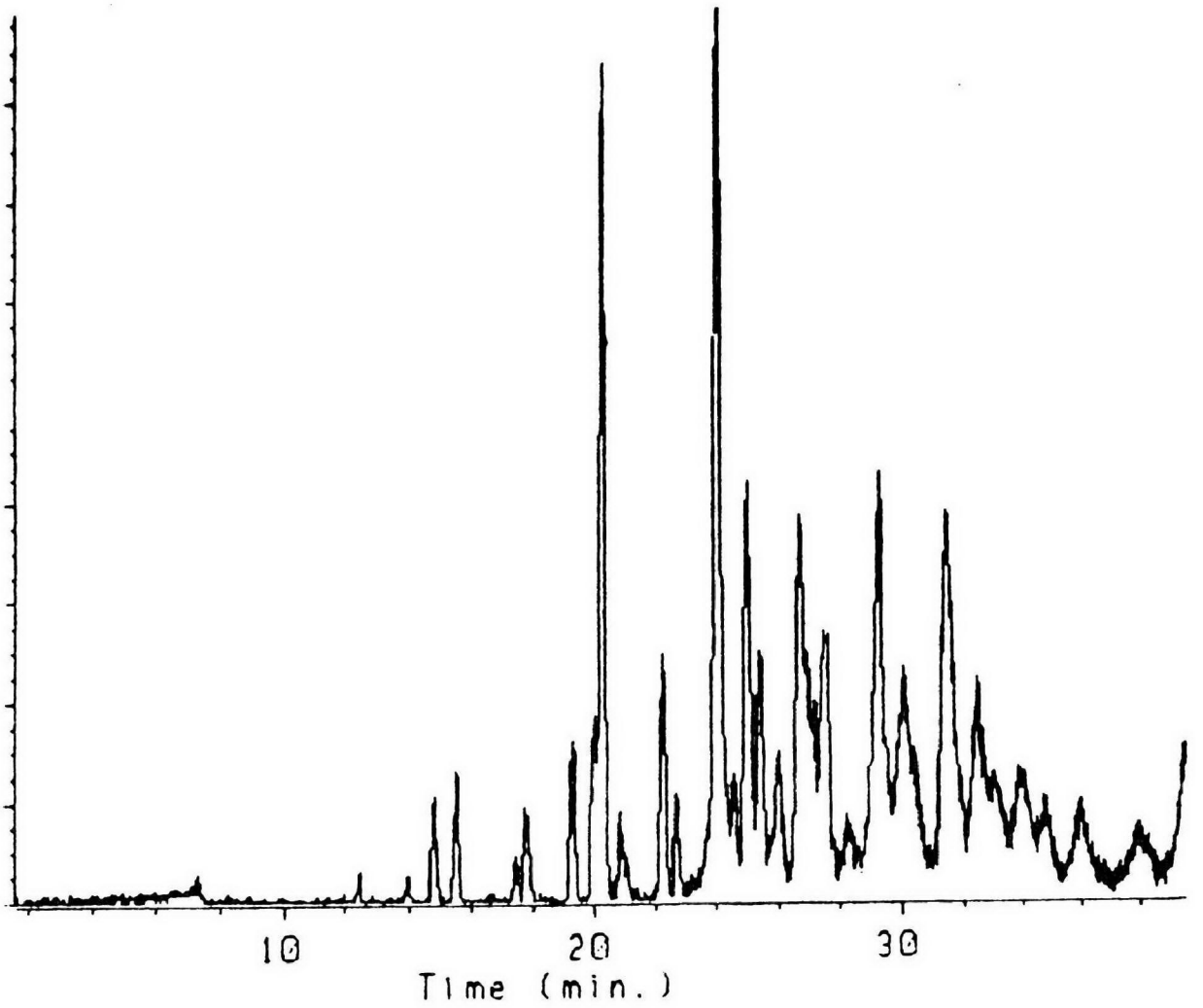

FIGURE 4

JP-4 PACKED COLUMN

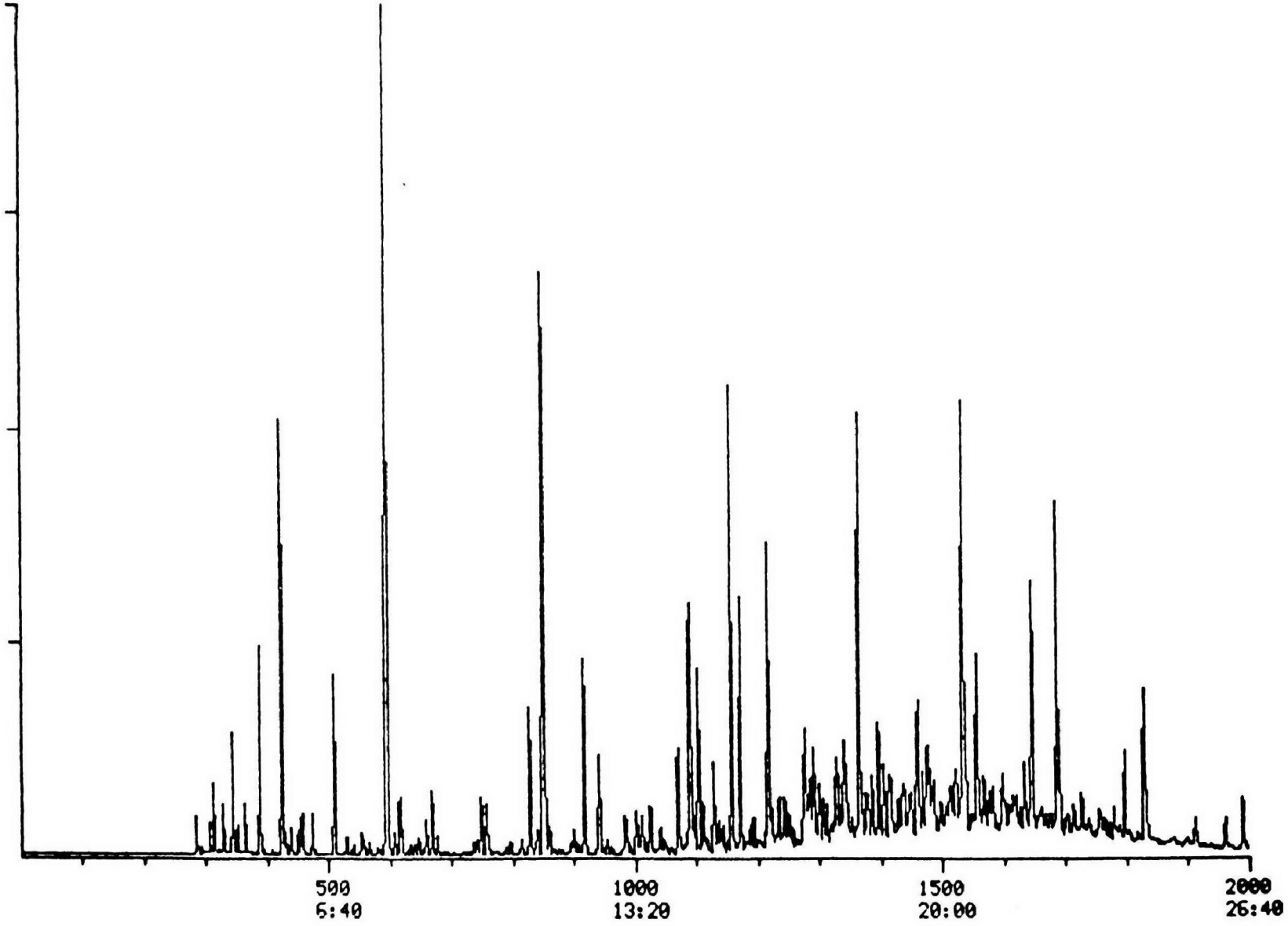

FIGURE 5

JP-4 CAPILLARY COLUMN

PROBLEMS WITH MSD

We could not use the MSD for capillary column purge and trap analyses on a consistent basis. When a capillary column is used with a GCMS the column is inserted directly into the source. When used with a purge and trap device, water vapor can be introduced with the sample. This water vapor triggered an error detection circuit in the MSD which shut down the source due to "excessive source pressure." The HP MSD was originally specified to allow 0.8 ml/min total flow into the source. Attempts to remove the water by employing the Tekmar 4000's "dry purge" option again failed to work consistently. Since the "excessive source pressure" error was triggered on an inconsistent basis we were unable to produce any MDL data from the MSD using capillary column. Since our capillary problem and those of other laboratories have been brought to their attention, HP has reinvestigated the maximum pressure limit and determined that the 0.8 ml/min was overly conservative. HP has since come up with a solution to the problem (by-passing the error detection circuit) and is offering it an option.

LIMITATIONS OF CAPILLARY TECHNIQUES

Although capillary columns provide much greater resolution and sensitivity then packed columns, this higher sensitivity also limits the linear range. An attempt to meet CLP protocols for standardization required by the CLP methods (20, 50, 100, 150 and 200 ug/l). Using capillary columns we can routinely see compounds below 0.1 ug/l, however above 20 ug/l the detector becomes saturated. This problem can be overcome by diluting samples so that the concentrations fall within the linear range of the standards.

SUMMARY

The EPA's publication of capillary column methods for volatile organic analysis will increase the sensitivity of the analysis and will allow more complex matrixes to be examined. However it is important to note the limitations of capillary columns. In our laboratory we feel that for low level samples containing complex mixtures capillary column analysis is preferred. For samples with only a few components at high levels we prefer the use of packed columns. For high level complex mixtures we prefer to dilute the sample and to analyze it using capillary columns.

AN EXAMPLE OF INTERLABORATORY METHOD VALIDATION STUDIES IN THE U.S. ENVIRONMENTAL PROTECTION AGENCY, METHODS 3510 AND 8270

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ABSTRACT

One of the activities of the Quality Assurance (QA) Branch of the Environmental Monitoring and Support Laboratory in Cincinnati (EMSL-Cincinnati) is to perform interlaboratory method validation studies. Through the use of a contractor, the QA Branch developed three mixes containing 59 compounds which were spiked into three matrices (reagent water, ground water from a dump site, and leachate from a dump site), at six different concentration levels. These 59 compounds represent the Appendix IX[1] list minus those compounds which already have performance data. The six concentration levels form three Youden pairs which are used to determine accuracy, single laboratory precision and overall precision. The mixes were tested in a control laboratory for applicability to Method 3510 (liquid/liquid extraction) and Method 8270 (gas chromatograph/mass spectrometer (GS/MS)) for extraction efficiency, sensitivity, resolution, and stability. Fixed fee contracts were awarded to ten laboratories. Each laboratory was required to analyze three matrices for all 59 compounds at six concentrations. A quality control sample and a blank were also required for analyses each day. The resulting data were evaluated statistically by the interlaboratory method validation study (IMVS) system of computer programs which is consistent with ASTM procedure D2777, "Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water". IMVS tests for the rejection of outliers (both whole laboratory per matrix and individual data points), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision and tests for the effects of matrices on accuracy and precision. A final report, containing a description of the study, statistical treatment of data, results, discussion and conclusions, completed the interlaboratory method validation process.

INTRODUCTION

The Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) develops analytical methods and provides quality assurance (QA) support for the various offices of U.S. Environmental Protection Agency (USEPA) for maximum reliability and legal defensibility of environmental data collected under the water and waste regulations. In EMSL-Cincinnati, QA responsibilities are

assigned to the Quality Assurance Branch. One of its activities is to conduct interlaboratory method validation studies to generate accuracy and precision statements for the analytes specified in each method. This paper describes one such study now being conducted for the Office of Solid Waste (OSW), on two of its methods, 3510 and 8270.

METHOD SUMMARIES

Method 3510 is an extraction and concentration procedure for water-insoluble and slightly water soluble organic analytes from aqueous samples. In Method 3510, one liter of water or wastewater is extracted successively at pH >11 with three 60 mL volumes of methylene chloride. The pH of the sample is then readjusted to <2 and again extracted successively, with three 60 mL volumes of methylene chloride. The extracts are combined, dried using a sodium sulfate column, and then concentrated to a final volume of 1.0 mL, using a Kuderna-Danish apparatus with a Snyder column. Method 8270 uses gas chromatograph/mass spectrometer (GC/MS) capillary column techniques to determine the concentration of the semi-volatile organic analytes in the extract.

STUDY DESIGN

A prime contractor was selected to develop, prepare, and verify the test sample series and to manage the performance of the study. Participant laboratories were obtained separately on contract by the QA Branch of EMSL-Cincinnati. These laboratories were shipped samples, sample instructions, study instructions and written analytical methods, for analyses within a set time frame.

The sample design was based on Youden's non-replicate plan for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs, each sample of a pair containing slightly different concentrations of the constituents. Each analyst is directed to perform single analysis and report the value for each analyte in the sample. Analyses in reagent water evaluate the proficiency of the method on a sample free of interferences whereas analyses in the other waters reveal the effects of interferences on the method.

The results from the study are returned to the QA Branch for evaluation using IMVS at the Agency computer center in Research Triangle Park, North Carolina.

SELECTION OF STUDY PARTICIPANTS

In accordance with the standard competitive bid process, an abstract of the scope of work was announced in the Commerce Business Daily. Over 100 laboratories asked for the request for proposal (RFP), which contained an abstract of the method, the scope of work, and the evaluation criteria upon which the offeror would be evaluated. The evaluation criteria for the technical proposal for this study were as follows:

* The offeror must demonstrate the Suitability of the Project Management Plan, which includes the experience of the project manager in managing contracts of a similiar nature as this contract, the suitability of the organizational plan in which roles, responsibilities and authorities are clearly identified. The offeror must demonstrate the ability of the offeror to provide the required number of analyses within the period of performance given in the contract.

* The offeror must demonstrate the experience of analysts involved in the method study.

* The offeror must describe the facilities and instrumentation which will be made available for this contract.

* The offeror must describe what efforts are to be made to insure the quality, quantity and timeliness of the data.

After proposals were evaluated and ranked, technically acceptable laboratories were sent a performance evaluation (PE) sample for analyses as per the written method and were required to use the same personnel and instrumentation specified in their proposal to complete the analyses. The PE sample contained ten priority pollutants. The offerors did not know the compounds or their concentrations. The offerors' data were evaluated based on statistics from an interlaboratory method validation study of Method 625, a similar GC/MS procedure. From laboratories performing acceptable, ten were chosen based on competitive costs. These are listed in Table 1.

STUDY DETAILS

Bionetics, Inc. in Cincinnati, Ohio, was selected as the prime contractor, and was responsible for the preliminary investigation of sample design, sample stability, extraction efficiences and practical concentration levels. Bionetics conducted developmental studies to determine the number of compounds that could be analyzed practically, in one mixture without chromatographic interferences, the stability of various mixtures in different matrices and the extraction efficiencies from different matrices.

The goal of this study was to include as many analytes as possible from the RCRA Appendix IX list yet still remain within resource limits. Of approximately 120 analytes, there were 48 analytes for which regression equations had been generated for bias and precision in a Method 625 study. These were deleted because Method 625 differs from Method 3510 and Method 8270 only in that packed column chromatography is used in Method 625 whereas Method 8270 uses capillary column chromatography. Each method uses mass spectrometry for the determinitive step.

Of the 72 remaining analytes, 13 were deleted from the study due to either instability, insolubility or poor recovery. Table 2 lists the compounds and the reasons for deletion from the study. The remaining 59 analytes (see Table 3) were divided into three mixes which exhibited no significant chromatographic interferences and were stable in methanol or acetone. Each mixture was injected repeatedly into the gas chromatograph/mass spectrometer at lower concentrations to estimate the instrument detection limit. When a reasonable level was established, these concentrates were spiked into the three matrices (reagent water, ground water, and leachate) used in the study to determine any adverse matrix effects on the chromatography and extraction procedure. Spiking ampul concentrations and standard solutions were stable for 90 days.

Each participating laboratory received copies of the analytical methods, instructions for preparation of the spiking solutions, standard solutions and quality control (QC) solutions, 54 ampuls of spiking solution, six 1-gallon bottles of ground water, six 1-gallon bottles of leachate, 12 ampuls of standard stock solution and six ampuls of QC solution. Spiking and standard solutions were heat-sealed in 5 mL glass ampuls. Each ampul contained approximately 2.5 mL of solution of which 1.0 mL was used to spike 1 liter of water. The ampul concentrations were analyzed for accuracy against standards prepared from the neat pure compounds, by Bionetics, prior to distribution. After the data were received from the participating laboratories, Bionetics again analyzed the ampul concentrations against standards freshly prepared from neat materials to verify the stability of solutions over the period of the study.

SAMPLE MATRICES

The ground water and leachate came from monitoring wells at industrial/municipal waste dumpsites. The wells were purged and samples were withdrawn. Waters were autoclaved to eliminate any biological activity and thoroughly mixed to ensure homogeneity. The waters were dispensed into bottles with Teflon lined caps and were shipped on ice in coolers to maintain the sample integrity.

DATA HANDLING

IMVS is used to evaluate the large number of data points in these studies (approximately 11,000 data points in this study). The data treatment tests for outliers using both Youden's laboratory-ranking test for laboratory outliers and the Thompson T-test for individual outlier values. Statistical parameters included estimates of mean recovery, single-analyst precision, overall precision, and tests for matrix effects.

A questionnaire was sent to each of the ten participating laboratories requesting information on the operating conditions of the instrumentation, problems encountered with the method and any other variables associated with the conduct of the method. Their comments will be addressed in the final report.

STUDY REPORTS

An in-depth report and a project summary report, will be generated from this interlaboratory method validation study. These differ in the depth and detail in the: introduction, conclusions, recommendations, descriptions, statistical treatment of data and discussion sections.

At this time, the data on Methods 3510 and 8270 from the ten participating laboratories are now being received. We anticipate that all data will be received, reviewed for major errors, processed through IMVS, a draft report generated and peer reviewed, and a final report available September 30, 1987.

REFERENCES

1. On July 24, 1986, the USEPA proposed to amend its regulations concerning groundwater monitoring at landbased hazardous waste treatment, storage, and disposal facilities. The amendment would require analysis of groundwater for a specific list of chemicals, Appendix IX to Part 264.

Table 1: Participating Laboratories

ACZ Inc.
Steamboat Springs, CO

Cambridge Analytical Associates
Boston, MA

Lancaster Laboratories, Inc.
Lancaster, PA

James M. Montgomery, Inc.
Pasadena, CA

Pacific Analytical, Inc.
Carlsbad, CA

PEI Associates, Inc.
Cincinnati, OH

Science Applications International Corp.
La Jolla, CA

Southwest Research Institute
San Antonio, TX

Thermo Analytical, Inc.
Ann Arbor, MI

UBTL, Inc.
Salt Lake City, UT

Table 2: 13 RCRA Appendix IX Analytes Not In Study

p-Benzoquinone	No recovery at both 20 and 600 ppb.
Benzenethiol	Unstable in spiking solutions, both methanol and acetone.
Pentachloroethane	Decomposes to tetrachloroethene with less than 2% recovery at 600 ppb.
Resorcinol	No recovery at both 20 and 600 ppb.
Hexachlorocyclopentadiene	Unstable by thermal decomposition and solvent reactivity.
p-Naphthoquinone	No recovery at both 20 and 600 ppb.
Aramite	No recovery at 50 ppb. 6% recovery at 600 ppb. Four peaks are produced from 96% pure material.
Hexachlorophene	No recovery at 50 ppb. 18% recovery at 600 ppb.
Dibenzo (a,h) pyrene	Insoluble in spiking solvents and commercially unavailable.
Dibenzo (a,i) pyrene	No recovery at 50 ppb. Detection limit approximately 150 ppb.
n-Nitrosodimethylamine	Compound coelutes with solvent. 30% recovery at 10 ppb.
1-Naphthylamine	20% recovery at 10 ppb.
Phthalic anhydride	No recovery at 100 ppb.

Table 3: Three Mixes Containing 59 Analytes

Mix 1 in methanol:

n-Nitrosomethylethylamine

n-Nitrosodiethylamine

Aniline

n-Nitrosopyrrolidine

a,a, Dimethylphenethylamine

p-Chloroaniline

n-Nitrosodi-n-butylamine

o-Nitroaniline

m-Nitroaniline

2-Naphthylamine

5-Nitro-o-toluidine

p-Nitroaniline

1,2-Diphenylhydrazine

4-Aminobiphenyl

Methapyrilene

Benzidine

p-Dimethylaminoazobenzene

3,3'-Dimethylbenzidine

4,4'-Methylene bis (2-chloroaniline)

3,3'-Dimethoxybenzidine

2-Methylnaphthalene

Table 3: Three Mixes Containing 59 Analytes
(continued)

Mix 2 in acetone

Methyl methane sulfonate

n-Nitrosomorpholine

p-Methylphenol

2,6-Dichlorophenol

1,2,4,5-Tetrachlorobenzene

Isosafrole

Dibenzofuran

n-Nitrosodiphenylamine

Phenacetin

Pronamide

2-Acetylaminofluorene

Tris (2,3-dibromopropyl) phosphate

Benzyl alcohol

Dihydrosafrole

1,3-Dinitrobenzene

Chlorobenzilate

Kepone

Table 3: Three Mixes Containing 59 Analytes
(continued)

Mix 3 in acetone

2-Methylphenol

Acetophenone

n-Nitrosopiperidine

Hexachloropropene

Safrole

2,4,5-Trichlorophenol

1,4-Dinitrobenzene

Pentachlorobenzene

2,3,4,6-Tetrachlorophenol

Diphenylamine

Pentachloronitrobenzene

2-sec Butyl 4,6-Dinitrophenol

7,12-Dimethylbenz (a) anthracene

3-Methycholanthrene

Dibenzo (a,e) pyrene

Ethyl methane sulfonate

1,2-Dibromo-3-chloropropane

1,2-Dinitrobenzene

1,3,5-Trinitrobenzene

Diallate

4-Nitroquinoline-N-oxide

DETECTING COELUTING COMPOUNDS IN GC/MS

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ABSTRACT

In recent years, more and more sophisticated analytical tools have been applied to the analyses of solid waste. High resolution fused silica capillary column gas chromatography/mass spectrometry has become a standard tool for examining environmental samples. However, the complex matrices often encountered makes it difficult even for such a powerful technique.

The GC/MS target compound approach is commonly used to screen for a list of suspected chemicals. This, by itself, is insufficient to characterize the sample. To identify the non-target compounds, one must perform a library search on the unidentified peaks. Peak identification and selection is not necessarily easy to do. Automatic peak selection may be performed on partially overlapping peaks but completely coeluting peaks will be missed. A skilled chemist may be able to spot coeluters by examining the mass spectral data. This manual process is very time consuming as well as dependent on the chemist's ability. In very complex cases, compounds will remain undetected.

We will survey the present techniques for co-eluting and overlapping compounds along with their limitations. Then we will discuss another software approach that can be used for these difficult cases. The process of data examination can be used in either a manual inspection or automated batch mode. Automatic screening makes it feasible to process more files in a more consistent manner than can be done manually.

INTRODUCTION

Solid waste samples can be very complex, requiring highly sophisticated tools for analysis. For semi-volatiles analysis, fused silica capillary column chromatography combined with mass spectrometry has become the standard analytical technique in environmental labs.

In spite of the chromatographic and spectrometric separation capabilities of HRGC/MS, instances of coeluting compounds are encountered more as the rule rather than as the exception. In this paper, we will review the software techniques available for identifying instances of coelution for both target and nontarget compounds.

IDENTIFICATION AND QUANTITATION OF TARGET COMPOUNDS

Many of the established GC/MS methods, such as 624 an 625 are designed for target compound analysis (determining whether a compound is present, and if so, in what quantity). Detection of these target compounds in a complex mixture is relatively easy to do with current software.

In the AQUARIUS automation software for the Hewlett-Packard RTE data system, one prepares an identification specification for each target compound including mass abundances and the expected retention time. The software allows the operator to enter in the permissible acceptance window for the mass abundances and retention time. This window is set globally with the option of individual specification for each target compound. The passing criteria for each component can be set in terms of spectral match to the specifications, retention time, or a combination of spectral match and retention time. The flexibility of the system in setting the passing criteria allows one to be very stringent or lenient in identification of target compounds.

One can also look for a specific compound without knowing the retention time or even injecting the standard if there is a reference mass spectra. Among the commands available is one which determines the cross correlation between a reference spectrum and the spectra over a chromatographic range. A plot is generated where the y-axis value represents the correlation of the spectra with the reference spectrum. The amplitude of the peak is an indication of the quality of the match. Thus, one can locate a target compound or class of compounds within a complex mixture.

These two methods, or variations thereof, are available on a variety of mass spectral data systems and are routinely used by chemists in environmental labs.

RECOGNITION OF COELUTING PEAKS AMONG TARGET COMPOUNDS

Coeluting peaks are easily recognized when spectral comparisons are displayed or printed out during target compound analysis. When one encounters a component that has many more peaks than the reference standard, even though it has been background subtracted or enhanced, one presumes that another component is involved. This component may be isolated by performing a subtraction of the standard or library spectrum of the target compound from the sample spectrum. Multiple, coeluting, target compounds may be successively removed to give a residual spectra. A subsequent library search may be used in an attempt to identify this residual spectra. In many cases, a reverse library search may be sufficient to identify the components.

IDENTIFICATION OF NON-TARGET COMPOUNDS

For high volume laboratories, it is desirable to reduce the amount of time spent by an analyst to hunt for these coeluters. One can write a

procedure for testing the contamination index or some other value in the library search results. If this value indicates the presence of extraneous peaks in the sample spectrum, a spectral subtraction followed by a library search of the residual spectrum is to be performed.

In the EPA Contract Lab Program, the contractor is to identify a target list plus the ten largest non-target peaks. This is typically done by examining a total ion chromatogram of the run and labeling the target compounds. Then, one selects the ten largest non-labeled peaks for a library search. This is not a difficult process, but when one considers many labs where there are a couple of mass spectrometers with autosamplers running around the clock, the peak selection, library search examination, concentration estimation, and report production can easily overwhelm a single operator.

In addition to the time-consuming nature of identifying the non-target peaks for a large number of samples, there is the problem of coelution. Unless one carefully examines the target compound spectrum while examining the chromatogram, one can very easily mark off a peak as a target compound when it consists of a non-target compound in much larger quantities than the target. One way to reduce errors is to use some of the alternative peak labeling options in the RTE data system. One can, for instance, label the target compound peaks with the determined concentrations. When looking at a relatively large peak with a small labeled concentration, one is alerted to the possibility that there is another compound present. While this labeling will help, one is nevertheless faced with visual examination of large numbers of samples.

AUTOMATION OF NON-TARGET COMPOUND IDENTIFICATION

To what extent can the process of identifying the largest non-target peaks be automated? After the qualitative and quantitative analysis, one has the retention time of the target compounds along with their starting and ending scan numbers or times. Thus, it is very easy to remove the target peak with a tangent skim between the first and last scans. After the target compounds are removed, a simple integration will select the ten largest peaks for library searching. The chemist would still have to use his judgment on the library search, but the quantitation and generation of the Contract Laboratory Program report form can be automated. This process is not just theoretically possible, but has been implemented with the RTE mass spectrometer data system. The procedure that performs these operations has been available and used by many labs.

The procedure just described performs what an analyst does with visual examination. However, we come back to the problem of the coeluting peak. How does one handle the case where a relatively large non-target compound coelutes with the target compound? In the above procedure, it will be removed if it is within the beginning and ending scans of the target compound.

Let us consider the technique of spectral subtraction. Ordinarily, we think of choosing a spectra before or after a peak and subtracting it from the apex or an average spectrum separate partially coeluting peaks. This process is usually done manually or, with some compromises, automatically. While it gives us relatively good spectra, it doesn't help us find the largest non-target peaks.

The latest revision (Revision E) of the RTF software has a new command, BSB, which performs background subtraction in a different manner than described. This command removes a reference spectrum from a portion or all of a data file rather than from a selected mass spectrum. Thus, if one removes the target compound spectrum from a retention time window, all that remains would be the non-target compound spectra. If this same process is repeated for all the non-target compounds, the residual total ion chromatogram represents the non-target compounds. From this point on, it is very easy to select the ten largest non-target compounds for library searching and quantitation.

[Although the BSB command has legitimate uses as illustrated above, it can be abused. Therefore, whenever it is used, a non-changeable flag is set for the data file indicating that something has been removed. This flag shows up in the annotation as "BSB" in any chromatogram (total or extracted) or mass spectrum that is produced from this modified file. The annotation will be displayed even on spectra from a region for which this command has not been applied. If this command is to be used, it is highly recommended that it be used on a copy of the original data file. Once used, there is no way to reset the flag for the data file.]

CONCLUSION

We have examined how coeluting peaks may be dealt with in GC/MS. Naturally, the same techniques have some application for LC/MS as well. The coelution problem may not be completely solved, but there are sufficient software solutions to handle some difficult cases. The selection and quantitation of the largest non-target peaks is no longer a problem than must be done completely by the analyst. Although a manual review is necessary (and desirable), identifying the peaks and completing a quantitation report can be automated.

THE IDENTIFICATION OF SELECTED SYNTHETIC SURFACANTS FOR A COMPLEX WASTE MATRIX USING THERMOSPRAY LIQUID CHROMOTOGRAPHY-MASS SPECTROMETRY

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ABSTRACT

Synthetic nonionic surfactants are present in many manufacturing processes which ultimately find their way into the environment. Although surfactants are generally considered nontoxic, they have a profound effect on the rates of absorption, leaching and/or movements of other more hazardous materials.

Currently the surfactants are not monitored by GC/MS methods due to their nonvolatile character. Also, the analytical isolation and characterization of surfacants from complex matricies requires lengthy work-ups.

This paper will describe an experimental approach which isolates and characterizes selected nonionic surfactants from a waste matrix. The analysis was performed rapidly using thermospray liquid chromatography-mass spectrometry which is well suited for non-volatile organic compounds.

EVALUATION OF METHOD 3640 (GPC CLEANUP) FOR APPENDIX VIII ANALYTES

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ABSTRACT

Sample cleanup gel permeation chromatography (GPC) is a useful technique for removing high molecular weight interferences from sample extracts. The technique was originally developed for removing lipids from biological samples, and has since been applied to a wide variety of environmental samples as Method 3640 of SW-846. The experiences of several laboratories using GPC for the cleanup of high concentration Superfund and RCRA wastes demonstrate that Method 3640 may not be sufficiently *rugged* for application as a *generic* cleanup procedure for all wastes. Work is not in progress to validate use of Method 3640 for the analysis of Appendix VIII analytes in a variety of wastes.

The GPC recovery of standards of most organic Appendix VIII analytes were determined by using GC/MS, GC/ECD, GC/FPD, and HPLC-UV. In addition, the GPC retention volume for each compound was also determined. Analytes that gave poor recoveries on GPC when the system was calibrated by using phthalate/PCP were identified. Recoveries of the same analytes were also determined for standards spiked into hazardous waste in order to evaluate method suitability for difficult sample matrices. Labeled *bis*-(2-ethylhexyl) phthalate (^{3}H) and benzopyrene (^{14}C) will be used used as marker compounds to monitor the effect of sample size on method performance.

Detailed guidance in the use of GPC for environmental samples is being developed for laboratories because many of the problems associated with the use of GPC appeared to be caused by inadequate training of instrument operators. Specific guidance is provided on maximum sample size, sample preparation techniques, and column packing procedures, and system maintenance.

INTRODUCTION

Gel Permeation Chromatography (GPC) is a size exclusion separation technique that is used to remove high-molecular weight interferences from

sample extracts prior to GC or GC/MS analysis. GPC was first used for environmental samples in the analyses of PCB's and dioxins in fish tissue. At that time, the protocol required the samples be eluted from the GPC column using a solvent mixture of methylene chloride and cyclohexane. Method performance studies were conducted at that time to establish the elution pattern and the recoveries of a variety of pollutants using the cyclohexane/methylene chloride solvent system.

In the last decade, GPC has come to be used as a generic technique for the cleanup of hazardous waste samples. During the period, it has been observed that recovery of a limited number of surrogate analytes was unchanged by using 100 percent methylene chloride as an elution solvent. GPC cleanup using methylene chloride as an elution solvent is now specified for the analysis of hazardous waste samples in Method 3640 of the third edition of SW-846. By virtue of its publication in SW-846, GPC has become the standard method for the preparation of hazardous waste samples to be analyzed for the presence of Appendix VIII compounds. Unfortunately, there is little data on GPC method performance for the majority of Appendix VIII analytes when methylene chloride is used as a solvent. Nor are there data available for analyte recoveries from spiked sample matrices.

MATERIALS AND METHODS

All standards were obtained from either the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina, or from commercial sources (Aldrich, Sigma, Chem Service, etc). Methylene chloride was HPLC or distilled in glass-grade. The GPC separations were accomplished using an Autoprep 1002A from ABC Laboratories. The column was 70 g of resieved Bio-beads SX-3 (200-400 mesh) packed using a 1:3 mixture of methylene chloride/cyclohexane. After packing, the column was flushed with methylene chloride overnight. Each column was calibrated by the fraction collection technique described in Method 3640; the dump and collection times were set in order to eliminate 85 percent of the corn oil. All standards and samples were run using automated collection, and collected GPC runs were concentrated on a steam bath in 500 mL or 1-L Kuderna-Danish (K-D) apparatus. Analysis was accomplished using GC/MS (Finnigan 4500, DB-5, Method 8270), GC/ECD or GC/FPD (HP5880; DB-5, DB-608, or DB-210; Proposed Method 1618). HPLC studies used a Spectra-physics terniary gradient pump, Model 8800, Spherisorb 5 μm ODS column, and a Hewlett-Packard diode array detector, Model 1040A. Elution was with 0-100 percent aqueous acetonitrile.

RESULTS AND DISCUSSION

Initial efforts in this study focused on determining the GPC retention volumes of Appendix VIII analytes and the precision and accuracy of their recovery using Method 3640. Mixtures of standards were prepared and run on the GPC using two different collection techniques. First, 20-mL (four-minute) fractions were collected and analyzed in order to determine the retention volume of the various analytes (Figure 1). Second, recoveries of the analytes (Table 1) were determined in triplicate using the phthalate/PCP calibration described in Method 3640.

Figure 1 shows that only organophosphorus insecticides elute as early as do phthalate esters on the GPC. Other classes of organic Appendix VIII compounds elute after phthalates. It has been our experience that if the laboratory does not need to determine phthalates or phosphates in a sample, significantly better sample cleanup can be achieved by calibrating the GPC to eliminate most phthalates.

Table 1 reports the range of mean recoveries and standard deviations for individual compounds in a chemical class. These data show that the GPC is capable of giving good-to-excellent recovery of Appendix VIII analytes, in terms of both precision and accuracy. If there is a weakness of technique, it is with strongly polar compounds, as evidenced by the lower recoveries of phenoxyacid herbicides and aromatic amines. The data presented in this table were collected using mixtures of standards. Work is in progress to establish the recoveries of analytes spiked into hazardous waste extracts.

Table 2 summarizes some of the problems that have been observed using GPC for the cleanup of hazardous waste samples. The problems have been observed by our laboratory or by other laboratories that use GPC on a routine basis for preparing samples. The first item listed in the table deals with:

(1) Acidic/corrosive samples. It has been our experience that one sample with a high concentration of hydrochloric acid will destroy a column. Washing the sample with acetate buffer or aqueous sodium chloride reduces the acidity of the extract and reduces column damage.

(2) Glass wool in the sample is a more insidious problem; small amounts of glass fibers can severely damage or destroy the 23-port valve that allows semiautomated operation with the Autoprep GPC. This problem seems to be worse with industrial wastes, but can occur with any sample when too much (or unrinsed) glass wool is used in preparing samples.

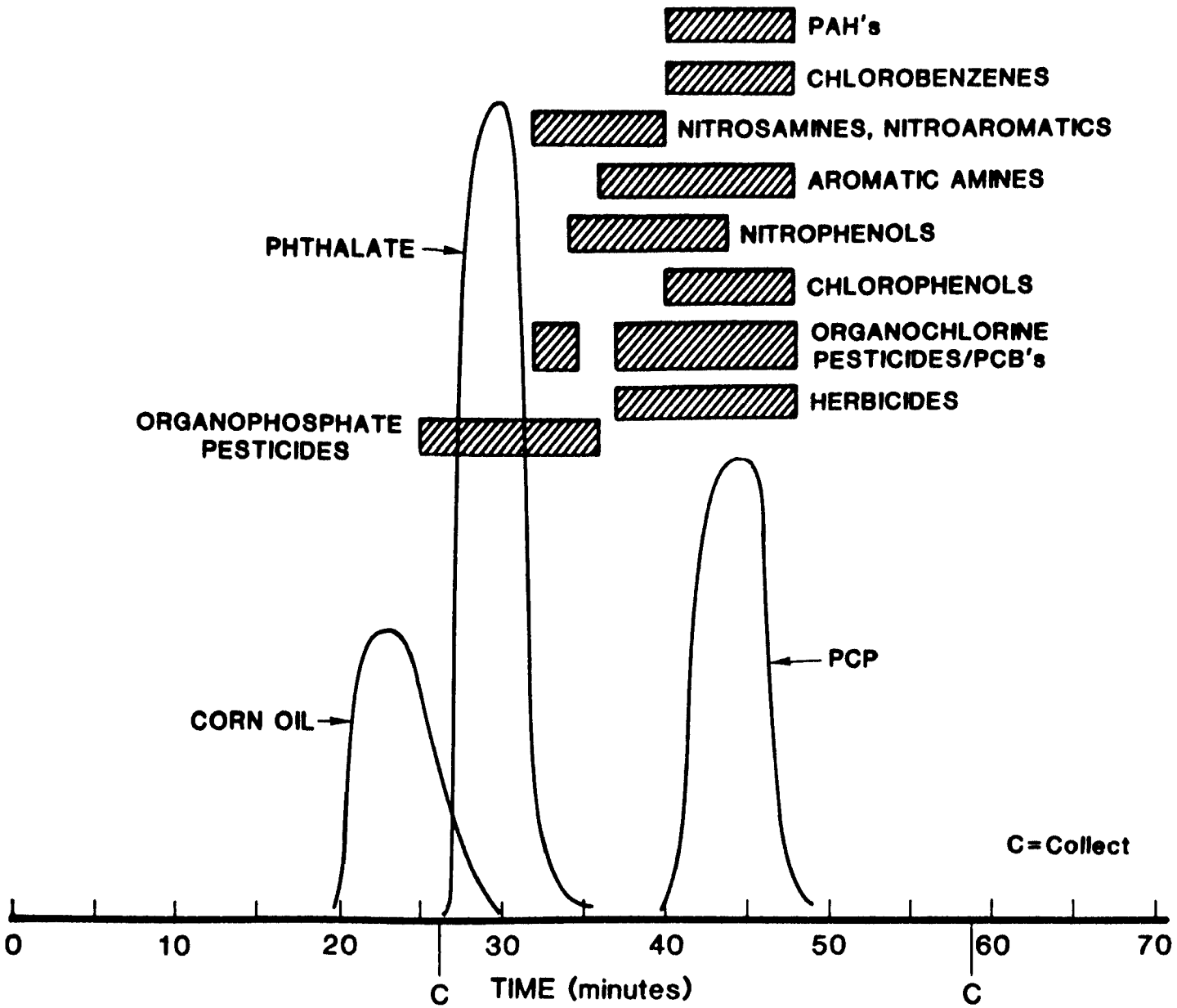

Figure 1. GPC Elution Curves

Table 1. GPC Recoveries of Standards

Compound Class	Range of Percent Recovery	Range of Standard Deviation
Organochlorine Pesticides	84-108	1-15
Phenoxyacid Herbicides	67-80	9-23
Chlorophenols	77-102	1-3
Nitrophenols	77-118	1-7
Aromatic amines	69-97	1-8
Nitroaromatics	93-101	2-4
Nitrosamines	83-99	1-13
Chlorobenzenes	81-96	1-2
Phthalates	89-104	1-4
Haloethers	76-98	1-2
PAHs	79-102	1-13

Table 2. Problems Observed with GPC Cleanup of Hazardous Waste

Cause	Symptom	Solution
Acid/Corrosive Sample	Permanently decreases PCP recovery, possibly breaks column cross-linking	Wash extract with aqueous NaCl or buffer prior to GPC
Glass Wool in the Sample	Clogs 23-port valve, may require factory repair	Reduce use of glass wool in sample preparation and rinse it thoroughly before use. Centrifuge extract with celite prior to loading the GPC.
Acetone in the Sample	Creates dead volume in the column, reducing recoveries.	Ensure that all acetone is exchanged to methylene chloride prior to loading the GPC.
Extract Precipitates in the Sample Loop	One or more loops show high-pressure problems, high carry-over between samples.	Use co-solvents for preparing GPC extracts (butyl chloride, ethyl acetate or benzene).
Column Overloading	High pressure shuts off pump, cross-contamination of samples.	Split the extract between several loops.

(3) Acetone in the sample will cause the Bio-beads to shrink, creating dead volume in the column and significantly degrading the chromatography. As acetone/methylene chloride (1:1) is a common extraction solvent for solids, it is important to emphasize the need to remove acetone prior to loading the GPC with Method 3640. Some extracts precipitate in the sample loop after loading (a sample can be held in the loop up to 24 hours in normal operation of the GPC). We have found that precipitation can be reduced or eliminated by using a mixture of methylene chloride with a second solvent to load sample extracts into the loop. Work at S-CUBED has demonstrated that ethyl acetate and butyl chloride are suitable for this application; Jean Czuczwa of Battelle has demonstrated that benzene can also be used.

(4) Finally, any chromatography system can be overloaded, including the GPC. Experienced operators learn to split extracts over several loops, based on their viscosity, nonvolatiles residue, etc. S-CUBED is gathering data on column capacity for different types of hazardous waste which will be made available in a GPC guidance document.

The solutions to GPC problems presented here have not been fully tested and should not be considered modifications to Method 3640. A proposed section on sample preparation, as well as a guidance document on applying GPC cleanup to samples, will be made available by S-CUBED to EMSL-Cincinnati and OSW for review this year.

CONCLUSION

GPC is a valuable cleanup technique that can be used for the preparation of extracts of a wide variety of hazardous waste samples. Many of the problems that have been observed with the technique seem to be caused by improper training of operators or by loading samples incompatible with the GPC. This is an interim report on a study that will develop a guidance document for laboratories that use GPC. The document will include specific requirements for sample preparation, column capacity for different types of waste, and precision and accuracy data for the recovery of analytes from the hazardous waste extracts.

NOTICE

The research described in this report has been funded by the United States Environmental Protection Agency under Contract 68-03-3375 with S-CUBED, a Division of Maxwell Laboratories, Inc., San Diego. This document has not been subject to Agency review and does not reflect its views. Mention of trade names or commercial products is for identification purposes only and does not constitute endorsement or recommendation for use.

USE OF WIDE-BORE CAPILLARY COLUMNS FOR THE GC ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

Two GC methods for environmental samples utilizing wide-bore (0.53-,mm I.D.) capillary columns have been demonstrated to be reliable, rugged techniques that provide data of good quality. One method for the analysis of 20 single component organochlorine pesticides, toxaphene, and PCBs was developed and validated for the Office of Emergency and Remedial Response (OERR). It is currently being considered for use as a Contract laboratory program (CLP) method. The second method was developed for 26 organophosphorous analytes during validation of the current SW-846 Method 8140. This study was conducted as a task from the Environmental Monitoring Systems Laboratory, at Las Vegas (EMSL-LV) for the OSW. Both methods were validated in separate single laboratory studies at S-CUBED for the analysis of water, soil, and hazardous waste samples.

These wide-bore capillary methods offer improved GC resolution over similar packed column techniques. The improved chromatography results in better separation of analytes from matrix interference, as well as more confidence in the identification of analytes by retention times. The larger capacity of wide-bore versus narrow bore capillary means that samples that would overload a 0.25 mm column give good chromatography on a 0.53 mm column. Minimal hardware changes are required to install a wide-bore capillary column in a packed column GC.

Summaries of both dual columns methods are reported along with the bias and precision of each. The improved chromatography achieved with wide-bore capillaries was demonstrated using chromatograms of mixtures of Appendix IX analytes and by comparing capillary versus packed column chromatograms of selected samples. In addition, the sample capacity of wide-bore capillary

columns, in terms of nanograms of nonvolatile residue injected, was determined for several types of environmental extracts.

INTRODUCTION

The state-of-the-art in chromatography has advanced beyond the packed column technology specified in many analytical methods for the determination of pesticides by GC and selective detectors. One major advance in GC chromatography was the development of wide-bore (0.53 mm) fused silica capillary column. These columns have efficiency and inertness comparable to narrow bore capillary columns with capacity close to packed columns. The use of these columns allows: more positive identification of method analytes based on retention time, better separation of analytes from matrix interference, and the ability to analyze more analytes in a sample that can now be done using packed column techniques. At the present time several very similar packed column GC methods have been developed for the analysis of pesticides in environmental samples. These include Methods 608, 608.1 and 617 (Method 8080) for halogenated compounds and Methods 614, 622 and 701 (Method 8140) for organophosphates. Validation studies at S-CUBED have demonstrated that it is possible to consolidate these methods into two GC procedures by the use of wide-bore capillary. This approach is particularly useful for multiresidue environmental analyses because a single extraction sample preparation procedure can be used for both analyses.

MATERIALS AND METHODS

Standards for this study were supplied by the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina, the manufacturers, or were purchased from Chem Services, Westchester, Pennsylvania. Solvents were pesticide grade or better.

Sample cleanup was achieved using an Autoprep 1002A by ABC Laboratories (Columbia, Missouri) and Diol bonded silica cleanup cartridges (Analytichem, J.T. Baker or equivalent). GC analyses were performed on HP 5880 chromatographs equipped with electron capture (EC), flame photometric (FP) or nitrogen-phosphorous (NP) detectors. Chromatographic separation was achieved using one of several 30 m wide-bore (0.53 mm I.D.) fused silica capillary columns including the DB-5, DB-608, DB-210 (J&W Scientific, Folsom, California), SPB-5 and/or SPB-608 (Supelco, Inc., Bellefonte, Pennsylvania).

The columns were plumbed into 1/4-inch packed column injector ports using a dual column injection tee kit (Supelco). The columns were plumbed into the detector ports using makeup gas adapters with argon/methane (P-5) for the ECD, nitrogen for the FPD, and helium for the NPD.

RESULTS AND DISCUSSION

The procedures for the extraction, cleanup and analysis of samples is summarized in Figure 1. The modular approach has been taken in developing these protocols. The samples are extracted using one of the four standard procedures, sonication or soxhlet for solids and liquid/liquid or separatory funnel extraction for waters. Soil extracts are then subjected to GPC cleanup using Method 3640. Although GPC retention volumes were somewhat different for the two classes of compounds (Marsden and Longbottom, this symposium), both were recovered using the standard phthalate/PCP calibration. Extracts from all samples are exchanged to hexane and cleaned up on Diol bonded silica columns. The organochlorine pesticides and PCBs are eluted from the Diol cartridge using 10 mL of 1:9 acetone in hexane. While this same solvent system elutes most organophosphates, recovery of all analytes for Method 8140 requires 10 mL of 4:6 acetone in hexane. GC analysis is accomplished on two columns for each set of analytes. The organochlorine pesticides/PCBs are determined using DB-5 and DB-608 (or SPB-5 and SPB-608) with a temperature program of:

T_i 140°, 0.5 minute	
Ramp 1,	8°/min to 180° C
Ramp 2,	3°/min to 275° C
T_F 275°, 10 minutes	

The organophosphates are determined using DB-5 (SPB-5) or DB-210 with a temperature program of:

T_i 50° C, 1 minute	
Ramp 1,	5°/min to 140° C
Hold 1, 140° for 10 minutes	
Ramp 2,	10°/min to 240° C
T_F 240° C, 10 minutes	

The recovery of the single component organochlorine pesticides are presented in Table 1. These values are comparable with what is achieved with packed column methods. Isodrin and HBB are not analytes of the CLP method are included as method surrogates which are added to every sample, blank and matrix spike QC sample in order to monitor method performance. These two

compounds are a significant improvement over dibutylchlorendate that was used previously as a surrogate in terms of both accuracy and precision of recovery as well as similarity in analytical behavior with other compounds on the CLP target compound list.

The recovery of organophosphates from solids using soxhlet extraction is presented in Table 2. These values are somewhat better than can be achieved using sonication. The values are somewhat lower and less consistent than those reported for the organochlorine pesticides, primarily because phosphate hydrolyze in environmental samples.

CONCLUSION

The use of wide-bore capillary GC analysis is a significant improvement over packed column techniques. The use of capillary analytical procedures has been validated for organochlorine and organophosphates in industrial/environmental samples.

NOTICE

The research described in this report has been funded by the United States Environmental Protection Agency as a Special Analytical Service of the CLP and under Contract 68-03-3375 with S-CUBED, a Division of Maxwell Laboratories, Inc., San Diego. This document has not been subject to Agency review and does not reflect its views. Mention of trade names or commercial products is for identification purposes only and does not constitute endorsement or recommendation for use.

Figure 1. Analytical Scheme

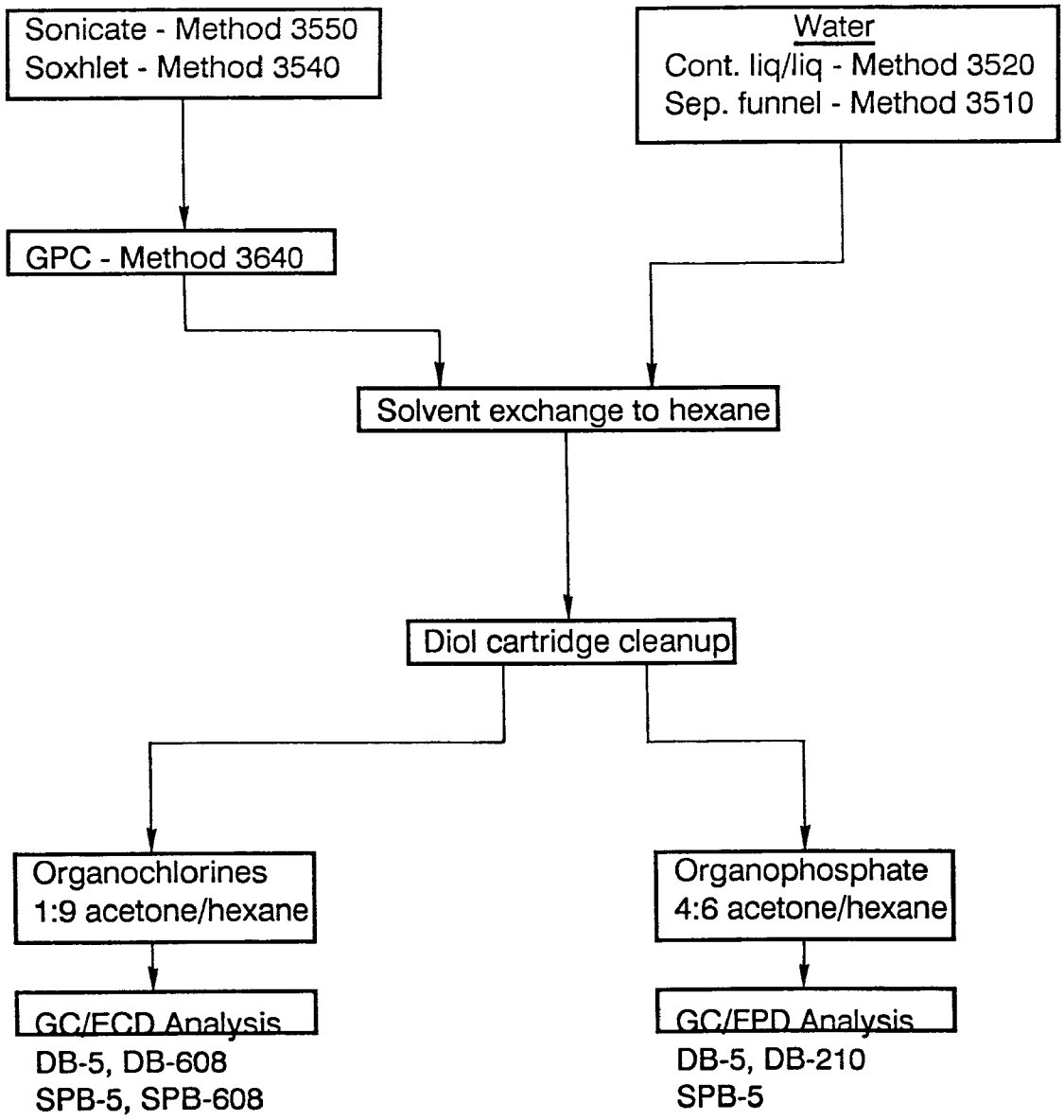

Table 1. Recovery of Single Component Organochlorine Pesticides

Compound	Matrix	
	Water	Soil
α-BHC	80	80
β-BHC	62	77
Δ-BHC	63	60
γ-BHC	87	95
Heptachlor	69	74
Aldrin	104	118
Heptachlor epoxide	74	98
Endosulfan I	101	85
Dieldrin	79	104
4,4′-DDE	73	67
Endrin	119	94

Compound	Matrix	
	Water	Soil
Endosulfan II	79	77
4,4′-DDD	87	112
Endosulfan sulfate	68	81
4,4′-DDT	91	104
4,4′-Methoxychlor	73	71
Endrin ketone	68	77
Endrin aldehyde	55	49
α-Chlordane	82	78
γ-Chlordane	85	75
Isodrin	97	94
HBB	63	69

Average of six recoveries CRQL to 120x CRQL.

Table 2. Recover of 27 Organophosphates by Soxhlet Extraction

Compound	Recovery	High
Azinphos methyl	110±6	87
Bolstar	103±15	79
Chlorpyrifos	66±17	79
Coumaphos	89±11	90
Demeton	64±6	75
Dimethoate	48±7	98
Diazinon	96±3	98
Dichlorvos	39±21	71
Disulfoton	78-	76
Ethoprop	70±7	75
EPN	93±8	82
Fensulfothion	81±18	111
Fenthion	43±7	89
Malathion	81±8	81
Merphos	53	60
Mevinphos	71	63
Monocrotophos	NR	NR
Naled	48	NR
Parathion, ethyl	80±8	80
Parathion, methyl	41±3	28
Phorate	77±6	78
Ronnel	83±12	79
Sulfotep	72±8	78
TEPP	34±33	63
Tetrachlorvinphos	81±7	83
Tokuthion	40±6	89
Trichloroate	53	53

NR = Not recovered.

A DATA BASE FOR ESTABLISHMENT OF PREANALYTICAL HOLDING TIMES

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ABSTRACT

Experiments aimed at precisely determining the preanalytical holding time for soil and water samples containing volatile organic compounds have been conducted. Three water samples, distilled water, surface water, and groundwater, as well as three soil samples, were fortified with a wide range of volatile organics. Aliquots of these samples were stored at three conditions for up to one year. Four replicates were analyzed by GC/MS at logarithmic time intervals. The objectives were to develop procedures for the preparation of the samples, to establish the holding time for each compound under each storage condition, and to develop or apply preservation techniques for the extension of the holding time.

The procedures for preparation of the water samples include the use of Tedlar bags for spiking and dispensing. The procedure gives a precision of less than 5% for almost all compounds. The procedure also allows for reproducible production of numerous samples. Soil samples were prepared by addition of ca. 0.5 mL water (containing the volatile organics) to a 1 g sample in a VOA vial. The VOA vial is then directly attached to the purge unit. The precision of this technique is dependent on the compound, but is generally about 10%. These techniques will be published and available for use in the production of performance evaluation samples.

Surprisingly, most of the volatile organic compounds are stable for at least eight weeks, and probably beyond. Those which are not stable either undergo dehydrohalogenation (tetrachloroethane to trichloroethylene) or bacterial degradation (aromatics). This can be reduced or eliminated by the use of HCl as a preservative. Data on the stability of preserved samples will be presented. Results on the stability of volatiles in soil will also be reported.

INTRODUCTION

Preanalytical holding times are defined as the time between sample collection and analysis. The degree to which a sample changes or is no longer representative is expected to be minimal during this period of time. In the absence of a definitive data base establishing this time period for individual analytes, recommendations have been made under various regulations limiting the holding times. These recommendations have been made based on available information, experience, and intuition. This paper

reports on the data base being established to support these recommendations.

For this study, two matrices have been chosen, water and soil. Analytes considered include a wide range of volatile organic compounds and a limited number of semivolatile organic compounds including four nitroorganics. Three samples have been chosen for each matrix. Distilled water (drinking water), groundwater, and surface water make up the aqueous samples, while three soils were chosen to give a variety of soil types. Storage conditions were chosen to provide an insight into the type of change which might occur to the samples under normal sampling and transportation to the laboratory, as well as storage in the laboratory prior to analysis. Thus, for each individual compound, a preanalytical holding time can be deduced based on storage condition and sample type. This information is also valuable for the development of performance evaluation samples for use by regulatory agencies and quality assurance officers.

MATERIALS AND METHODS

Materials. All analytes were obtained from either the USEPA repository (volatile organic compounds) or in the case of nitroorganics from the U. S. Army Toxic and Hazardous Materials Agency (USATHAMA) as Standard Analytical Reference Materials (SARMs). Volatile organics were obtained in solution and used as received. Nitroorganics were dissolved in ethanol prior to addition to the samples. All solvents were distilled-in-glass grade.

Methods. Multiple aliquots of volatile fortified water samples were prepared as follows. Four liters of the sample were added to a Tedlar gas sample bag (SKC, Inc. Eighty Four, Pa.). The methanol solution of the volatiles was then added to the bag and the contents mixed thoroughly. The samples were then dispensed into 40 mL vials using a length of Teflon tubing sufficient to reach the bottom of the vial. Thus, while the samples were aliquotted, no headspace was formed in the bag, and minimal mixing of the sample with air occurred during the filling of the vials.

Soil samples containing volatile organic compounds were prepared in a similar manner. The soils were all obtained after air drying. A measure of the amount of water required for saturation was then made. This amount ranged from 80-100% by weight. Approximately half of this amount was added to the soil three days prior to the addition of the volatiles. This was done in order to activate any microbial activity and to assure a steady state microbial population on Day 0. The remaining water, containing the volatile organics, was added from a Tedlar bag as described above.

For the semivolatile organic compounds, addition of the solution directly to the sample was performed. For the soils, prior incubation with water was again used. For the water samples, 1 dram vials were used, and for the soil samples, 40mL vials were used. All samples were stored immediately after preparation.

For the analysis of volatile organic compounds, standard Contract Laboratory Program (CLP) methods were employed. Gas Chromatography/Mass Spectrometry (GC/MS) was used exclusively. For the analysis of the nitroorganics, standard USATHAMA methods were employed (1, 2). These methods utilize High Performance Liquid Chromatography (HPLC) with ultraviolet absorbance detection. Water samples were analyzed directly, while soil samples were extracted in an ultrasonic bath with acetonitrile.

RESULTS AND DISCUSSION

Volatile organic compounds in water. Analysis of the three water samples was carried out at 0, 3, 7, 14, 28, 56, and 112 days. At each time point, four replicates were analyzed at two levels of fortification. The results are summarized in Tables 1-6. Each of the water samples behaves slightly differently. In the case of the distilled (drinking) water sample, almost all of the components are stable through 28 days. The exception is 1, 1, 2, 2-tetrachloroethane, which degrades to trichloroethylene. This is seen much more quickly in the case of room temperature storage than under refrigeration, although the refrigerated storage does not prevent this degradation. Otherwise, there are no significant changes through Day 28.

For the groundwater sample, no changes were noted through Day 28 which were significant, with the exception of ethyl benzene, styrene and o-xylene. This is probably due to chemical oxidation, although groundwater in general may be more likely to remain stable than other water samples. This is a conclusion which must be validated by the use of additional samples.

For the surface water sample, several significant changes were noted. The aromatic compounds benzene, toluene, ethyl benzene, xylene and styrene all appear to be degraded at rates far greater than distilled water. Again, this is probably due to oxidation of the compounds and subsequent degradation. This oxidation may either be due to microbial or chemical reactions, although microbial action is more likely to be the cause in this case.

In general, it is perhaps surprising to note that there appears to be little or no loss of these compounds due to volatilization, at least at refrigerator temperature. This is supported by the fact that even the gases (bromomethane, chloroethane) are not lost at rates greater than the less volatile compounds. This is an

indication that the containerization of water samples for volatile organic analysis using septum capped vials with no headspace is sufficient as a sampling/storage technique.

All of the degradation which occurred during the original study was due either to dehydrohalogenation or to microbial oxidation. Therefore, the addition of HCl to the samples was considered to be an appropriate preservation technique for volatile organics in general. This has been suggested in the past, particularly for drinking water. A second experiment was performed in order to evaluate the ability of acid preservation to extend the holding time of volatile organics in these samples. The study was repeated, at one concentration level, under refrigeration, at day 0, 14, 28, and 56 for the three samples. Data for the distilled water and groundwater through Day 28 are presented in Table 7. The extent of dehydrohalogenation of tetrachloroethane has clearly been reduced, while no significant deleterious effects of the HCl were noted. For the groundwater sample, the data indicate a significant reduction in the rate of degradation of the aromatics. For both samples, higher levels of the early eluting components were found on Day 0 than either Day 14 or 28. We believe that this is due to a bias in the internal standard rather than to degradation, since the target level in this case was 50 μg/L, and no change was noted from Day 14 to Day 28. The data for the surface water are not yet available, although if the data support the use of HCl as a preservative for volatile organics, it would appear that the preanalytical holding time for these compounds could be increased to 28 days. This would have a dramatic impact on the ability of the contract laboratories to handle large numbers of analyses without exceeding the holding times.

Volatile organic compounds in soil. For the purpose of establishing the holding times of volatile organic compounds in soil, a preliminary experiment was carried out in order to determine the proper containers for longer term storage. Three types of bottles were used: 40 mL septum-capped vials, 120 mL septum-capped vials (Shamrock Glass), and 120 mL wide-mouth vials with Teflon cap liners (I-Chem). These containers were chosen on the basis of current use in the sampling of soils for volatile organic compounds. Replicate samples were prepared for each type of vial containing 100 μg/kg of a range of volatiles. The samples were analyzed in triplicate at day 1, 3, and 8. Storage was at refrigerator temperature. In the case of the 40 mL vials, the entire 5 g sample was analyzed using a modified purge and trap device capable of accepting the vial directly. The larger vials were analyzed after weighing a 5 g aliquot into the purging device. The results of this study are given in Tables 8-10.

The results indicate that for all of the vials, recovery was not quantitative even on Day 1. Not surprisingly, recovery dropped off

with increasing molecular weight in all cases. The best recovery was seen using the 40 mL vials. Recovery was essentially similar with the two larger vials, and lower than the 40 mL vials. The more volatile components were affected more by the transfer and weighing steps than the later eluting components. It is likely that recovery can be improved by the heating of the purging device, although this technique has problems as well. However, the losses which apparently occur in the weighing and transfer steps are not easily eliminated. These results recommend the use of preweighed vials with a know mass of soil added, and no further operations on the sample before purging.

With respect to the holding times, all samples showed degradation, even on Day 3, and dramatic losses were seen on Day 8. The 1, 2-dichloropropenes degraded rapidly, and had disappeared by Day 8. Many of the compounds showed significant deterioration in all containers by Day 8. The losses are attributable in part to microbial degradation, but are probably mostly due to volatilization. In all cases, headspace will be present in a vial containing soil. While the volatiles come to equilibrium rather quickly in a sealed container, the caps are also permeable. Therefore, gas exchange will occur between the headspace and the outside of the container, causing the loss of volatile organics. This effect is not seen when using the vials for water samples, since there is no headspace, and diffusion is five orders of magnitude slower in water than in air. A further indication of the diffusion through the vial cap is the fact that methylene chloride, not present in the original samples, had accumulated in the samples by Day 8. This effect was again most dramatic with the wide mouth bottles. These bottle caps actually tend to loosen as the temperature is reduced in the refrigerator. These particular samples were stored in a refrigerator containing methylene chloride solutions so that the effects seen here are not unexpected. It appears that additional development will be required in order to assure that volatile organic analysis of soil samples is reliable and meaningful.

The data set for the explosives in water is also complete, although this data will only be summarized here. Aromatic compounds degrade faster than aliphatics, refrigerated storage is essential for maintaining these compounds, and only slight degradation is noted for any of the compounds at refrigerator temperature after 28 days. Here again, preservation with HCl may extend the holding time well beyond 28 days.

An additional feature of this work is the ability to evaluate laboratory performance over time with respect to the analysis of these compound/matrix combinations. Initially, it was thought that when lowered concentrations of a particular analyte were noted, the holding time would be declared to have been exceeded. However, the

combination of slight changes in the internal standard or calibration with normal day to day variability in the methods, can cause erroneous assumptions about the stability of the compounds. In many cases, when one compound is found to have a lowered concentration, all of the compounds integrated against that particular internal standard are lowered by about the same amount. These same concentrations may then be elevated at the next time interval. It now appears that the best approach to determining the holding times from a statistical standpoint may be to compare the found concentrations with the known starting concentrations, using all of the replicates to develop a precision statement on the method. This approach is currently being taken.

Table 1. Volatile organics in water, low level in distilled water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	53	49	53	57
1,1-Dichloroethene	58	48	58	59
1,1-Dichloroethane	64	57	64	53
Chloroform	60	53	60	53
Carbon tetrachloride	51	50	51	53
1,2-Dichloropropane	50	49	50	47
Trichloroethene	66	66	66	91
Benzene	50	46	50	45
1,1,2-Trichloroethane	47	49	47	38
Bromoform	34	45	34	43
1,1,2,2-Tetrachloroethane	42	33	42	0
Tetrachloroethene	50	48	50	44
Toluene	50	50	50	49
Chlorobenzene	52	53	52	54
Ethylbenzene	49	49	49	48
Styrene	52	46	52	47
o-xylene	54	49	54	50

Table 2. Volatile organics in water, high level in distilled water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	464	562	464	533
1,1-Dichloroethene	473	502	473	616
1,1-Dichloroethane	515	596	515	552
Chloroform	489	533	489	487
Carbon tetrachloride	446	481	446	453
1,2-Dichloropropane	421	504	421	481
Trichloroethene	287	710	287	663
Benzene	400	455	400	432
1,1,2-Trichloroethane	440	550	440	281
Bromoform	619	678	619	631
1,1,2,2-Tetrachloroethane	531	85	531	2
Tetrachloroethene	370	371	370	294
Toluene	383	440	383	405
Chlorobenzene	382	416	382	387
Ethylbenzene	378	376	378	340
Styrene	394	361	394	341
o-xylene	398	411	398	379

Table 3. Volatile organics in water, low level in ground water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	66	46	66	44
1,1-Dichloroethene	61	49	61	50
1,1-Dichloroethane	66	61	66	56
Chloroform	61	64	61	59
Carbon tetrachloride	56	50	56	47
1,2-Dichloropropane	34	61	34	56
Trichloroethene	108	90	108	92
Benzene	55	50	55	47
1,1,2-Trichloroethane	55	62	55	59
Bromoform	50	56	50	46
1,1,2,2-Tetrachloroethane	48	58	48	58
Tetrachloroethene	53	69	53	67
Toluene	54	52	54	44
Chlorobenzene	55	49	55	42
Ethylbenzene	51	24	51	14
Styrene	63	12	63	2
o-xylene	53	12	53	12

Table 4. Volatile organics in water, high level in ground water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	396	474	396	508
1,1-Dichloroethene	383	667	383	617
1,1-Dichloroethane	389	727	389	748
Chloroform	385	705	385	725
Carbon tetrachloride	551	763	551	684
1,2-Dichloropropane	590	612	590	698
Trichloroethene	570	631	570	730
Benzene	570	560	570	585
1,1,2-Trichloroethane	584	647	584	808
Bromoform	583	756	583	923
1,1,2,2-Tetrachloroethane	544	1190	544	980
Tetrachloroethene	531	577	531	521
Toluene	550	605	550	633
Chlorobenzene	547	492	547	526
Ethylbenzene	532	312	532	285
Styrene	535	187	535	188
o-xylene	531	173	531	169

Table 5. Volatile organics in water, low level in surface water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	69	62	69	62
1,1-Dichloroethene	53	53	53	50
1,1-Dichloroethane	64	57	64	54
Chloroform	69	62	69	59
Carbon tetrachloride	47	50	47	30
1,2-Dichloropropane	55	51	55	53
Trichloroethene	60	56	60	70
Benzene	56	50	56	49
1,1,2-Trichloroethane	59	53	59	55
Bromoform	55	48	55	45
1,1,2,2-Tetrachloroethane	54	52	54	31
Tetrachloroethene	57	52	57	50
Toluene	54	48	54	45
Chlorobenzene	56	48	56	44
Ethylbenzene	52	5	52	29
Styrene	58	0	58	15
o-xylene	58	47	58	43

Table 6. Volatile organics in water, high level in surface water

Name	Storage cond. 1 (4°C) Day 0	Storage cond. 1 (4°C) Day 28	Storage Cond. 2 (25°C) Day 0	Storage Cond. 2 (25°C) Day 28
Methylene chloride	556	603	556	509
1,1-Dichloroethene	420	543	420	419
1,1-Dichloroethane	608	650	608	545
Chloroform	586	608	586	508
Carbon tetrachloride	690	542	690	409
1,2-Dichloropropane	560	569	560	528
Trichloroethene	507	566	507	531
Benzene	480	555	480	482
1,1,2-Trichloroethane	651	622	651	609
Bromoform	775	739	775	701
1,1,2,2-Tetrachloroethane	818	781	818	537
Tetrachloroethene	416	438	416	295
Toluene	473	487	473	404
Chlorobenzene	488	483	488	394
Ethylbenzene	427	260	427	299
Styrene	495	416	495	334
o-xylene	483	475	483	383

Table 7. Volatile organics in HCL-treated waters

	Water 1 (distilled water)			Water 2 (ground water)		
	Day 0	Day 14	Day 28	Day 0	Day 14	Day 28
Bromomethane	65 ± 1	47 ± 3	49 ± 1	66 ± 2	47 ± 1	48 ± 2
Chloroethane	78 ± 1	59 ± 2	63 ± 3	78 ± 2	58 ± 3	66 ± 2
1,1-Dichloroethene	71 ± 1	58 ± 2	58 ± 1	71 ± 3	50 ± 5	58 ± 2
1,1-Dichloroethane	77 ± 1	64 ± 2	63 ± 2	74 ± 1	64 ± 2	64 ± 1
Chloroform	70 ± 1	57 ± 2	60 ± 2	69 ± 2	58 ± 2	60 ± 1
Carbon tetrachloride	63 ± 1	63 ± 1	59 ± 2	62 ± 1	62 ± 3	59 ± 3
1,2-Dichloropropane	62 ± 1	59 ± 2	53 ± 1	62 ± 1	58 ± 1	54 ± 1
Trichloroethene	59 ± 1	53 ± 2	50 ± 0	62 ± 1	54 ± 1	53 ± 1
Benzene	60 ± 2	53 ± 2	53 ± 1	57 ± 1	49 ± 2	50 ± 1
1,1,2-Trichloroethane	62 ± 3	60 ± 3	59 ± 2	63 ± 3	61 ± 3	61 ± 0
Bromoform	54 ± 2	56 ± 2	59 ± 2	55 ± 2	58 ± 2	61 ± 2
1,1,2,2-Tetrachloroethane	61 ± 4	61 ± 4	59 ± 1	64 ± 2	63 ± 1	61 ± 2
Tetrachloroethene	57 ± 1	49 ± 1	46 ± 1	57 ± 1	49 ± 1	45 ± 0
Toluene	57 ± 1	50 ± 1	49 ± 1	55 ± 1	48 ± 1	49 ± 1
Chlorobenzene	54 ± 0	50 ± 1	49 ± 1	55 ± 1	51 ± 1	50 ± 1
Ethylbenzene	54 ± 1	48 ± 1	46 ± 1	51 ± 1	45 ± 1	46 ± 0
Styrene	44 ± 1	39 ± 2	36 ± 2	41 ± 1	35 ± 1	32 ± 0
o-xylene	54 ± 1	48 ± 2	45 ± 1	51 ± 1	46 ± 1	45 ± 0

Table 8. Volatiles in soil (storage in 40 mL septum-capped vials). n = 3, CONC = µg/kg.

Number	Compound	Day 1		Day 3		Day 8	
		Conc.	Std dev.	Conc.	Std dev.	Conc.	Std dev.
1	t-1,2-Dichloroethene	87.39	1.64	86.94	4.37	54.42	9.99
2	1,2-Dichloroethane	67.54	22.69	86.68	5.72	64.65	5.83
3	1,1,1-Trichloroethane	81.84	3.32	81.25	9.92	67.89	13.07
4	Bromodichloromethane	64.33	6.82	67.17	6.67	58.99	5.19
5	t-1,3-Dichloropropene	44.21	1.07	21.73	11.01	1.26	0.61
6	c-1,3-Dichloropropene	53.34	0.66	19.43	12.00	1.48	1.00
7	Benzene	78.38	0.41	82.40	4.01	58.08	7.34
8	Bromoform	42.81	3.98	41.68	6.44	29.87	1.25
9	1,1,2,2-Tetrachloroethane	49.72	7.26	57.55	8.16	44.86	2.51
10	Toluene	65.11	8.95	74.15	2.62	45.31	5.83
11	Ethyl benzene	57.22	2.40	55.42	1.22	32.13	8.06
12	Methylene chloride*	4.47	0.03	6.97	0.55	25.06	0.39
13	Acetone**	189.42	47.65	137.99	21.69	77.95	10.70

*Not added to soil.

**Not added, but found in blank.

Table 9. Volatiles in soil (storage in wide-mouth bottles). n = 3, CONC = μg/kg.

Number	Compound	Day 1		Day 3		Day 8	
		Conc.	Std dev.	Conc.	Std dev.	Conc.	Std dev.
1	t-1,2-Dichloroethene	256.43	409.45	12.82	7.31	2.97	1.93
2	1,2-Dichloroethane	54.57	5.13	45.23	11.18	24.26	10.89
3	1,1,1-Trichloroethane	14.00	2.54	10.17	4.61	2.54	1.60
4	Bromodichloromethane	39.81	4.41	29.39	9.94	13.74	7.41
5	t-1,3-Dichloropropene	26.78	1.96	17.68	6.67	2.34	0.56
6	c-1,3-Dichloropropene	37.76	1.92	24.30	7.45	1.04	0.23
7	Benzene	28.92	5.60	21.29	7.86	15.59	1.45
8	Bromoform	39.33	0.16	37.28	3.64	17.98	3.78
9	1,1,2,2-Tetrachloroethane	53.55	0.78	61.02	3.91	43.68	3.63
10	Toluene	27.78	3.40	29.21	5.86	27.65	3.88
11	Ethyl benzene	23.05	2.41	22.58	6.24	10.62	3.22
12	Methylene chloride*	16.15	19.76	87.44	67.32	442.77	199.70
13	Acetone**	115.63	25.43	149.06	44.98	165.14	30.20

*Not added to soil.

**Not added, but found in blank.

Table 10. Volatiles in soil (storage in 120 mL septum-capped vials). n = 3, CONC = μg/kg.

Number	Compound	Day 1		Day 3		Day 8	
		Conc.	Std dev.	Conc.	Std dev.	Conc.	n = 1
1	t-1,2-Dichloroethene	21.27	0.32	26.92	0.73	17.56	
2	1,2-Dichloroethane	54.98	4.62	68.09	9.10	49.19	
3	1,1,1-Trichloroethane	14.21	0.28	17.63	0.43	16.36	
4	Bromodichloromethane	39.68	2.49	44.60	2.73	39.56	
5	t-1,3-Dichloropropene	28.29	3.15	24.62	1.53	1.99	
6	c-1,3-Dichloropropene	39.58	3.07	30.70	3.52	0.56	
7	Benzene	30.49	1.35	35.65	0.57	27.43	
8	Bromoform	40.51	2.48	40.73	1.54	29.22	
9	1,1,2,2-Tetrachloroethane	54.98	2.19	60.35	0.75	56.01	
10	Toluene	72.93	5.61	38.34	2.57	28.18	
11	Ethyl benzene	49.76	2.83	29.59	2.46	21.65	
12	Methylene chloride*	5.76	1.86	4.12	0.32	18.04	
13	Acetone**	122.82	24.30	116.22	11.93	47.90	

*Not added to soil.

**Not added, but found in blank.

THE DETERMINATION OF CHLOROPHENOXYACID HERBICIDES BY LIQUID CHROMATOGRAPHY USING CARBON-14 TRACERS

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ABSTRACT

The determination of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4,5-trichloro) phenoxypropionic acid (Silvex) in both solid and liquid environmental samples by several liquid chromatographic approaches has been studied. The extractive recovery was evaluated for both a soil matrix and water using Carbon-14 tracers of both 2,4-D and Silvex. For water, the extractive recoveries were evaluated as a function of both pH and ionic strength. Recoveries from the soil matrix were evaluated for both Soxhlet extraction and ultrasonic extraction. This evaluation of the sample preparation methods with the assistance of Carbon-14 tracers allowed the distribution of each herbicide to be estimated in all phases of the procedure.

Several approaches to the liquid chromatographic determination of these herbicides were studied. One approach employed a heavily loaded (18% carbon by weight), completely endcapped C18 reversed phase column eluted with an aqueous solution of 30% (v/v) acetonitrile that contained 0.001 M concentration of a pH 4.6 acetate buffer. The effluent from this column was monitored at 280 nm. The minimum amount detected by this approach is 100 ng of either Silvex or 2,4-D in the injected sample. A second approach avoids the use of a buffered eluent by employing a very high performance reversed phase column and an aqueous methanol (27% v/v) eluent. This second column has been monitored at multiple wavelengths with a diode array detector. The sensitivity of detection can be greatly increased at wavelengths below 240 nm; however, very short wavelengths (<230 nm) may not be practical for real environmental samples.

There will be some discussion of interferences and sample clean-up procedures. However, an important advantage of these methods is that most organic compounds that are either higher in molecular weight or less polar than the herbicide acids will be retained longer by the reversed phase column.

NOVEL EXTRACTION SOLVENTS FOR ENVIRONMENTAL SAMPLES

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ABSTRACT

Extraction of organic compounds from environmental matrices occurs when the solvent is brought into contact with the sample. If the analyte of interest has a higher affinity for the extracting solvent, it will partition into the solvent. The percent of analyte extracted into the solvent phase (%E) can be calculated by

$$\%E = \frac{100\ K_D}{K_D + \frac{W_s}{W_o}}$$

where K_D is the distribution coefficient of an analyte between the solvent and the martrix and W_s and W_o are weights of the sample and solvent, respectively. From this equation, it is obvious that high analyte recoveries will depend upon either a large distribution coefficient or a small sample:solvent ratio.

The choice of solvent is critical to liquid-liquid extraction (LLE) procedures. As discussed above, the solvent must have a large distribution coefficient for the compounds of interest. Extensive listings of partition coefficients from water are available for various solvent systems. Along with having a high extraction efficiency for the analytes of interst, the extracting solvent should be immiscible with the sample, not contain contaminants which might compromise subsequent analysis, be chemically inert, be specific for the compounds of interest, and be amenable to the analytical method of choice. Since solvent evaporation may be employed to further concentrate sample extracts, solvents with low boiling points are preferred.

Solvents such as benzene and chloroform were used extensively in the past, but now have limited applicability because they have been identified as carcinogens or cocarcinogens. Methylene chloride has become the solvent of choice for most procedures. Unfortunately, methylene chloride is not a universal solvent and does not have high distribution coefficients for many polar compounds. Alternate solvents and solvent systems have been tested for this purpose. Methyl-t-butyl ether has been demonstrated as a good solvent choice for phenols and organic acids. Data for a variety of solvent systems will be presented.

Although part of the research described was funded wholly or in part by the U.S. Environmental Protection Agency through Contract Numbers 68-03-2704 and 68-03-2845, it has not been subjected to the Agency's required peer and administrative review and does not necessarily reflect the views of the EPA, and no official endorsement should be inferred.

AN EXPERT SYSTEM TO AID IN USING USING SW-846

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ABSTRACT

An automated system is being developed to aid in the use of the manual "Test Methods for Evaluating Solid Waste" (SW-846). This system will assist users in choosing the appropriate methods from SW-846 to meet RCRA regulatory requirements, such as determining if a waste is hazardous, analyzing a sample for specific compounds, analysis of ground water monitoring samples, analyzing used oil to be sold for burning in non-industrial boilers, etc.

This system will provide a basis for the interfacing of analytical requirements, techniques and methods with regulatory requirements and guidance to enable the regulated community to better understand the analytical requirements and more easily interpret analytical data. Additional benefits of the system include obtaining a greater degree of uniformity in the selection of methods for similar tasks, and making the quality control requirements more accessible to the laboratory chemist and the regulated community.

So far, a demonstration system has been developed. This demonstration system handles only one of the above types of problems: analyzing used oil to be sold for burning in non-industrial burners.

The user interacts with the system through a sequence of menus. As the user answers the questions, the system provides guidance in understanding the applicable regulations and in understanding the tradeoffs involved in the various decisions he must make about testing his used oil.

The system is designed to run on an IBM PC/AT and is written in ARITY/PROLOG.

LIQUID CHROMATOGRAPHY MASS SPECTROMETRY: AN EVOLVING TECHNIQUE

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ABSTRACT

Historically the U.S. Environmental Protection Agency has utilized GC/MS as the primary technique for environmental analyses. Clearly, GC/MS methods are limited to those analytes that are both volatile and chromatographable. These requirements can severely hinder or make MS environmental characterization of compounds of regulatory or other interest either impossible or less than ideal. Because accurate regulatory work or accurate characterization of environmental phenomena can require characterization of labile organic compounds or both labile and non-chromatographable pollutants, GC/MS can give only a partial view of the analytes being characterized.

Liquid chromatography/mass spectrometry offers one of the obvious solutions to this dilemma. Since the mid-seventies, various LC/MS interface designs have been proposed and tested which have given varying degrees of success. The technology has not been widely disseminated or accepted in the environmental monitoring community. The purpose of this article is to discuss the potential of newer LC/MS technology called, generically, particle beam liquid chromatography-mass spectrometry (PB/LC/MS), to show why such technology has the potential to enhance mass spectral based environmental monitoring and to indicate where the implementation of such technology could help fulfill scientific and regulatory environmental needs.

INTRODUCTION

Particle beam liquid (PB/LC/MS) technology was introduced by Willoughby and Browner (1). More recent efforts, Apffel and Willoughby (2,3) have demonstrated significant important development. These include production of NIH/EPA library matchable electron impact mass spectra, and sensitivity in the nanogram range for a wide range of non-volatile and volatile (or gas chromatographable) analytes.

These properties coupled with the ease of interfacing PB/LC/MS technology directly to quadruple mass spectrometers routinely used for GS/MS analysis with little or no ion source modification will result in rapid, cost effective deployment of such technology. Although the practicality of this concept requires significant further rigorous testing, it appears that such is the case.

The importance of a rugged, routine LC/MS technique for environmental analytical organic (and potentially inorganic and/or oreganometallic) chemistry is of practical significance to environmental, biomedical, defense and drug studies related to characterization of environmental contaminants, drug metabolites, characterization of chemical deterent agents, and analysis of explosives. PB/LC/MS techniques also have application in routine targeted compound analysis scenarios related to analysis of U.S. EPA RCRA Appendix VIII and IX lists, and the priority pollutants. All of these applications have in common the analysis of either labile or labile and non-chromatographable analytes to characterize the phenomena or interest. The routine availability of such technology could, therefore, have a major impact in the analytical chemistry of environmental contaminants, and eventually reorient how such characterizations are performed.

The purpose of this article is to briefly show recent applications of PB/LC/MS to the appendix VIII and IX compound list and to discuss the implications of such results for environmental testing in general. While it is clear that such technology is still evolving, it appears the refinement of LC/MS interfaces could be as significant to the dissemination of LC/MS technology as the glass jet separator was to the routine application of GC/MS technologies. Because the availability of routine electron impact LC/MS technology has the potential to analyze both non-volatile or labile analytes in one MS experiment, LC/MS technologies could assist with providing a more accurate approach to characterization of environmental phenomena, hazardous wastes, hazardous waste sites and other chemical mixtures or processes.

EXPERIMENTAL

All data reported were provided by R. C. Willoughby, Pittsburgh, Pennsylvania, and A. D. Sauter, (under contract to the U.S. EPA), or J. A. Apffel, Hewlett Packard in Palo Alto, California.

Experimental Parameters

Consisted of a 100 X 2.1mm 3um Spherisorb ODS2 with a mobile phase of A(.01M NH_4OAC) and B(Acetonitrile) using a 0-90% B/5 min gradient at a .4 ml/min flow rate. The MAGIC helium flow rate was 1.2L/min with the desolution chamber operated at 40°C. The MS (Hewlett Packard) was scanned at 50-500 amu/sec with the source temperature at 330°C. The quantity injected was 100ng/component.

The Thermabeam experiments utilized a 15cm X 2.0mm C18 reverse phase HPLC column operated at ambient temperatures. A gradient of 20% .1M NH_4OAC to 90% methanol at 4%/minate at a flow rate of .5ml/min was utilized. The MS (Model EL750) was operated at 70eV, scanning the mass range 70-550 amu with an ion source temperature of 200-350°C.

Thermospray experiments utilized a 25cm X 4.6mm C18 reverse phase column operated at ambient temperature. A solvent gradient of 10% .1M NH_4OAC to 80% methanol at 2%/min with a flow rate of 2.ml/min was utilized. The MS (Model El-1000) was scanned from 70-550 amu.

RESULTS AND DISCUSSION

The thermospray technique employs a thermal nebulizer. Although there are several different designs offered by instrument manufacturers, they all have in common the entertainment of ions formed via charge transfer from an ionic buffer. There have been variations of the thermospray technique which allow electron ionization as well as discharge ionization. Typically the technique has applicability to those compounds with proton affinities greater than ammonia derived from the ammonium acetate buffer commonly employed.

Both Thermabeam and MAGIC use a nebulization technique, a thermospray in the former and a gas nebulizer in the latter. Ionization in both techniques occurs after desolution of the analyte followed by electron ionization. A nebulizing interface has also been used in conjunction with an atmospheric pressure ionizer using a corona discharge as the ionization mechanism (4).

It is not the purpose or intent of this article to make judgment on the relative merits of these approaches, rather, it is our purpose to demonstrate exciting recent results acquired by two separate approaches and to demonstrate where such technology or related technology is required to ensure the fundamental application to the characterization of hazardous wastes, hazardous waste sites and other environmental media. Obviously, such technology has apparent merit to many aspects of analytical organic (and potentially inorganic) chemistry, as well.

Because PB/LC/MS interfaces eliminate most of the LC solvent or sample only a small portion of the solvent, subsequent ionization of the analyte in the source can take place at pressures conducive to the generation and observation electron ionization mass spectra. In Figure 1 we show 70eV electron ionization mass spectra for the selected Appendix IX compounds, warfarin, thiram, and dichlorobenzidine, and the RIC for several other analytes, all generated with the MAGIC interface. In Figure 2 the spectra of propylthiouracil, 2,4-D and brucine as well as the RIC for other selected Appendix VIII compounds were generated with the Thermabeam interface. We draw attention to the chemical and structural diversity of the analytes for which apparent 70eV electron ionization mass spectra have been generated. Comparison of mass spectra with the NIH/EPA library is shown for selected analytes, Figure 3, as well as the difference spectra. Without more detailed

statistical analysis, it is apparent that particle beam technologies show good fragmentation spectra of numerous analytes.

For comparison, we show Thermospray mass spectra acquired in a recent U.S. EPA funded project (5), Figure 4. This study performed a very preliminary comparison of the particle beam LC/MS technique and thermospray analysis of Appendix VIII listed analytes. The difference in information content is apparent between the two techniques, compare Figures 2 and 4.

The difference between thermospray and particle beam LC/MS technology can be seen in application to the Appendix VIII listed analyte, auramine-0. In Figure 5, we show a 3-dimensional plot of a particle beam experiment with reverse phase gradient elution LC conditions. In this experiment, auramine-0 was identified at nanogram levels, but another structurally related analyte was also identified. Auramine-0 can undergo hydrolysis to the ketone, producing a species whose molecular weight is increased one amu compared to auramine-0 268 vs. 267. The thermospray spectra of a freshly prepared solution of auramine-0, Figure 6, is dominated by the MH^+ species at m/z 268. While auramine-0 and the hydrolysis produced auramine ketone were separated under the LC analysis conditions figures, and hence could be detected in one LC/MS assay, it is clear that fragmentation information is required to unambiguously identify the two species when the occurrence of the latter was unexpected. This example shows an important property of PB/LC/MS and the value of electron ionization mass spectra compared to techniques that generate pseudo molecular ion information. Due to the lack of structural information contained in thermospray spectra, collision induced spectra have proven valuable (6). A comparison of thermospray and PB/LC/MS techniques must consider other sensitivity benefits that thermospray ionization possesses. It is clear that the work to date is preliminary and requires further in-depth examination and comparison.

One of the most appealing aspects of environmental LC/MS is the possibility of making injection volumes a factor of 100 to 1,000 times greater than commonly employed in FSCC-GC/MS. Consequently, given the nanogram range for full scan electron ionization PB/LC/MS spectra, the capability for large injection volumes, and other analytical options (e.g., SIM or NCI), the issue of sensitivity does not appear to be the limiting factor. Clearly, though, significantly more data are required to evaluate the relative merits of particle beam, thermospray and other LC/MS techniques as applied to environmental problems or regulatory or more fundamental interest. Nevertheless, these data show considerable promise.

A primary prerequisite for the development of powerful LC/MS methods is the capability to be utilized in the reverse phase gradient elution LC domain. In Figures 1 and 2, we show gradient elution

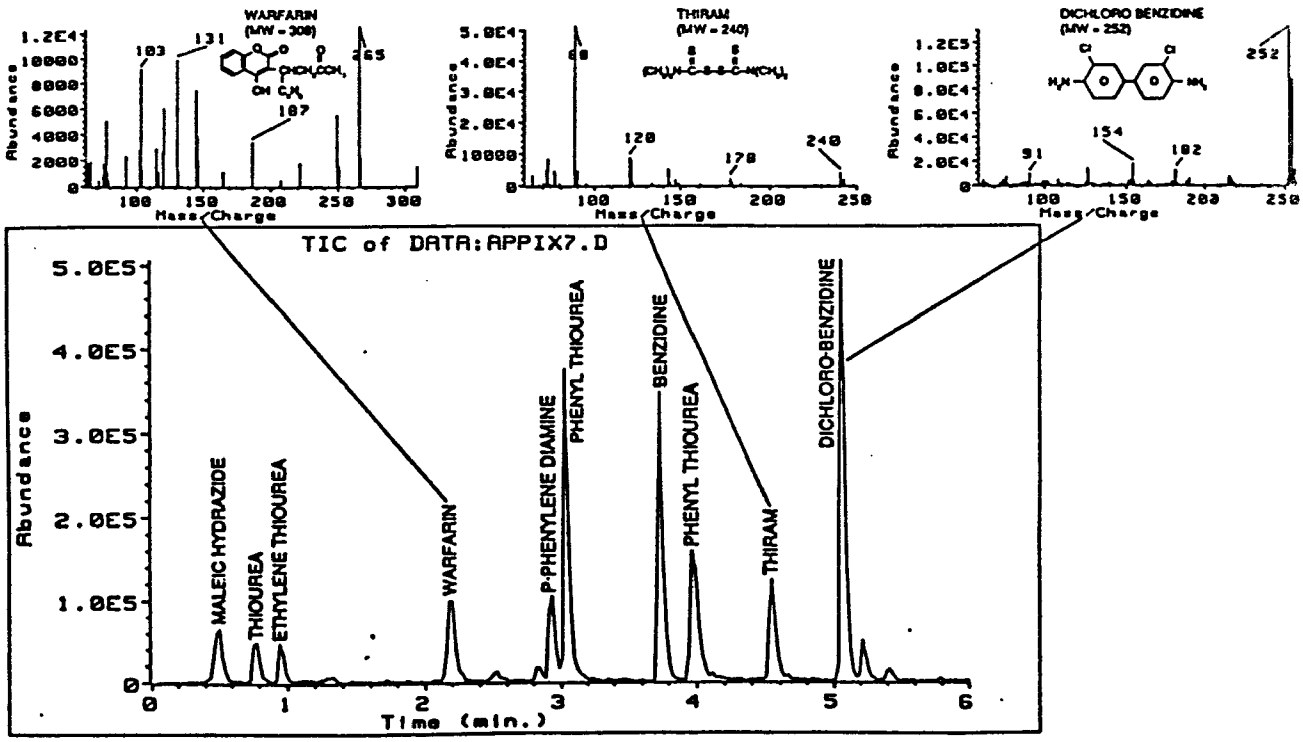

Figure 1. MAGIC spectra of selected Appendix IX analytes

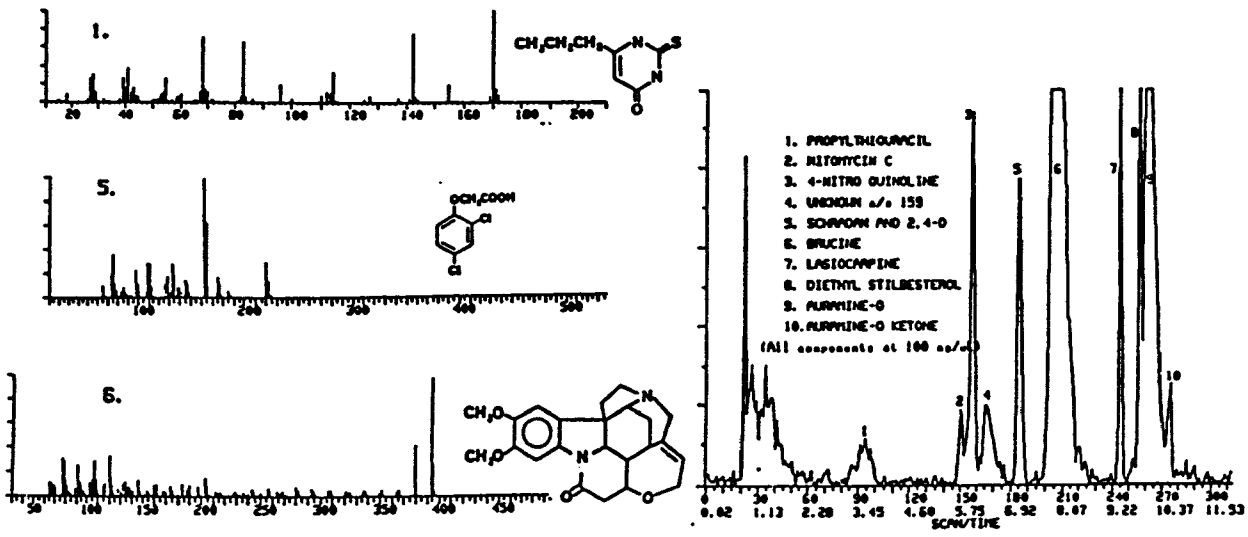

Figure 2. Thermabeam spectra of selected Appendix VIII analytes.

PB/LC/MS data under the conditions noted. The observed peak shape with detection limits in the nanogram range represent important observations, as these data show good response and other analytical characteristics for a diverse range of chemical species.

CONCLUSION

Having shown the ability to generate 70eV/EI mass spectra for a wide range of diverse species using PB/LC/MS and the potential of two different PB/LC/MS interfaces to employ gradient LC conditions, the issues of sensitivity and ruggedness become important as do the practicality of PB/LC/MS.

As discussed previously, and as shown in a recent study funded by the U.S. EPA Office of Solid Waste (5), response characteristics appear to allow the response factor equation to be employed. The study used a prototype PB/LC interface and it yielded nanogram sensitivities for many Appendix VIII listed analytes which could not be done by GC/MS techniques. In this work, ion current was found to be highly correlated with injected weight even when internal standards were not employed. Many of these experiments, however, were conducted under flow injection analysis conditions. In the referenced study, and in subsequent recent work, it appears that for a wide variety of analytes, low nanogram sensitivities are possible using electron impact conditions. We would note, however, that the lack of "real-world" data on actual samples is due to a variety of factors foremost of which is the study of the rapid developing technology. Nevertheless, data does exist which suggest that PB/LC/MS is useful and powerful for the analysis of real world samples. However, we are cautious about stating its useability, although the data of Willoughby suggests this technology represents a major advance in the state-of-the-art of LC/MS and will have significant impact in characterization or non-chromatographable analytes of regulatory interest.

Given the previous data and its qualification it is instructive to consider exactly when, how and why such technology is important in environmental chemistry. It is also of importance to identify potential problems and limitations. In terms of application to existing programs in the RCRA and Superfund area, it is known that such technology is important to accurately characterize hazardous waste or hazardous waste sites at which labile compounds or their degradation products are present. Obviously, such applications could include what has been termed "exotic" RCRA Appendix VIII compounds. In the Superfund area, the technique can have application to the characterization of hazardous waste sites "known" to contain nonvolatile, (i.e., non-gas chromatographable analytes) species at high concentration levels, but that are not well characterized due to current measurement methodology. Also, application too difficult to analyze priority pollutants is expected

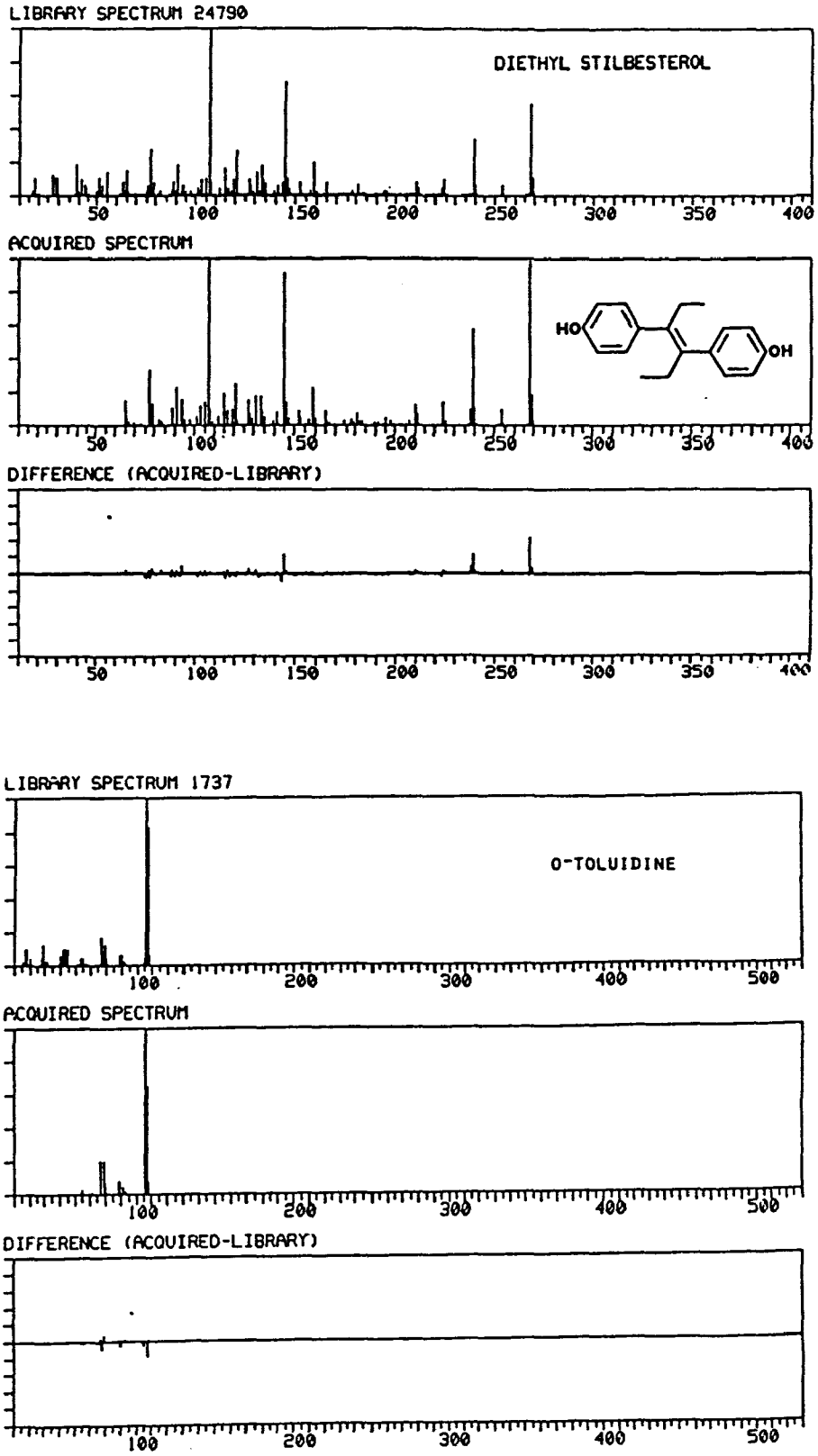

Figure 3. Library matched, Thermabeam spectrum of DES and O-Toluidine

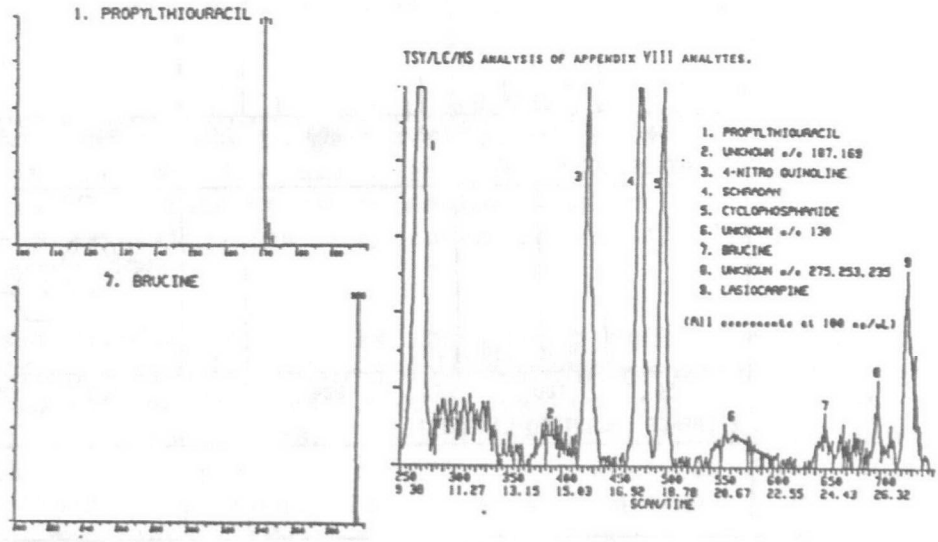

Figure 4. Thermospray analysis or Appendix VIII analytes

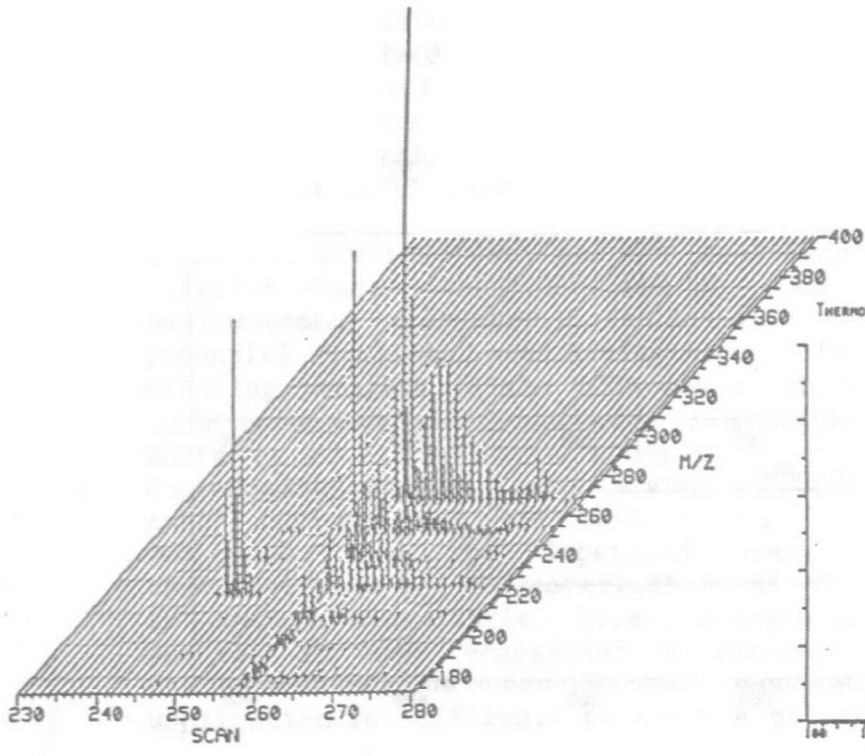

Figure 5. Three dimensional plot of Auramine-O PB/LC/MS spectrum

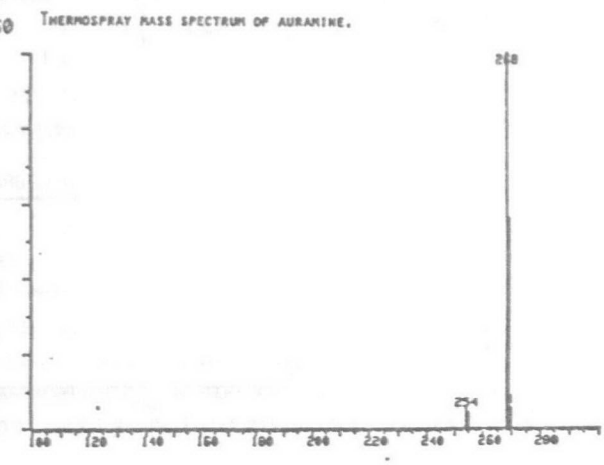

Figure 6. Flow Injection Thermabeam Spectrum of Auramine

by be straight forward (i.e., Benzidine). Implementation of the technology would, of course, require further testing and method development and validation, but given our observations, it would appear as if existing systems with appropriate ion optics and source design could be retrofit for relatively small cost (compared to a complete LC/MS systems), and given the national quadruple GC/MS resource system, introduction of such technology could be made more rapidly, than technology requiring special modification or complete systems purchase. Perhaps, more important, PB/LC/MS technology or similar technology could provide the necessary tools to regulate a wide range of analytes. If in fact, such technology proves to be robust enough, then the "target compound approach" associated with regulatory lists could be eliminated or significantly reduced.

DISCLAIMER

This article has not been subjected to Agency policy review, and therefore does not necessarily reflect the views of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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MINIMUM DETECTION LIMITS AND DATA ANALYSIS

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ABSTRACT

Many of the Agency's regulation require collection of chemical or environmental data, then a summarization of this data to a mean or variance, and finally the comparison of these estimates to some standard in order to determine compliance status. Providing the contaminants or variables in question occur at sufficiently high levels that that measurement can be done with high precision, the determination of compliance or non-compliance with a regulation is relatively straightforward. When data are recorded as being "Below the Detectable Limit" or "Trace," the calculation of meaningful summary estimates becomes somewhat tenuous, owing to the absence of numerical values.

This paper looks at the results of making simple approximations to unrecorded data when calculating means and variances. The consequences of setting all below-detection-limit values to a constant (such as the detection limit itself) are discussed in the context of comparison of data to a standard. The method due to Cohen for normally distributed data will be demonstrated and the work of Gilliam and Helsel for lognormally distributed data will be discussed.

DEVELOPMENT OF ROBOTICIZED ANALYTICAL METHODS

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ABSTRACT

The Research Triangle Institute (RTI) has undertaken a robotics-related task to assist the Technology Assistance Branch, Office of Solid Waste, Environmental Protection Agency (OSW, EPA). OSW is encouraging producers of analytical instrumentation to develop robotic assisted methods as adaptations of SW-846 (Test Methods for Evaluating Solid Waste Physical/Chemical Methods, 3rd Edition) for determination of hazardous constituents. Laboratory robotics will improve the precision and accuracy, overall analytical data quality, safety, and efficiency of analyses. It has been demonstrated that rather than eliminating jobs and upsetting the work environment, laboratory robots have enriched the work of technicians and professionals by providing new intellectual challenges and eliminating repetitive tasks. Although laboratory robotics have only recently begun to be successfully applied, their impact on analytical methods development is certain to be important.

Robotics can be defined as the study and use of machines capable of manipulation and/or mobility with some degree of autonomy. The autonomy may be almost complete -- as in the case of an industrial manipulator which follows a sequence of preprogrammed moves, or limited, as with teleoperators used in nuclear and undersea operations. Robots become more autonomous and flexible when they incorporate sensory capabilities, such as machine vision or tactility, or are controlled by computerized expert knowledge or heuristic decision-making programs. Therefore, laboratory robotics utilize machine intelligence and flexibility rather than simple, "fixed automation" instruments.

A few vendors are supplying laboratory robot systems for such operations as sample weighing, transfer, separation, and mixing. Research areas in robotics which will become more important for laboratory applications include: development of sensors, improvement of speed and accuracy, development of better internal models of the environment in which the robot works, interface standardization (both for software and hardware), incorporation of mobility, improved robot teaching methods (including off-line programming), and reformulation of control architectures and path control. Robots will eventually become incorporated into laboratory information management systems (LIMS). Mobile field sampling and analytical robots are also being investigated.

The initial RTI task is a step directed toward development of laboratory work cells interfacing robots, automated instrumentation and personnel in the most efficient manner. The task is coordinated with an interagency agreement between EPA the National Bureau of Standards, which will serve as a technical expert responsible

for standardization of roboticized analytical methods. Enlistment of a producer of analytical instrumentation is also planned. The participation of such agencies as the National Aeronautics and Space Administration will be solicited, e.g. related to the transfer of such technology as automated laboratory designs for Space Station and Space Shuttle experiments. The study will incorporate review and evaluation of existing and planned robotic-related methods which may be important to hazardous constituents determinations.

Initial emphasis will be placed upon development and demonstration of a flexible robotic technique for a specific solid waste test method. Incorporation of flexibility in this case will emphasize statistically-based experimental design. Test method optimization by such techniques is ideal in a computer-based robotic work cell. Analysis results may be continuously evaluated and the analytical plan updated and optimally redefined using the robot, since it is capable of altering function and sequence without human intervention. The human scientific knowledge required for making such decisions will eventually be incorporated into expert systems related to all the functions of a particular laboratory work cell.

EXPERT SYSTEM FOR INTERPRETATION OF THE INFRARED SPECTRA OF HAZARDOUS WASTE DRUM SAMPLES

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INTRODUCTION

In order to satisfy the requirements of hazardous waste analysis at Superfund and at licensed disposal sites [1-6], a program for automated waste mixture identification (PAWMI) through the interpretation of the infrared (IR) spectrum of the waste mixture was developed [7,8] and tested on hazardous waste drum samples [9]. This approach, which utilizes the speed and sensitivity of Fourier transform infrared (FT-IR) spectrometry meets many of the requirements of a near real-time, principal component screening technique for organic hazardous waste samples [1].

Two limitations of PAWMI were that once a training set, consisting of a library of reference of spectra, was defined, the rules for the inference engine (PAIRS) [10-16] had to be generated manually. The second limitation was that the PAWMI compound identification software only uses peak location information.

An approach to the automated generation of functional group interpretation rules for PAIRS was previously developed (17).

Efforts by other investigators have been successful for the interpretation of IR spectra using computerized interpretation or matching procedures (18-27).

This paper describes a program for the identification of the principal components of mixtures based on computer assisted interpretation of the mixture's infrared spectrum. This program (intIRpret), which was developed as a preliminary screening tool for unknown organics handled on hazardous waste remedial action sites, has five main subroutines: the interferogram processing and peak selection subroutine (PUSHSUB) [8], the automated knowledge acquisition subroutine (AUTOGEN) [17], the system optimization subroutine (STO), the interpretation subroutine (PAIRS) [7, 10-16], and final processing subroutine to subtract spectral similarity (PAIRSPLUS) [8].

Many of these subroutines are substantial modifications of the programs previously reported [7,8,17]. Principal advantages of this system compared to the previously reported PAWMI system are speed (all spectral information is encoded automatically),

flexibility (changes in the data base and in interpretation rules are readily accommodated) and accuracy (interpretation is based on peak position, frequency of occurrence and peak size, each of which is weighted in an optimal fashion).

The method has been evaluated using the 62 most commonly identified organic compounds on hazardous waste sites [18]. IntIRpret was designed to be automatic, self-training, and self-optimizing so it could be operated on-site (in a mobile laboratory) during a remedial action project, by personnel with limited training. Other applications of the intIRpret technique would include screening incoming organic waste at licensed disposal facilities or for interpreting gas phase spectra obtained during industrial hygiene air monitoring.

EXPERIMENTAL SECTION

Spectra were acquired on a Nicolet 20-SX optical bench. Each spectrum was generated with a background and sample signal averaging of 128 scans. The number of data points collected was 16,384, resulting in a nominal spectral resolution of 2 cm-1. All programming and spectral analysis, including rule writing, compiling and spectral interpretation, was performed with a Nicolet 1280 computer equipped with a 160 Mbyte Winchester disk system.

RESULTS AND DISCUSSION

IntIRpret has five main subroutines: the interferogram processing and peak selection subroutine (PUSHSUB) [8], the automated knowledge acquisition subroutine (AUTOGEN) [16], the system optimization subroutine (STO), the inference engine (PAIRS) [7, 10-16], and the final processing subroutine which subtracts spectral similarity (PAIRSPLUS) [8]. Figure 1 is a flow chart of the intIRpret process, where the logic of each of the five major subroutines is diagrammed.

Because PUSHSUB, AUTOGEN, PAIRS and PAIRSPLUS have been explained in detail in the above referenced papers, the reader will have to study those papers in order to understand the details of the operation of those subroutines. However, a summary of those subroutines is given in this publication. In his publication, emphasis is placed on describing STO, which is central to the operation of the self-training, self-optimizing mode of operation of intIRpret. In addition, the linkage of all of the subroutines is explained.

This system is used in conjunction with spectral library SEARCH programs to optimize the ability of the system to identify unknowns.

PUSHSUB

In order to automate PAWMI, a peak selection of subroutine PUSHSUB, was developed that does not require the operator to set a peak selection threshold, and successfully follows non-linear baselines [8]. Figure 2 shows an example of the operation of PUSHSUB. In tracing A, the IR spectrum of a hazardous waste drum sample is shown. Tracing B shows the spectral baseline automatically established by PUSHSUB. Tracing C shows the resulting spectrum, with the peaks of importance for the identification of the principal components of this mixture separated from the non-linear baseline.

STO

This subroutine accesses the peak tables generated by PUSHSUB. The peaks in a spectrum that are chosen for the purposes of decision making are called rule peaks. Not all spectral peaks are rule peaks. Each rule peak is assigned a "goodness value" that indicates the probable presence or absence of each compound in the training set.

Three factors are used to weight the goodness values assigned to each rule peak listed by AUTOGEN: k1 (frequency of occurrence), k2 (intensity), and k3 (frequency of occurrence X intensity). These three factors are designed to follow the logic used by an expert during the interpretation of the infrared spectra of mixtures. In this respect, the underlying intellectual framework is similar to that described in the work of McLafferty in which Match Factors were automatically calculated for the interpretation of mass spectra [28,29].

The factors k1, k2 and k3 are defined by the program. The goodness available to each peak window is divided between k1, k2 and k3, with the default value for the constraints set equal. These default values can be changed by the operator.

K1, which is a measure of frequency of occurrence of peaks in the training set within a given wavenumber window, essentially states that a peak should be given added importance (or goodness) if it is in a region of the spectrum in which there are few peaks in the other spectra in the training set. K1 is equal to:

$$\frac{\textbf{number of peaks present in the rule peak window}}{\textbf{number of peaks in that window in all spectra in the training set}}.$$

K2 essentially states that added significance should be attached to the presence of a peak that represents a large fraction of the total peak intensity for the spectrum of a compound. K2 is equal to:

$$\frac{\text{rule peak intensity}}{\text{total intensity for all peaks in the spectrum of that compound}}.$$

K3, which is the cross-term between frequency of occurrence and intensity, essentially states that a large peak should be given added importance if it is in a region of the spectrum in which there are few large peaks in the other spectra of the training set. K3 is equal to:

$$\frac{\text{rule peak industry}}{\text{intensity of all peaks in that window in all spectra in the training set}}.$$

As stated earlier, the default values chosen for this study were: window widths of +/- 3, 5, and 10 cm-1; goodness values divided between these windows of 50%, 30%, and 20%, respectively; and k1 = k2 = k3. It is not known if these are the optimal values for this training set, for all possible mixtures that can be prepared for compounds in this training set, or for other training sets. Studies are underway to define the optimal window width based on experimentally determined peak shifts.

STO is a very significant departure from the practice previously reported for PAWMI [7,8]. In that program, only peak position information was used. Using the STO portion of intIRpret allows the optimization of goodness values for each rule peak in each training set.

AUTOGEN

The automated generation of rules for a defined training set is essential to the success of this approach. The nature of these rules is dealt with in great detail in references 7 and 10-16, and is described in brief in the section of this text describing PAIRS (below). Without AUTOGEN, PAIRS and PAWMI are hampered by the potential for errors that always occurs when data is manually encoded, and by the constraints imposed by the length of time it takes to enter data for new or modified training sets. Because of these problems, such a system is inherently inflexible. AUTOGEN solves these problems.

PAIRS

As previously reported, PAIRS [10-16] was modified in the PAWMI

program [7,8]. The mixture interpretation software uses peak location information and is based on a three-level filter algorithm designed to compensate for potential peak shifts in the mixture spectrum. If a peak falls in a relatively wide frequency window assigned to a certain compound, a percentage of the overall goodness value will be added to the total. "Goodness" is a measurement of closeness of match between the spectrum of the pure compounds used for rule generation and the spectrum of the unknown compound(s). The goodness scale ranges from 0.001 for a complete mismatch to 0.999 for a complete match.

In the intIRpret program, peaks in the library spectra are picked by PUSHSUB, the goodness values are weighted by STO, and the three level rules are written by AUTOGEN. A peak table is then created for the unknown mixture by PUSHSUB. PAIRS accesses that table and generates goodness values that indicate the probable presence of compounds in the mixture of unknowns.

PAIRSPLUS

PAIRSPLUS was developed to limit the effect of spectral similarity. A detailed description of PAIRSPLUS can be found in reference 8.

An example of the spectrum of a four-component mixture that was analyzed using intIRpret is shown in Figure 3. 1,1,1-trichloroethane, chlorobenzene, toluene, and benzene were correctly identified in this mixture.

LIBRARY SEARCH

Many hazardous waste samples, when analyzed by GC-MS show an incomplete material balance [9]. This is due to the presence of polymeric, thermally labile and/or highly polar components. Using this FTIR technique, simple air drying of the sample will frequently be sufficient to leave a residue containing only the commercial polymer that makes up a bulk of the sample. Figures 4 and 5 show two examples of this. In each case, the analysis performed by GC-MS showed only the presence of volatile solvents comprising less than 30% of the sample weight. The dried specral library file, when searched against the Aldrich library of 4,000 compounds and commercial mixtures, resulted in the identification of Polyamide Resin and Igepal polymer as the principal components of these hazardous waste drum samples.

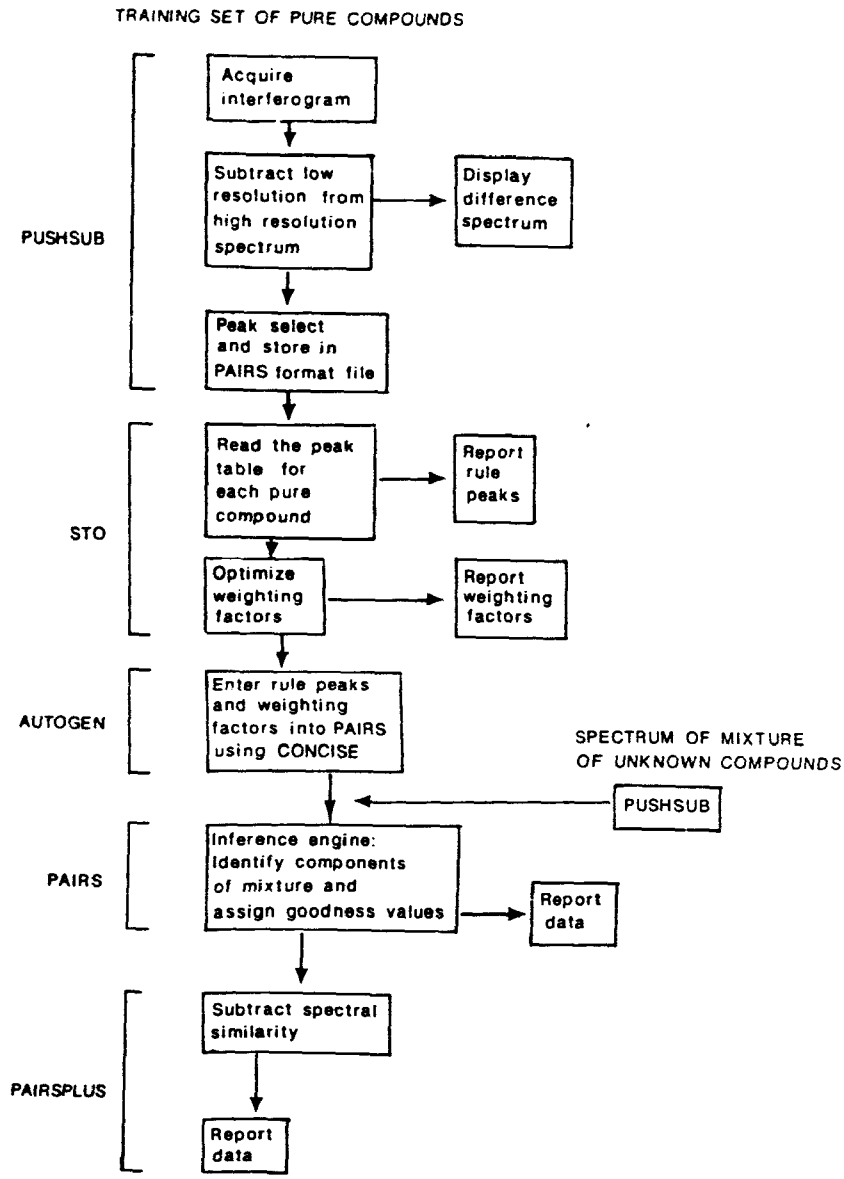

Figure 1. Flow chart of the intIRpret process, showing the logic of each of the five major subroutines.

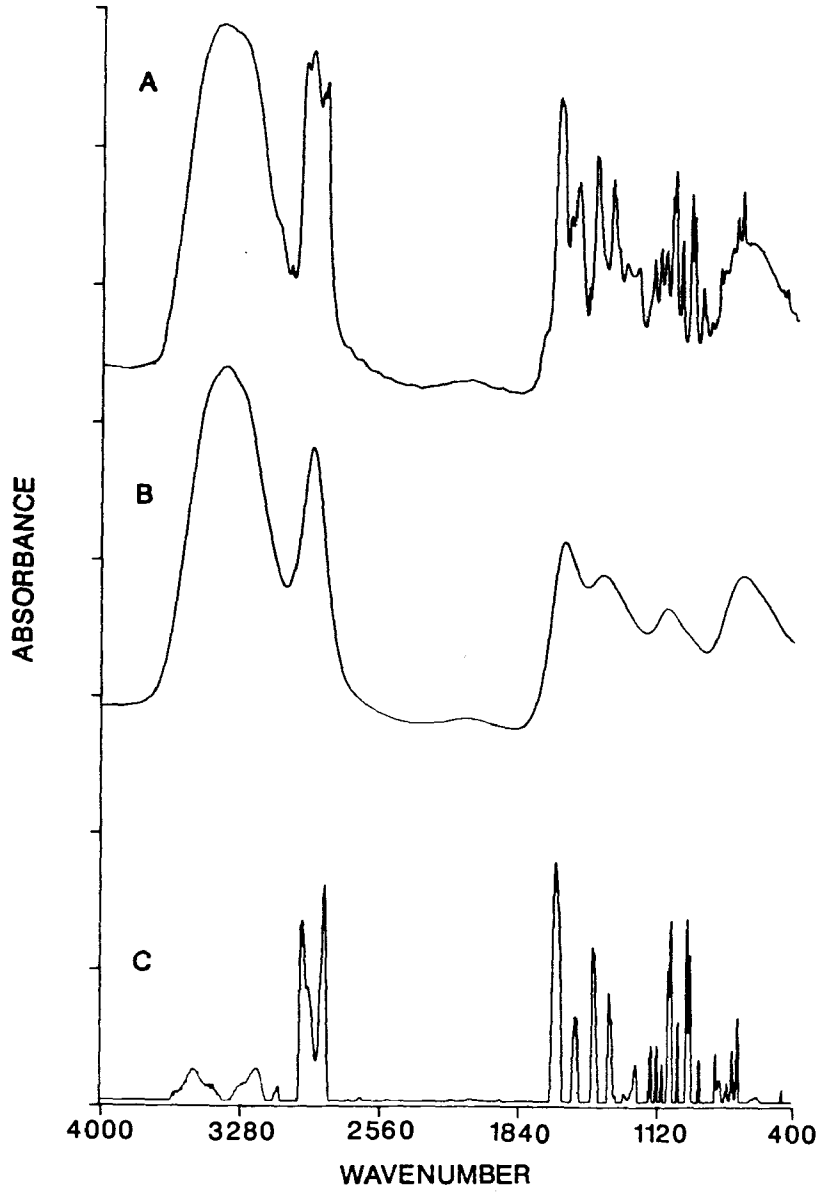

Figure 2. Spectral tracings showing the operation of PUSHSUB. A = spectrum of hazardous waste sample; B = baseline automatically generated by PUSHSUB; C = difference between A and B, which is used to identify peak locations for spectral interpreatation.

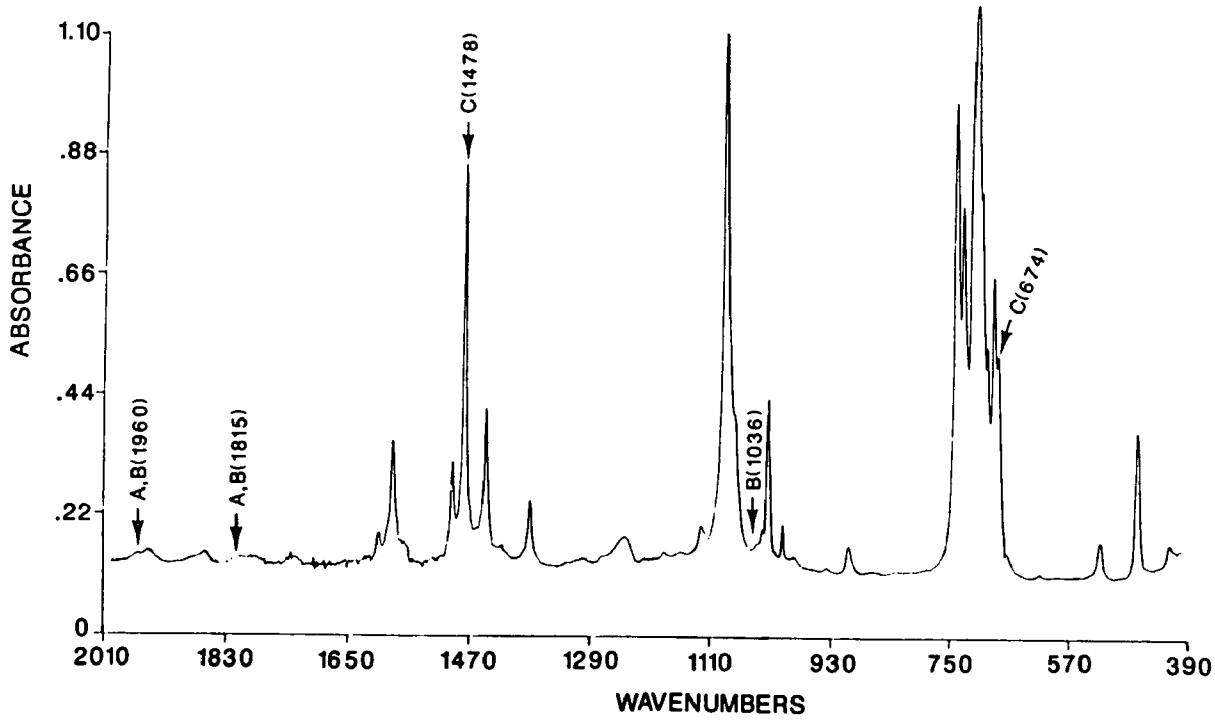

Figure 3. Portion of the spectrum of the mixture chlorobenzene + 1,1,1-trichloroethane (TCE) + toluene + benzene in 1 : 1 : 0.5 : 0.1 ratio (w/w). Peaks used as PAWMI rule peaks but not intIRpret rule peaks are shown by (A); peaks missed by PUSHSUB are shown by (B); peaks heavily weighted in the spectrum of benzene by intIRpret that fall within the +/-3 cm-1 window are marked by (C).

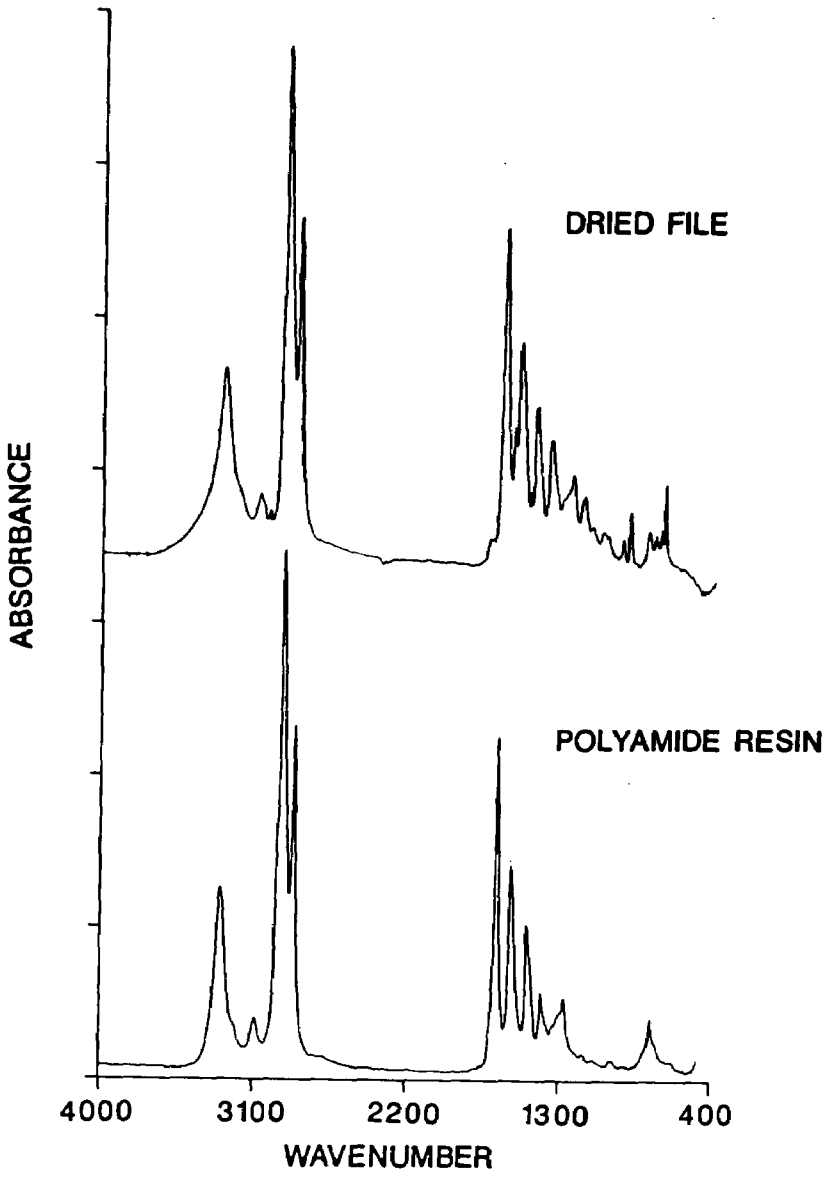

Figure 4. Spectrum of hazardous waste drum sample after air drying for five minutes (Dried spectral File), and closest library match (Polyamide Resin).

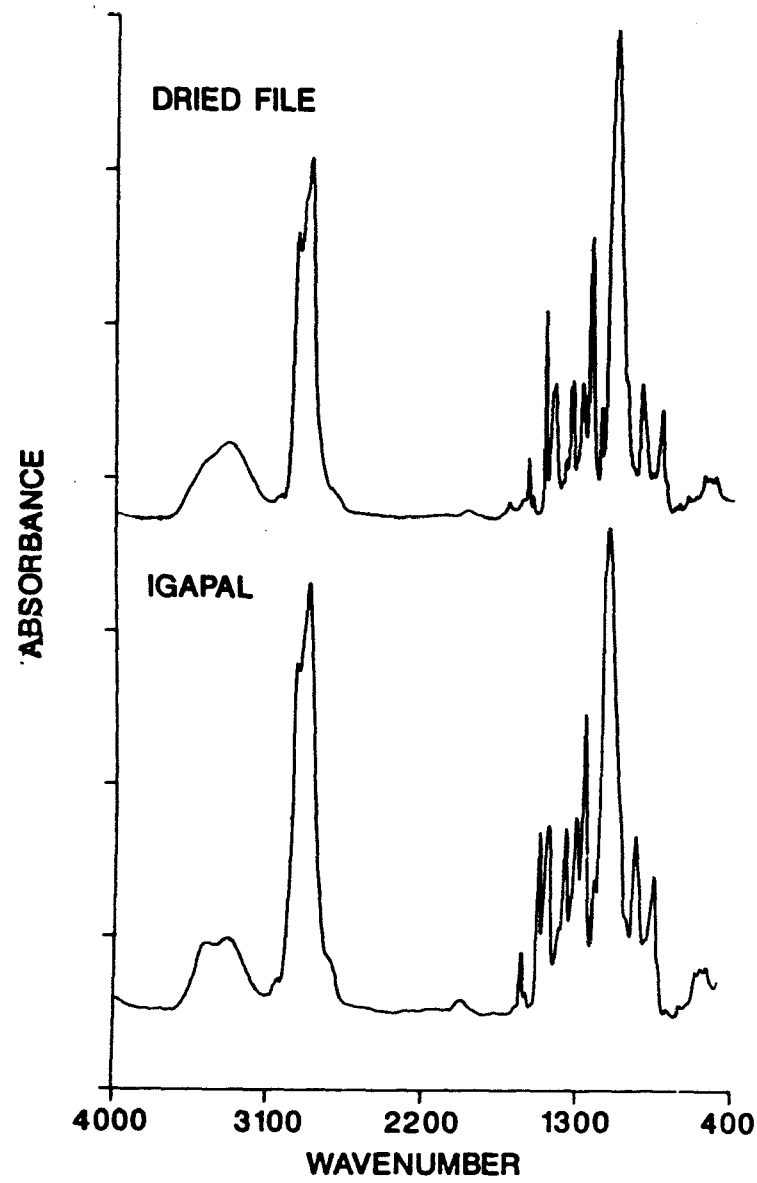

Figure 5. Spectrum of hazardous waste drum sample after air drying for five minutes (Dried spectral File), and closest library match (Igepal).

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CREDIT

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IMPROVING SONICATION TECHNIQUES IN CLP ORGANICS ANALYSIS AND SOLID WASTE EXTRACTION

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ABSTRACT

EPA laboratories and contractors and others following EPA protocols use sonication for analysis of extractable organics and pesticide/PCBs in sediment/soil in the CLP (Contractor Laboratory Program). Sonication is also used in evaluating solid waste by SW-846 Method 3550. Proper tuning of ultrasonic liquid processors and proper use of new half wave extender tips will greatly improve reproducibility and reduce costs to contractors and the Government. Tuning the processor is a means of assuring optimum operation at the highest efficiency. Techniques for tuning virtually every model of ultrasonic processor in current use are discussed. Use of half wave extender tips avoids solvent erosion of the replaceable tip joint and allows top insertion through the neck of flasks and bottles while lowering disposables costs.

INTRODUCING THE THIRD EDITION OF SW-846: TEST METHODS FOR EVALUATING SOLID WASTE

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ABSTRACT

On March 16, 1987, the U.S. EPA announced the availability of the Third Edition of the manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" EPA publication SW-846 (52 FR 8072). The manual contains methods suitable for specified hazardous waste testing and monitoring purposes, and provides a source of information on sampling and analysis for compliance with the Resource Conservation and Recovery Act (RCRA) regulations. This poster session presents an introduction to the information contained in the manual, the information required to use the manual, and an example of a decision tree which can be applied to the analysis of a sample containing organic compounds.

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in the manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

REGULATORY SIGNIFICANCE

SW-846 is a collection of methods suitable for specific hazardous waste testing and monitoring purposes. The manual does not establish testing requirements. Rather, the various testing requirements are

established in the appropriate sections of the Code of Federal Regulations.

EPA is not incorporating the Third Edition into the RCRA hazardous waste regulations at this time because of the significant changes which have been made in the methods. The Agency plans to replace the existing methods with the revised versions in the near future, after allowing time for comment in the revised methods. Until that time, however, the methods described in the Second Edition of SW-846 must continue to be used where the Second Edition is incorporated be reference or mandated by particular regulation.

CONTENTS

The manual is provided in four 4" D-ring binders. The first binder contains Volume 1A, which includes Chapters One through Three. Chapter One addresses quality assurance and quality control considerations which apply to all methods described in the manual. The chapter is not intended as a comprehensive guide to QA/QC programs, but emphasizes that data generated by the analytical methods contained in the manual are meaningless unless supported by appropriate quality control procedures and documentation.

Chapter Two contains information designed to aid the experienced analyst in selecting the appropriate methods from the maual, based on characteristics of the sample and the objectives of the analysis. Figures and tables are included to assist the user in identifying cleanup, preparation, and determination methods for various combinations of analytes and sample types. A table of containers, preservation techniques, and holding times is also provided.

Chapter Three covers sample preparation and determinative methods for metallic analytes. Preparation methods include acid digestion and dissolution procedures, while the determinative methods are Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA).

The second binder is labelled Volume 1B, and contains Chapter Four, Orgainc Analytes. Sample preparation methods cover a variety of extractions and cleanups, while the determinative methods include gas chromatography, gas chromatography/mass spectometry, and high performance liquid chromatography.

The third binder, Volume 1C, comprises Chapters Five, Six, Seven, and Eight, addressing miscellaneous analytes, properties, and characteristics. Miscellaneous test methods covered in Chapter Five include TOX, TOC, cyanide, sulfide, sulfate, phenolics, oil and grease, total coliform, nitrate, chloride, and radium. Chapter Six addresses properties such as pH, specific conductance, cation exchange capacity, liner performance and compatability, paint filter liquids, and radioactivity. Chapters Seven and Eight discuss the characteristics of hazardous waste, as defined by the Code of Federal Regulations. Regulatory definitions are covered in Chapter Seven and test methods appear in Chapter Eight.

Volume Two is contained in the fourth binder, and includes chapters Nine through Thirteen, which addresses sampling methods and monitoring procedures. Design, development, and implementation of sampling plans is discusses in emissions. Monitoring of groundwater, land treatment facilities, and incinerators is covered in chapters Eleven, Twelve, and Thirteen, respectively.

AVAILABILITY

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846, is available from the U.S. Government Printing Office, Washington, D.C. 20402, order number 955-001-00000-1, for a cost of $110, which includes future updates.

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U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY INSTALLATION RESTORATION QUALITY ASSURANCE PROGRAM

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ABSTRACT

The Army's Installation Restoration Program (IRP) was established in the mid-1970s to identify, evaluate and clean-up contamination resulting from past waste disposal activities on property under Army control. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) was assigned to execute this mission as the IRP central manager. In order to assure that high-quality, verifiable data was produced from chemical analyses of environmental samples, USATHAMA developed and implemented a state-of-the-art Quality Assurance (QA) Program. Since the implementation of the USATHAMA QA program in the mid-1970s, we have continued with a policy of reevaluation and revision of the program's concepts and methods. Our process of review and analysis includes experts from industry,m national laboratories, academia, and other government offices.

The main objectives of the USATHAMA QA Program are to: (1) provide a consistent framework for the generation of good analytical data; (2) require contractor laboratories to demonstrate their ability to analyze for all of the compounds of interest in the appropriate sample matrices over a range of concentrations; (3) require the laboratory to analyze daily quality control (QC) samples, and to evaluate laboratory performance on a daily basis; (4) require the laboratory to provide USATHAMA with daily QC charts on a weekly basis, and to provide detailed accounts of problems encountered and corrective actions taken; (5) provide the means (e.g., software) to perform certification calculations, daily QC and data entry, and internal and external audits of data, facilities, and sampling excursions; (6) require documentation of all aspects of sampling and analysis; (7) provide Standard Analytical Reference Material (SARM's) which are NBS traceable whenever possible; (8) use analytical methods based on those of the U.S. Environmental Protection Agency (EPA), AOAC, and methods in the open literature; (9) develop methods for military unique compounds; (10) participate in interagency cooperative studies as the EPA/DOD/DOE Holding Time Study; and (11) re-evaluate and improve the USATHAMA QA Program.

Presented here will be a discussion on how USATHAMA accomplished these objectives and some major differences between USATHAMA's QA Program and other programs in common usage.

INTRODUCTION

The main goals of any Quality Assurance (QA) program are: (1) to produce high quality, verifiable data from chemical analyses, or put another way, to ensure that one gets what is paid for (i.e., good analytical data); and (2) to prove to oneself and others that the data

is representative of the environment from which the samples were collected. There is, of course, more than one way to accomplish these goals, and reviewers of environmental data and regulators should keep an open mind to this fact. To do otherwise would result in dismissing a great deal of analytical data collected at great expense, and result in delaying crucial remedial actions, as well as the additional costs associated with resampling and reanalysis of samples from a previously studied site. In addition, to impose a de facto QA program without any provisions for making changes or achieving equivalency with the existing regulatory requirements would stifle scientific debate on QA issues, stagnate further developments in QA, and inhibit the peer review process which is so important in the scientific field.

USATHAMA developed a state-of-the-art QA program when the Agency was organized in the mid-1970s. This was about the same time that the EPA promulgated the drinking water regulation and associated QA/QC requirements. It was well before the passage of CERCLA in 1980 and the CLP in 1981. From the beginning, we adopted a policy of continued reevaluation within the Army, to debate and implement changes to the QA program. This process of review and analysis has expanded over the years to include experts from industry, national laboratories, academia, and other government offices.

Our main objectives in formulating the USATHAMA QA program have been: (1) to provide a consistent framework for the generation of good analytical data. We have accomplished this objective by establishing a formal QA program in which all QA program requirements are contained within a single document; in addition, (2) we require the laboratories to demonstrate their ability to analyze for all of the compounds of interest in the appropriate sample matrix; (3) the laboratories are required to analyze daily quality control (QC) samples, and to evaluate their performance on a daily basis; (4) we also require the laboratories to provide USATHAMA with all of their QC charts on a weekly basis, and to provide detailed accounts of problems encountered and corrective actions taken; (5) we provide the laboratories with tools such as software to perform certification calculations and daily QC; and we have automated data entry/data reporting to expedite the review process; (6) we require documentation of all aspects of sampling and analysis; (7) we provide standard analytical reference materials (SARM's) which are traceable to NBS whenever possible; (8) we use analytical methods published by the USEPA, AOAC, and in the open literature; (9) whenever methods are not available, such as military unique compounds, we conduct research and development efforts and ruggedness testing of new methods; (10) we participate in inter-Agency cooperative studies such as the EPA/DOD/DOE Holding Time Study and the DA/EPA evaluation of field portable instruments and methods; and finally, (11) we continue to reevaluate the effectiveness of our QA program taking into consideration new analytical, statistical, and software developments, and changes in the resources available to us (i.e., manpower and budget).

In developing the strategy to accomplish our goals, we considered factors such as the individual program and site specific requirements.

In addition, we considered the cost of performing analyses, since every QC ample, blank, duplicate, etc., that is analyzed impacts the total cost of an environmental study. We have striven to limit or reduce the number of samples, or lots of samples, that will be rejected due to poor lab QC, exceeding holding times, high lab blanks, etc. In determining the number of QC samples to be run in each lot, we evaluate the instrument and method limitations so we can optimize the ratio of the number of environmental samples to QC samples that must be analyzed. Further, we assess the intended use of the data to determine the amount of QC required and the confidence level to which the data will be reported. In the mid-1970s when our QA program was being formulated, we elected to set the reporting limit at the 90% confidence level where both the alpha and beta errors are 5% each. Even though this was an arbitrary decision, we have elected to stay with the 90% confidence level primarily because our experience has shown that the data produced is technically acceptable for the intended use, and at a reasonable cost. Finally, we have designed a QA program that is manageable with the manpower that we have available.

As mentioned previously, we continue to reevaluate and revise our QA program to make it among the best of the QA programs available. We believe that we have a technically sound QA program; however, we also recognize that it can still be improved. There have been many changes in the USATHAMA QA program since its inception in the mid-1970s, the most significant being a trend toward tighter restrictions on the laboratories operating under the program. When we began our program, we recognized that there were differences between laboratories, such as instruments, equipment, and personnel. We, therefore, designed the USATHAMA QA program to be flexible enough to accomodate these differences. Not long after establishing the original program, it became apparent that some laboratories would take advantage of every ambiguity in the QA program. Since that time, we have systematically made the USATHAMA QA program less flexible. We have taken actions such as requiring QC on a more frequent basis and spelling out the exact QC required; we have required more documentation of problems and corrective actions taken; we have improved our control charting procedures to make them more responsive to our needs; we increased the frequency of laboratory and field sampling audits; we began holding quarterly QA/QC meetings with all laboratory QA personnel in attendance. At these meetings, the laboratory QA personnel discuss problems which they are experiencing with methods, instruments, QC, etc., and they arrive at common solutions which are implemented by each laboratory; more recently, we have required six of our laboratories to use identical analytical methods where options that are found in some methods, such as flowrates, column temperatures, extraction solvent, etc., have been standardized. We have seen a significant reduction in the variances among these laboratories. We have now begun a study to evaluate a variety of commonly used methods, standardized the options of each method, and write the methods in a standard format. Each method will then be validated following the USATHAMA certification procedure. Upon completion of each standard method, our analytical laboratories will be required to follow the method(s) explicitly. When a new method becomes available, it will be

evaluated against the standard method, and depending on the result of the evaluation, it may be adopted as the standard method.

Some of the specific aspects of the USATHAMA QA program include a formal QA program document which contains all of the program requirements, except the analytical methods. The analytical methods are maintained separately. The USATHAMA QA program has existed as a formal document for more than ten years, and it has been the subject of extensive peer review during that time. The program was designed to provide real-time information on the analytical process so that deficiencies can be detected and corrected on-the-spot. The USATHAMA QA program has been highly automated in order to expedite the transfer of data and its review. This program has been instrumental in the early detection of deficiencies and their ultimate correction, and it has been effective in the detection of deficiencies in laboratories following other QA programs.

A major aspect of the USATHAMA QA program is that we require our laboratories to certify that they can actually perform the required analysis(es) using the equipment and personnel that will be used on "real" samples. Laboratories must demonstrate their proficiency before any field samples are analyzed. The laboratory certifies for each compound of interest and in each sample matrix they will be analyzing. Provisions are made for those methods where it would be impractical to analyze for every compound (e.g., GC/MS). Proficiency is demonstrated over a range of concentrations rather than at a single concentration. The method certification data established the baseline that future laboratory performance must fall within (i.e., upper and lower control limits) to be acceptable. We have observed improved laboratory performance as a result of the certification process. We also develop reporting limits for each method using the data collected during certification. These reporting limits become the USATHAMA Certified Reporting Limit (CRL) for each method. The CRL is the minimum quantification level that USATHAMA laboratories may report. The CRL should not be confused with the classical approach of comparing signal to noise under ideal conditions (limits which are difficult to achieve under routine laboratory conditions). The CRL is determined by application of regression theory to target (known analyte concentrations) versus found (values determined by actual analysis of spiked samples) curves generated by the analysis of real, spiked samples over a range of concentrations. The technique is based on principles described by Hubaux and Vos[1]. The reporting limits derived from this procedure are more representative of a laboratory's capabilities on a day-to-day basis and provide confidence that an analyte present at a concentration above the reporting limits will consistently be found.

Another major aspect of our QA program is the evaluation of a laboratory's performance on a regular basis. The laboratories are

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[1]Hubaux, A., and G. Vos, 1970, "Decision and Detection Limits for Linear Calibration Curves." Analytical Chemistry, Vol. 42, No. 8, pp.849-855.

required to analyze quality control (QC) samples on a daily basis. The results of these analyses are plotted daily on QC charts. The control limits used on the QC charts are those which were developed from the laboratory certification data collected prior to the beginning of routine laboratory analysis. Therefore, if a laboratory uses its best personnel and equipment at the beginning of the certification process, they will have to maintain that same level of performance throughout the analytical performance period. Should an attempt be made to make the control limits artificially wide, certification will likely be denied based on acceptance criteria developed by other laboratories using the same method(s). Control limits are periodically revised based on laboratory performance as more data is collected. Experience has shown that the control limits generally become narrower due to improved laboratory performance as more experience is gained with a particular method. When out of control situations do occur, the laboratory is required to investigate the probable cause(s), and to document the causes(s) and action(s) taken. The control charts are submitted to USATHAMA on a weekly basis for review. These reviews verify that the laboratory is performing a daily review of the analytical and QC data. If a laboratory's performance declines, or if they do not comply with the provisions of the QA program, the laboratory will be decertified for the method(s) in question. USATHAMA has decertified laboratories for poor performance under the USATHAMA QA program.

Another part of the USATHAMA QA program is the performance of laboratory and field audits, and quarterly QA/QC meetings of the USATHAMA certified laboratories. Each laboratory performing work for USATHAMA is randomly audited to ensure that the QA/QC procedures are being followed, that appropriate records are being maintained, and that good laboratory practices are being followed. Particular attention is given to those laboratories that have been experiencing problems. Audits are also conducted of field sampling operations to ensure that samples are being collected following the proper protocols (i.e., sample storage conditions, proper collection bottles, sample identification, etc.). In addition, we hold quarterly QA/QC meetings with the QA personnel from each laboratory present in order to discuss problems and find common solutions.

In summary, I would like to emphasize that we are striving to get high quality data from our contractors. We have developed a QA program that has worked for more than ten years and continues to work. We have gained a lot of experience with QA/QC programs, and have experience with laboratories working under their own or other QA programs. Our experience with some of these laboratories has been disappointing in some instances since their performance has not been what was expected given the programs being followed. We also realize that we can continue to improve our program with assistance from other experts in the field, and we hope that meetings such as this, and those in the future will help us to accomplish this objective.

AUTOMATED MAINTENANCE AND REPORTING OF ANALYTICAL QUALITY ASSURANCE ON A PERSONAL COMPUTER

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ABSTRACT

In order to support the validity of analytical results, a certain amount of overhead work is required for quality control. This overhead involves not only additional analyses of spiked samples, duplicates, and quality control samples, but also requires additional bookkeeping to track, document, and report quality assurance data. TELECATION ASSOCIATES has developed a software package for personal computers, which aids in the bookkeeping chore and automates the generation of quality control data and reports.

SMARTLOG (R) and SMARTLAB (R) are two laboratory data management programs which vary in the amount of laboratory information maintained in the data files. Both programs store analytical results for all analyzed samples, including all quality control work. After analysis, data may be reviewed and evaluated on the computer screen. Quality control data is identified and processed according to the type of QC calculation to be performed. The basic techniques of analytical quality control include calculation of spike recovery, determination of agreement between sample replicates, and analysis of quality control standards to verify the accuracy of the analysis. The programs support all of these techniques, generating both tabular and graphical output of results.

For laboratories involved in the EPA's Contract Laboratory Program, SMARTLOG and SMARTLAB will offer automatic generation of sample analysis and QC reports, compatible with CLP specifications. A report generation package will report sample data, automatically appending all appropriate flags and producing the various required QC reports. Report formats may be customized for individual purposes or to allow for changes which may occur in the CLP reporting protocols.

INTRODUCTION

The analysis of environmental samples involves the manipulation of vast amounts of data. In addition to actual analytical results, information about the sample, including who submitted it, where it came from, and what is to be determined, must be recorded. Finally, to completely document sample handling, a "chain-of-custody", listing the movement and treatment of the sample, must be maintained.

In addition to the information which must be kept on each actual sample, additional analyses must be performed to verify the validity of sample analysis. While this quality control work is necessary, if the laboratory is to have any credibility regarding the reliability of its data, it must be recognized that maintenance of a QC program will add significantly to the analytical work load of the laboratory.

Figure 1 illustrates the additional analyses required to fulfill the requirements set forth in the CLP protocol for ICP analyses. The left column tabulates measurements which relate directly to determining sample results. The right column lists the quality control measurements which are called for in the CLP QA/QC procedures. As can be seen from this table, a full 50% increase in the number of analytical measurements is required to support the minimum standards of quality control. It should be noted that this table assumes 20 samples of a similar type. If the 20 samples included different types, such as ground water and soil extracts, additional preparation blanks, spiked samples, and duplicate samples would have to be run to verify the accuracy of the different sample treatments.

ANALYTICAL MEASUREMENTS FOR SAMPLE ANALYSIS AND QUALITY CONTROL

SAMPLE MEASUREMENTS		**QC MEASUREMENTS**	
Calibration:	blank	**Init Calib Verif:**	QC solution
	3 standards		Calib blank
			Interf check
			Linear range
	4		4
Analysis:	10 samples	**Continuing Verif:**	QC solution
			Calib blank
	10 samples		QC solution
			Prep blank
			Spiked sample
			Dup sample
			Lab control
			Interf check
	20		8
Total:	24		12

QC Measurement Overhead = 12/24 = 50%

Figure 1. Analytical overhead for Quality Control.

Since the amount of work to maintain the necessary quality control is substantial, it is worth evaluating methods which will streamline the process. Nothing will shortcut the need to actually make the quality control measurements. However the work is not done when the measurements are complete. Figure 2 itemizes the data handling which begins once the data has been collected.

First, the data must be maintained by some kind of bookkeeping system, either manual or computerized. The specifics regarding the sample must be entered into the system, followed by entry of the analytical results. Then for quality control samples, the QC purpose must be identified. In other words, a sample must be identified as a spike, duplicate, etc. A calculation must then be performed, depending on the nature of the quality control technique. And finally the outcome of the QC measurement must be reported. While we cannot reduce the task of generating QC data, we can do things to expedite QC data management.

DATA MANAGEMENT REQUIREMENTS FOR QUALITY CONTROL

1. QC identification and login
2. Data entry
3. QC calculations
4. Reporting

GOAL: to expedite processing of QC information

Figure 2. Data management overhead for Quality Control.

SMARTLOG (R) and SMARTLAB (R) are two laboratory data management programs written for the IBM PC-XT, AT or compatible computers. Both programs store analytical results and offer quality control routines, which automate the treatment and reporting of QC data. SMARTLOG is designed to collect analytical data, perform simple calculations, and print reports. SMARTLAB, which maintains additional sample handling and business information, functions as a mini Laboratory Information Management System. The programs may be used separately or together, as indicated in Figure 3. To illustrate how the quality control functions integrate into the other laboratory functions, a description of each program follows.

LABORATORY SOFTWARE FROM TELECATION ASSOCIATES

SMARTLOG: The PC Data Station
* Collect data automatically through direct instrument interface
* Perform calculations for precision, sample weight and dilution factor correction
* Print customizable reports
* Manage QC information
* Transfer data to another computer or LIMS system including automatic transfer to SMARTLAB

SMARTLAB: Laboratory Information Management System
* Login sample information and results
* Track sample status
* Generate work sheets and status reports
* Manage QC information for evaluating completed samples
* Report results and generate invoices
* Archive results and chain-of-custody

SMARTLOG/SMARTLAB: Data Station/LIMS system combination
* Collect data with dedicated SMARTLOG System interfaced to analytical instrument
* Transfer data to SMARTLAB to merge with main data base, when convenient

Figure 3. Features of SMARTLOG and SMARTLAB systems.

COLLECTING DATA WITH SMARTLOG

The main purpose of SMARTLOG is to provide a means of collecting, storing, reviewing, and reporting the results of laboratory analyses. For many analytical instruments, data may be collected automatically by simple connection of the instrument serial output to the RS-232 input of the computer. Or data may be entered manually through the computer keyboard. Once in the data base, results may be grouped by test or by sample number and selected data isolated for easy review. Figure 4 illustrates a SMARTLOG data base record and the information which can be maintained for a single analyte on a single sample.

```
                SAMPLE ANALYSIS RESULTS FOR CADMIUM

Report Name: water1                          Test: Cd
------------------- SAMPLE INFORMATION --------------------
            Lab # 704551  Date: 04/23/87  Sample type: water
      Sample ID: ground water from well #87-7
    Client Name: Peterson and Company
- INSTRUMENT----- EDITED DATA ------------------------------
105          |                      | weight:
   2.4600    |  2.4600  Average     | volume:      alt.result:
   1.9000    |  1.9000      2.1867  |  units: ug/L
   2.2000    |  2.2000  SD          |
             |             0.28024  |
             |          CV   12.82  |         RESULT:  2.1867
             |                      |
             |                      |----- QUALITY CONTROL ----
             |                      | Trend: 87-7   QC: spike51
             |                      |            Spike: 0
-------------------------------------------------------------
F2 list  F3 find    F5 prev   F7 prt record   F9  copy   HOME
         F4 update  F6 next   F8 prt report   F10 menu   END
```

Figure 4. Data maintained in SMARTLOG record.

After data is entered, you may add additional information about the sample, such as sample identification, sample type, and who submitted the sample for analysis. Up to ten replicate determinations of an analytical measurement can be entered into the data base. Where replicate measurements are made, the average result, standard deviation, and coefficient of variation are automatically calculated. Additional mathematical manipulations can be made on each result, to correct for such things as sample weight variations, or dilution factor differences.

If data has been collected automatically from an instrument, the results will be shown under the "instrument" section of the screen. This data area is inaccessible to manual entry or change. Automatically collected data can be edited in the "edited data" window to eliminate biasing effects of obvious outlying results, while retaining the original instrument data to support the validity and credibility of the analysis.

All functions of the software are controlled by selection of a computer function key, the functions for which are always labeled at the bottom of the screen (as shown in Figure 4). Therefore, operation is self-prompting and quick to learn. To print a report of the selected data, for instance, one would simply depress the F8 function key.

The format of a data report is completely customizable. A report generation utility guides the user through the

creation of customized report formats, starting with previously existing formats, which can be used as examples or templates. Any number of customized report formats may be created and stored for later use.

One of the most valuable functions of SMARTLOG is its application as an interim data collection station, for subsequent data transfer to a larger "Laboratory Information Management System" (LIMS). Using SMARTLOG and an appropriately configured personal computer, data from a laboratory instrument can be collected and stored, until it is convenient to transfer the data into the laboratory's main data base.

The instrument/personal computer interface requires only simple direct connection for serial data transfer. The PC/LIMS connection may be made through a PC network, RS-232, modem, or even by simple disk transfer. While a built-in utility provides automatic transfer of SMARTLOG data to the SMARTLAB PC LIMS system, data can be transferred to any computer capable of receiving standard ASCII information.

RUNNING THE LABORATORY WITH SMARTLAB

SMARTLAB is a laboratory information management system designed for the personal computer. SMARTLAB tracks the completion status of every sample, from login to archiving of the results. SMARTLAB identifies what samples are in the laboratory; what preparations have to be performed; what analyses have to be run; and what samples have been completed. When a sample is completed and the results approved, reports and invoices may be automatically generated. Old sample data and complete chain-of-custody documentation can be archived on floppy disk and accessed as needed. Figure 5 illustrates the main functions of SMARTLAB.

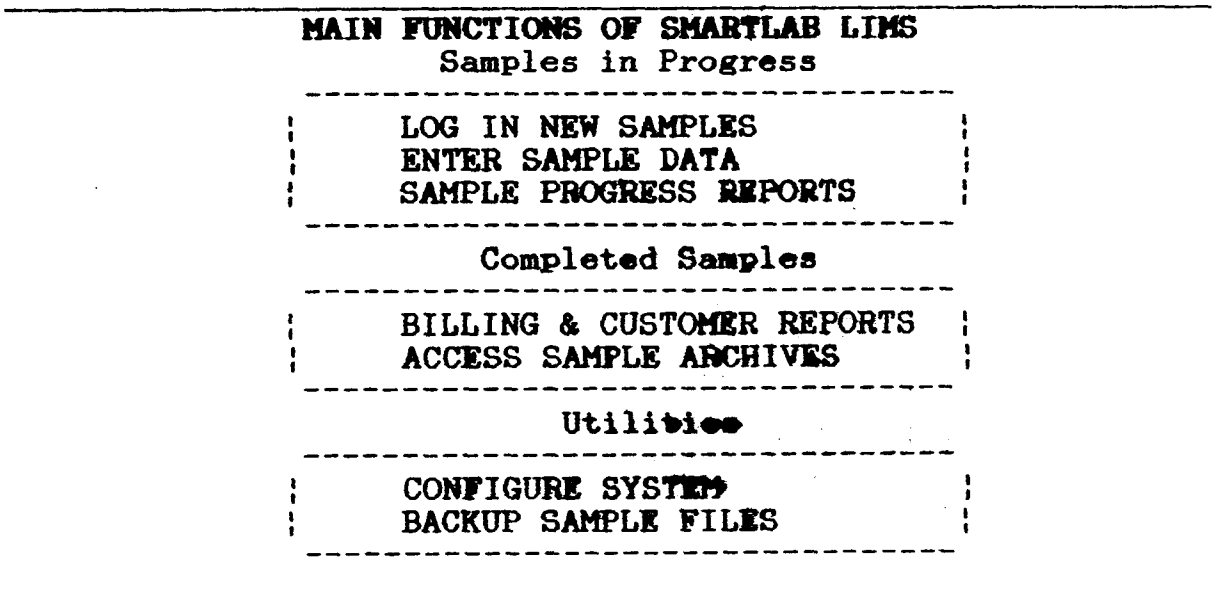


Figure 5. SMARTLAB Main Menu.

All of the functions of SMARTLAB are accessed by making a selection from the main menu. The choices clearly designate basic laboratory functions. There are no hidden commands to memorize. Functions under a main heading are similarly accessed by selecting from a clearly labeled menu. Further control is exercised by selecting one of 10 labeled function keys, similar to that already illustrated for SMARTLOG.

SMARTLAB: ENTRY OF SAMPLE INFORMATION

Many details must be entered into a sample entry log, if complete documentation and definition of the sample is to be maintained. Complete name and address information for the client, sample collection details, and of course, the tests to be performed on the sample, must all be entered. An example of the information to be entered for a sample is shown in Figure 6.

SAMPLE LOGIN INFORMATION

Client information:

Client Ajax Manufacturing Company
Quality Control Department
Address 1500 Broadway
Suite A
City Denver **State** CO **Zip** 80001

Contact Dan Wallace **Phone** (303)555-8500

Sample information: **Description** effluent **Trend** platte
QC Reference

Collection information: **Location** Platte River outlet #1
by Whom K. Jones
Preservation method refrigeration

Test information:

SECTION	TEST	FEE ($)
metals	As	15.00
metals	Pb	15.00
organic	2,4-D	25.00
organic	endrin	25.00
wet	F	15.00
wet	NO3	15.00

Figure 6. Client & sample information stored in SMARTLAB.

The goal for using a computer for laboratory information management is to expedite the handling of data and information. This includes information entry, as well as information access. SMARTLAB provides two means to speed the process of information entry. When multiple samples from the same client are logged in at the same time, one key stroke will copy information from a previous sample into the record for each additional sample. And where a regular client is concerned, login is even simpler. By typing in the client ID, all of the client details are instantly looked up, and automatically entered. Frequently encountered series of analyses can similarly be identified and automatically entered into the log. Even client-specific pricing will be recalled and used at invoicing time.

SMARTLAB: DETERMINING SAMPLE STATUS

One of the most powerful benefits of SMARTLAB is its ability to determine the status of samples in the laboratory. SMARTLAB maintains cross-referenced sample indices, listing the samples in a variety of useful orders. Samples may be displayed in any of the menu selectable orders by simply selecting the desired report from the Progress Report menu, shown in Figure 7. This mode may also be used to generate lists of work to be done in each analysis section of the laboratory. Examples of some of the progress report options are shown in Figures 8 through 11.

SAMPLE PROGRESS REPORTS

Printed Reports

Sample Analysis Backlog by:	==>Lab #
	Client
	Test
	Due Date
	Anal Method
Sample Prep Backlog by:	Prep Method

Screen & Printed Reports

Selected Test Status by:	Lab #
	Client
	Section
	Test
	Anal Method
	Prep Method
	CUSTOMIZED

Figure 7. SMARTLAB report selection menu.

ANALYSIS BACKLOG BY LAB NUMBER December 10, 1986

lab #	client	description	due date	section test
610032	Western Utilities Company	boiler water	11/29/86	metals Ca
		boiler water	11/29/86	metals Cu
		boiler water	11/29/86	metals Fe
		boiler water	11/29/86	metals Mg
610033	Western Utilities Company	boiler water	11/29/86	metals Ca
		boiler water	11/29/86	metals Cu
		boiler water	11/29/86	metals Fe
		boiler water	11/29/86	metals Mg
610103	Burrow Enterprises	ore	11/25/86	metals Ag
		ore	11/25/86	metals Au
		ore	11/25/86	metals Cu
		ore	11/25/86	metals Mo
610104	Burrow Enterprises	ore	11/25/86	metals Ag
		ore	11/25/86	metals Au
		ore	11/25/86	metals Cu
		ore	11/25/86	metals Mo
610116	Waterford Engineering Laboratory	ground water	12/06/86	metals As
		ground water	12/06/86	metals Pb
		ground water	12/06/86	organic 2,4_D
		ground water	12/06/86	organic endrin
		ground water	12/06/86	wet F
		ground water	12/06/86	wet NO3
610117	Waterford Engineering Laboratory	ground water	12/06/86	metals As
		ground water	12/06/86	metals Pb
		ground water	12/06/86	organic 2,4_D
		ground water	12/06/86	organic endrin
		ground water	12/06/86	wet F
		ground water	12/06/86	wet NO3
610118	Ajax Manufacturing Company	effluent	12/07/86	metals As
		effluent	12/07/86	metals Hg
		effluent	12/07/86	organic chloroform
		effluent	12/07/86	wet CN
610119	Ajax Manufacturing Company	effluent	12/07/86	metals As
		effluent	12/07/86	metals Hg
		effluent	12/07/86	organic chloroform
		effluent	12/07/86	wet CN
610120	Western Utilities Company	boiler water	12/08/86	metals Ca
		boiler water	12/08/86	metals Cu

Figure 8. List of incomplete samples sorted by laboratory number.

ANALYSIS BACKLOG BY TEST AND DUE DATE December 10, 1986

section	test	lab #	client	description	due date
organic	2,4_D	610116	Waterford Engineering Laboratory	ground water	12/06/86
		610117	Waterford Engineering Laboratory	ground water	12/06/86
metals	Ag	610103	Burrow Enterprises	ore	11/25/86
		610104	Burrow Enterprises	ore	11/25/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610126	Geophysical Exploration, Incorpo	sediment	12/10/86
metals	As	610116	Waterford Engineering Laboratory	ground water	12/06/86
		610117	Waterford Engineering Laboratory	ground water	12/06/86
		610118	Ajax Manufacturing Company	effluent	12/07/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610126	Geophysical Exploration, Incorpo	sediment	12/10/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610131	Ajax Manufacturing Company	effluent	12/13/86
metals	Au	610103	Burrow Enterprises	ore	11/25/86
		610104	Burrow Enterprises	ore	11/25/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610126	Geophysical Exploration, Incorpo	sediment	12/10/86
metals	B	610121	Brown Farms	soil	12/09/86
		610125	Brown Farms	soil	12/12/86
		610127	QC	soil	12/10/86
metals	Ca	610032	Western Utilities Company	boiler water	11/29/86
		610033	Western Utilities Company	boiler water	11/29/86
		610120	Western Utilities Company	boiler water	12/08/86
organic	chloroform	610118	Ajax Manufacturing Company	effluent	12/07/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610131	Ajax Manufacturing Company	effluent	12/13/86
wet	CN	610118	Ajax Manufacturing Company	effluent	12/07/86

Figure 9. List of incomplete samples sorted by test.

SAMPLE PREPARATION BACKLOG — December 10, 1986

prep method	test	lab #	client	description	due date
acetate leach	B	610127	QC	soil	12/10/86
		610121	Brown Farms	soil	12/09/86
		610125	Brown Farms	soil	12/12/86
	Mn	610127	QC	soil	12/10/86
		610125	Brown Farms	soil	12/12/86
		610121	Brown Farms	soil	12/09/86
	Mo	610127	QC	soil	12/10/86
		610125	Brown Farms	soil	12/12/86
		610121	Brown Farms	soil	12/09/86
	NO3	610121	Brown Farms	soil	12/09/86
		610125	Brown Farms	soil	12/12/86
		610127	QC	soil	12/10/86
	P	610121	Brown Farms	soil	12/09/86
		610125	Brown Farms	soil	12/12/86
		610127	QC	soil	12/10/86
benzene extract	2,4_D	610117	Waterford Engineering Laboratory	ground water	12/06/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
	chloroform	610129	Ajax Manufacturing Company	effluent	12/13/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
		610118	Ajax Manufacturing Company	effluent	12/07/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610131	Ajax Manufacturing Company	effluent	12/13/86
	endrin	610116	Waterford Engineering Laboratory	ground water	12/06/86
		610117	Waterford Engineering Laboratory	ground water	12/06/86
distillation	CN	610119	Ajax Manufacturing Company	effluent	12/07/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
		610131	Ajax Manufacturing Company	effluent	12/13/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610118	Ajax Manufacturing Company	effluent	12/07/86
	F	610117	Waterford Engineering Laboratory	ground water	12/06/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
HNO3 digestion	Ag	610103	Burrow Enterprises	ore	11/25/86
		610104	Burrow Enterprises	ore	11/25/86
		610126	Geophysical Exploration, Incorpo	sediment	12/10/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86
	As	610130	Ajax Manufacturing Company	effluent	12/13/86
		610118	Ajax Manufacturing Company	effluent	12/07/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86

Figure 10. List of incomplete sample preparations.

ANALYSIS BACKLOG BY ANALYTICAL METHOD December 10, 1986

anal method	test	lab #	client	description	due date
Ag titration	CN	610131	Ajax Manufacturing Company	effluent	12/13/86
		610118	Ajax Manufacturing Company	effluent	12/07/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
	F	610116	Waterford Engineering Laboratory	ground water	12/06/86
		610117	Waterford Engineering Laboratory	ground water	12/06/86
brucine	NO3	610127	QC	soil	12/10/86
		610117	Waterford Engineering Laboratory	ground water	12/06/86
		610121	Brown Farms	soil	12/09/86
		610125	Brown Farms	soil	12/12/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
cold vapor	Hg	610118	Ajax Manufacturing Company	effluent	12/07/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
		610131	Ajax Manufacturing Company	effluent	12/13/86
		610130	Ajax Manufacturing Company	effluent	12/13/86
		610129	Ajax Manufacturing Company	effluent	12/13/86
		610128	Ajax Manufacturing Company	effluent	12/13/86
flame AA	Ag	610126	Geophysical Exploration, Incorpo	sediment	12/10/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
	Au	610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610124	Geophysical Exploration, Incorpo	sediment	12/07/86
		610126	Geophysical Exploration, Incorpo	sediment	12/10/86
		610123	Geophysical Exploration, Incorpo	sediment	12/07/86
furnace AA	As	610122	Geophysical Exploration, Incorpo	sediment	12/07/86
		610119	Ajax Manufacturing Company	effluent	12/07/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
	Pb	610117	Waterford Engineering Laboratory	ground water	12/06/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
GC	2,4_D	610117	Waterford Engineering Laboratory	ground water	12/06/86
		610116	Waterford Engineering Laboratory	ground water	12/06/86
ICP	B	610127	QC	soil	12/10/86
		610125	Brown Farms	soil	12/12/86
		610121	Brown Farms	soil	12/09/86

Figure 11. List of incomplete analyses, sorted by analytical method.

SMARTLAB: CUSTOMIZABLE REPORTS & INVOICES

SMARTLAB will automatically find completed samples, print out the results in a report, and if desired, automatically generate an invoice. The form of the sample report and invoice are easily customizable to your preferred format. Figures 12 and 13 illustrate the standard format for analytical reports and invoices.

GOLDEN ANALYTICAL SERVICES, INC.
P.O. Box 1486 * Golden, Colorado 80043

phone: (303) 555-2100

- SAMPLE ANALYSIS REPORT -

To: Burrow Enterprises
Route 2
Box 955
Cheyenne WY 89335

Attn: Ed Burrow (490) 888-5525

Our Lab No: 610101 Report Date: 12/10/86
Sample Description: ore
Your Sample ID: sample 1

COLLECTION INFORMATION
Date/Time/Location: 11/15/86 10:15 am Claim N5W
Collected by/Preserved by: E.B.

ANALYSIS RESULTS

TEST	RESULTS	TEST	RESULTS
Ag	28 oz/ton		
Au	12 oz/ton		
Cu	57 oz/ton		
Mo	93 oz/ton		

All methods in accordance with Environmental Protection Agency recommended procedures.

Submitted:
GOLDEN ANALYTICAL SERVICES, INC.

Chemist

Figure 12. SMARTLAB sample analysis report

GOLDEN ANALYTICAL SERVICES, INC.
P.O. Box 1486
Golden, Colorado 80043
phone (303) 555-2100

To: Burrow Enterprises
Route 2
Box 955
Cheyenne WY 89335

Invoice date 12/10/86
Attn: Accounts Payable
Invoice no. 144207

- INVOICE -

Lab #	Submitted	Sample Identification	Charge
		Burrow Enterprises	
610101	11/19/86	sample 1	$47.96
610102	11/19/86	sample 2	$30.56
		Total	$78.52

Terms: net 30
Thank you.

Figure 13. SMARTLAB standard invoice.

In addition to the reports and invoices which go out to your customers, SMARTLAB can generate useful in-house accounting reports, such as the accounts receivable report, shown in Figure 14.

GOLDEN ANALYTICAL SERVICES, INC.
- ACCOUNTS RECEIVABLE -
Samples Completed and Billed

client	lab #	inv #	invoice date	charges
Ajax Manufacturing Company	610016	144204	11/27/86	$140.20
	610114	144205	11/28/86	$48.00
			Client Total	$188.20
Burrow Enterprises	610101	144207	12/10/86	$47.96
	610102	144207	12/10/86	$30.56
			Client Total	$78.52
Western Utilities Company	610113	144206	11/28/86	$32.00
	610110	144206	11/28/86	$32.00
	610112	144206	11/28/86	$32.00
			Client Total	$96.00
			Total Receivables	$362.72

Figure 14. SMARTLAB accounts receivable report.

SMARTLAB: ACCESS TO SAMPLE DOCUMENTATION

The completion of a sample does not mean that there will never be a need to review the results. Further, for environmental and legal work, it is becoming more and more important to document the movement and treatment of every sample, with name, date, and treatment information ("chain-of-custody"). SMARTLAB saves all completed sample information on the system's hard disk storage, with long-term archiving possible on floppy disk. Figures 15 and 16 show examples of archived sample results and chain-of-custody.

SAMPLE ARCHIVES REPORT for:

Ajax Manufacturing Company
Quality Control Department
1500 Broadway
Suite A
Denver CO 80101
Joe Collier (303) 555-8500

Lab # 610016
Logged in: 10/28/86
Completed: 11/19/86
Description: effluent
Sample ID: Platte #1-861025

TEST	RESULTS
As	38 ug/L
Cr	58.2 ug/L
Hg	0.4 ug/L
Pb	25 ug/L
Se	83.8 ug/L
chloroform	0.71 ug/L
meth chloride	1.63 ug/L
toluene	5.1 ug/L
vinyl chloride	0.81 ug/L
CN	26.4 ug/L
F	73 ug/L

Figure 15. SMARTLAB sample archives.

Chain-of-Custody Report

Lab #: 610016
Description: effluent
Sample ID: Platte #1-861025

Ajax Manufacturing Company
Denver CO 80101

COLLECTION INFORMATION

Date/Time/Location: 10/25/86 3 pm Platte River output #1
Collected by/Preserved by: K. Jones refrigeration

LABORATORY HANDLING INFORMATION

Test	Sample Preservation	Sample Preparation	Sample Analysis	Approval
As	0.5% HNO3	HNO3 digestion	furnace AA	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
Cr	0.5% HNO3	HNO3 digestion	ICP	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
Hg	0.5% HNO3	HNO3 digestion	cold vapor	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
Pb	0.5% HNO3	HNO3 digestion	furnace AA	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
Se	0.5% HNO3	HNO3 digestion	furnace AA	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
chloroform	refrigeration	benzene extract	GC	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
meth chloride	refrigeration	benzene extract	GC	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
toluene	refrigeration	benzene extract	GC	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
CN	refrigeration	distillation	Ag titration	
	KLG 10/28/86	RAN 10/28/86	DLB 10/28/86	RDB 11/19/86
F	refrigeration		ion electrode	
	KLG 10/28/86		DLB 10/28/86	RDB 11/19/86

Figure 16. SMARTLAB chain-of-custody report.

MAINTENANCE OF LABORATORY QC DOCUMENTATION

Both SMARTLOG and SMARTLAB offer similar QC capabilities. In SMARTLAB access to QC routines is available to the user at the time that sample results are approved, thus providing the necessary information to make an informed decision on the validity of the results. Standard techniques of quality control addressed by SMARTLOG and SMARTLAB include: determination of spike recovery, repeatability of replicate analyses, and agreement of results with known or certified values. Tabulated and graphed quality control documentation can be stored for later reference and printed for distribution.

Control of the QC function is exercised by first identifying the QC samples in the data base. This is done by providing a "QC Reference" name in the designated field of a sample record. For spiked samples, a spike value must also be indicated in the data field provided. In addition to standard quality control procedures, long-term trends for designated samples may be monitored by entering a "Trend" name in the data field provided for this purpose.

When the user wishes to process QC or Trend information, the desired data is isolated from all other data in the data base by selecting a specified QC or Trend name. Then by simply depressing the labeled function key indicating the desired QC technique, calculations are performed and the data is tabulated in a standard format determined by the quality control procedure selected. Figures 17 through 20 present examples of printed output from the QC routines.

In addition to the standard QC displays, both tables and graphs are customizable to accomplish various additional graphing and tabulating functions, which might be required by a particular laboratory. A graph generation utility aides the user in designing custom graphs.

For laboratories involved in the Contract Laboratory Program or who wish to report data in the CLP format, a new quality control report option, which will automatically generate CLP reports and quality control forms, is under development. When complete, this option will automatically determine the flags to be appended to data, as well as generate all of the QC forms to be submitted to the EPA. Working prototypes based on the current CLP protocols have been demonstrated. Completion of this work is pending the establishment of the new protocols by the EPA.

GENERAL SOFTWARE TOOLS FOR THE LABORATORY

SMARTLOG and SMARTLAB are dedicated laboratory software programs. A user may operate these programs fully, without any knowledge of the software system used. However, for those who wish to use it, additional capability exists.

SMARTLOG and SMARTLAB were written around Innovative Software's SMART System, an integrated software package providing a word processor, data base manager, spreadsheet, communications capability, and more. SMART was hand picked as a basis for Telecation's laboratory software, due to its power, speed and programmability. As a result, all of the functions of SMART are available to the SMARTLOG or SMARTLAB user. In addition, many of the features of SMARTLOG and SMARTLAB may be customized beyond the utilities provided, by the experienced SMART user. All of the documentation which accompanies the SMART system is provided to assist the user, who wishes to take advantage of this capability.

SPIKE RECOVERY

lab #	test	units	result	spike	Recovery	% Recovery
610032	Ca	ug/L	1000.0	0.0		
610033	Ca	ug/L	1090.0	100.0	90.0	90.0
610032	Cu	ug/L	20.0	0.0		
610033	Cu	ug/L	48.0	25.0	28.0	112.0
610032	Fe	ug/L	30.0	0.0		
610033	Fe	ug/L	74.0	50.0	44.0	88.0
610032	Mg	ug/L	2000.0	0.0		
610033	Mg	ug/L	2487.0	500.0	487.0	97.4

Figure 17. Spike recovery table.

QUALITY CONTROL TABLE
Lead Precision

lab #	test	units	result	Average	- 10 %	+ 10 %
610227	Pb	ug/L	26.0	25.2	22.7	27.7
610228	Pb	ug/L	24.6	.	.	.
610229	Pb	ug/L	24.2	.	.	.
610230	Pb	ug/L	25.6	.	.	.
610231	Pb	ug/L	28.8	.	.	.
610232	Pb	ug/L	23.2	.	.	.
610233	Pb	ug/L	23.4	.	.	.
610234	Pb	ug/L	24.2	.	.	.
610235	Pb	ug/L	26.7	.	.	.
610236	Pb	ug/L	25.3	25.2	22.7	27.7

Figure 18. Quality control table.

Figure 19

SMARTLAB

Lead Quality Control Chart
Precision Range: +/- 10%

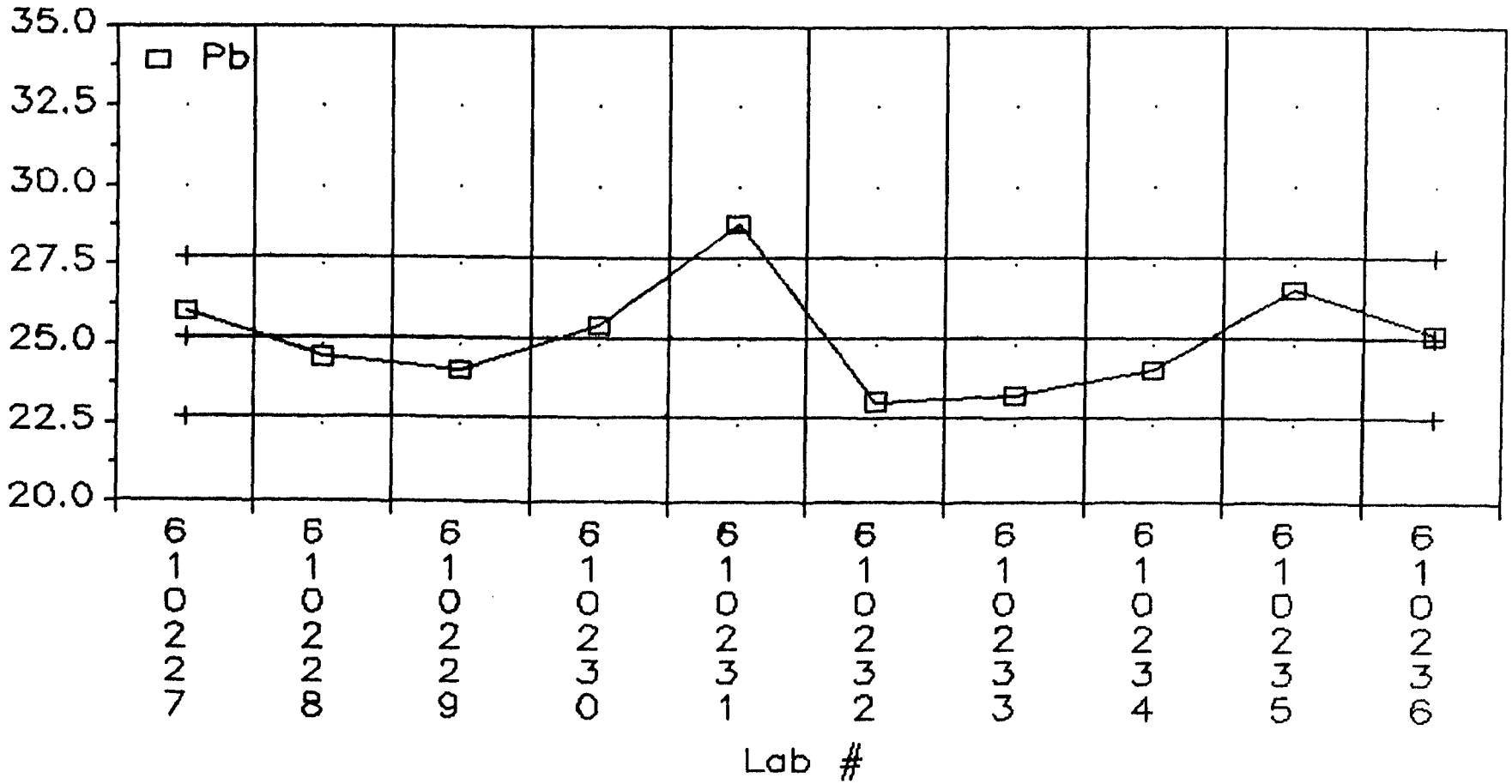
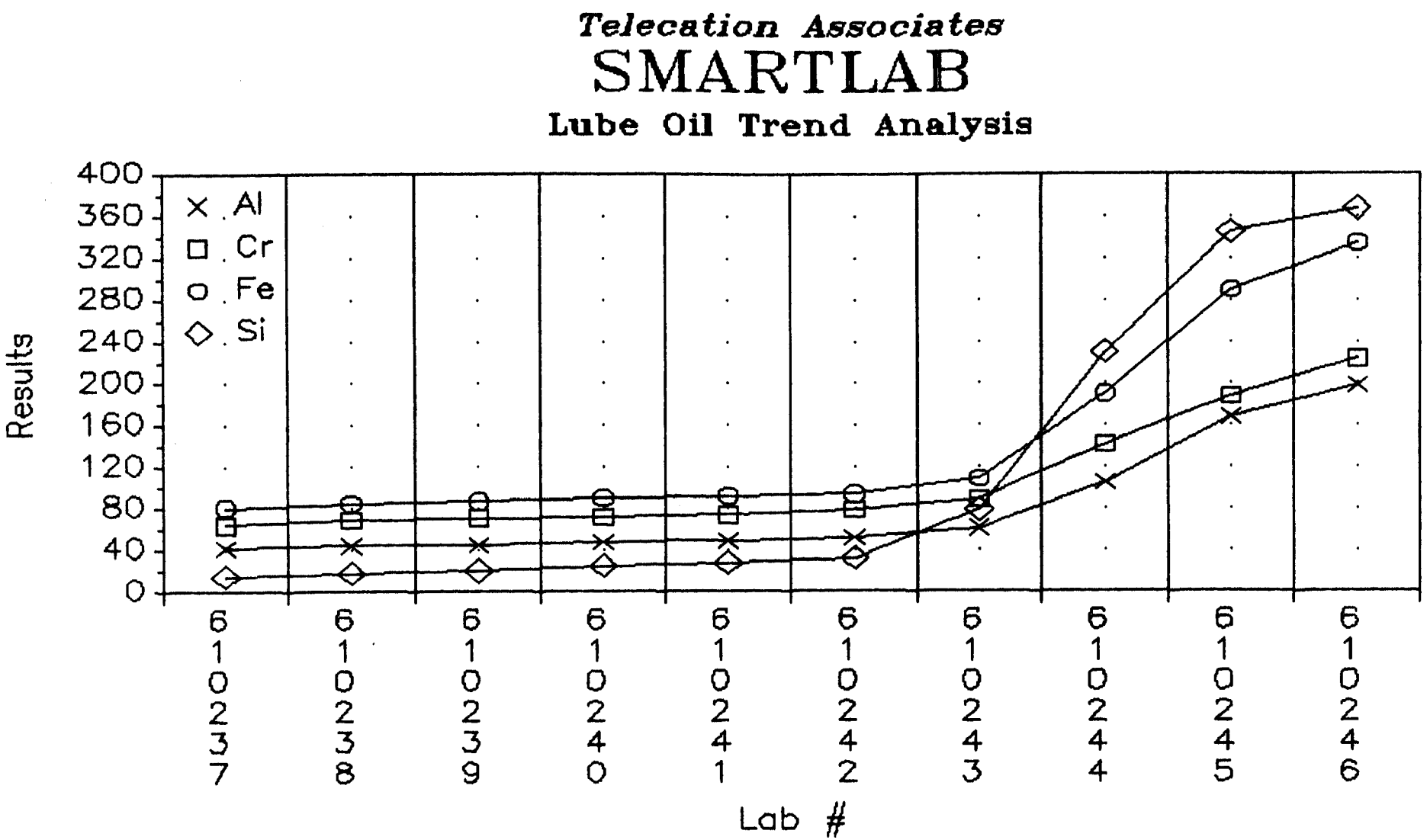


Figure 20


Telecation Associates
SMARTLAB
Lube Oil Trend Analysis
Results
400
360
320
280
240
200
160
120
80
40
0
Al
Cr
Fe
Si
6102437
6102438
6102439
6102440
6102441
6102442
6102443
6102444
6102445
6102446
Lab #

LABORATORY AND FIELD AUDITS AS PART OF THE EPA HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY (HWERL) QUALITY ASSURANCE PROGRAM

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ABSTRACT

Audits are an important and integral part of the EPA HWERL Quality Assurance Program. As part of this overall QA Program, audits are used to determine contractor compliance with quality assurance plans and to assess the overall quality of data collected during data gathering or data generation activities. Additionally, audits are useful in evaluating the procedures used in collecting and analyzing samples, in all facets of data quality, and in management of the activity. Often, an audit of a sampling or analytical activity will reveal a problem which otherwise may have gone undetected until the end of the project. In such cases, on-site Corrective Action Recommendations are made.

Four different types of audits are performed under the EPA HWERL QA Program: Management Systems Audits (MSA), Technical Systems Audits (TSA), Performance Evaluation Audits (PEA), and Audits of Data Quality (ADQ). Such audits of HWERL projects are conducted by the Quality Assurance Officer or a designated representative. Each type of audit has established Standard Operating Procedures and has a well-defined direction in evaluating a particular aspect of field and/or laboratory operations.

INTRODUCTION

Audits are an important and integral part of the EPA Hazardous Waste Engineering Research Laboratory (HWERL) Quality Assurance Program. As part of this overall QA Program, audits are used to determine the compliance of contractors, in-house groups, and academic groups with previously approved Quality Assurance Program and/or Project Plans. Also, audits can be implemented to assess the overall quality of data collected during data gathering or data generation activities, in evaluating sampling and analytical procedures, and assessing the management of an activity.

Four different types of audits are conducted under the HWERL QA Program:

(1) *Technical Systems Audit (TSA)* - a qualitative on-site evaluation of all components of the measurement systems, including personnel.

(2) *Performance Evaluation Audit (PEA)* - a quantitative evaluation of critical measurements through an organization's analysis of Performance Evaluation (PE) samples.

(3) *Audit of Data Quality (ADQ)* - an on-site assessment of the methods used to collect, interpret, and report the information used to characterize data quality.

(4) *Management Systems Audit (MSA)* - an on-site evaluation of an organization's quality assurance management system.

In general, audits of HWERL projects are performed by the Quality Assurance Officer (QAO), or by a designated representative.

AUDIT DESCRIPTION AND PROCEDURES

Technical Systems Audit

The Technical Systems Audit (TSA) is one of the most utilized types of audits of the four types of HWERL audits. All aspects of sampling or data generation can be evaluated and the TSA may be project-specific or organization-specific. The TSA is particularly valuable in that it can be quickly implemented and completed, thus identifying potential problems and recommending corrective action while the subject project is still in progress. The TSA is conducted by one or two scientists or engineers, depending upon the nature of the project. These reviewers are generally chosen on a project-specific basis, based upon a combination of their quality assurance and related technical expertise. The QA Project Plan provides the basis for the audit, which generally takes one to two days to complete.

Some questions which may be of relevance to a TSA include:

- Is the project adequately staffed with personnel of relevant background to accomplish the objectives of the project? Is project organization and management sufficient to meet these same objectives?

- Does the organization devote sufficient resources and personnel (i.e., a Quality Assurance Officer) to an established Quality Assurance Program?

- Is the equipment used on the project being used for the purpose for which it was intended and is it being used properly?

- Are proper chain-of-custody and sample handling procedures being followed?

- Are personnel involved with the project knowledgeable, properly trained, and adequately supervised?

- Are the facilities being used sufficient to meet the needs of the project?

- Are sampling and analytical equipment being maintained properly, calibrated properly, and used in an appropriate manner?

- Are quality assurance and quality control procedures outlined by the organization in such documents as Work Plans and Quality Assurance Project Plans being followed according to planned procedures?

- Do standard operating procedures exist and are they up to date and complete?

- Do data validation procedures exist and is there sufficient review of data to minimize reporting of calculation errors?

- Is documentation of sampling and analytical procedures, data, QA/QC information, and corrective action adequate and well organized?

The audit proceeds in five phases:

(1) A pre-visit planning phase is begun where the reviewers familiarize themselves with relevant documents (i.e., QA Project Plan) and make contact with on-site project management. A *Pre-Visit Worksheet* is sent to project

management, which is returned to the reviewers prior to the site visit. This worksheet provides the reviewers with current information regarding project organization, personnel, and equipment, as well as any changes to procedures given in the QA Project Plan.

(2) The site visit begins with an initial meeting conducted by the reviewers and attended by key project personnel. Review procedures and objectives are discussed and an agenda is agreed upon. Following this discussion, the QA Project Plan is examined and questions or clarifications needed by the reviewers are addressed.

(3) A facilities tour is conducted where project-related measurement equipment is viewed and responsible analysts are interviewed. In the case of a sampling effort review, sampling equipment and locations are seen. If possible, actual sampling and analytical work in progress is observed.

(4) A review of documentation and data handling procedures is conducted. Usually, this is accomplished by selecting one or more samples at random and tracing their progress through sampling and analytical procedures and up to final data reporting.

(5) Following an adjournment where the reviewers assimilate notes and observations, a debriefing and summary meeting is held. The reviewers discuss concerns and rank them in order of importance (i.e., critical, major, and minor). Project personnel are encouraged to engage in a constructive discussion with the reviewers and offer clarifications or additional information to the reviewers in response to the noted concerns. In concluding this meeting, and in consideration of discussions with project personnel, Corrective Action Recommendations (CAR) may be made. These are documented, on site, on a CAR Form (Figure 1). The HWERL Technical Project Officer receives this form within three days and is responsible for implementation and follow-up of any identified corrective action.

6.6.2

CORRECTIVE ACTION RECOMMENDATION (CAR) FORM FOR HWERL

Lab Workplan No: ☐☐☐☐☐☐ Project Category:_____

QA I.D. No.:_____

Organization Reviewed:_____

Project Title:_____

_____

Reviewer:_____ Affiliation:_____

Review Type:_____ On-Site Location:_____

Rating:_____ Technical PO:_____

I. Date Problem Identified:_____

Problem serious enough that Part II must be completed by the HWERL technical project officer and submitted to the HWERL QA Officer? Yes ____ No ____

Nature of Problem:

Recommended Action:

Corrective Action Recommendation Form (Part I) has been reviewed by the organization's on-site representative:

Signature: _____ Date:_____

(Organization's On-Site Representative)

II. Date Corrective Action Taken:

Summary of Corrective Action:

QA Activity Implemented to Prevent Future Occurrences:

Effectiveness of Corrective Action:

Signature (HWERL technical PO):_____ Date:_____

HWERL (CAR)
(April 1987)

Figure 1. Corrective Action Recommendation (CAR) Form

Within one week following the on-site portion of the TSA, the reviewing group submits to the reviewed group a Draft TSA Summary Report detailing the positive aspects of the review, any concerns ranked by order of importance, and any corrective action recommendations, along with an audit rating (see Table 1). The reviewed group is allowed one week to read and respond to the TSA Summary Report. This response is included with the Final TSA Summary Report, which is then forwarded to the HWERL Technical Project Officer with a copy to the HWERL QAO. An important aspect of the HWERL TSA procedure is that the review is conducted, corrective action recommendations made on site via the CAR Form, and a report submitted to the HWERL Technical Project Officer in about three weeks. This timeliness allows for prompt resolution of any problems which may be present and gives the Technical Project Officer an immediate assessment of the quality of sampling and analytical activities associated with the subject project.

Performance Evaluation Audit

A Performance Evaluation Audit (PEA) is a quantitative evaluation of measurement systems. Usually, only the most critical measurements, as designated in the QA Project Plan, are evaluated. The PEA involves measurement or analysis of a reference material having associated with it a known value or composition. The value or composition of the reference material is certified, or at least verified, prior to use. The USEPA Environmental Monitoring and Support Laboratory in Cincinnati is active in preparation and certification of these materials.

Among the questions that may be determined from a PEA are:

- What is the bias and precision of the measurement system at the time of the audit?
- Under the ideal conditions presented in analysis of a performance evaluation sample, are the results generated by a given instrument and from a given method under control?
- If the results of previous audits are available, has data quality significantly changed?

Ideally, the performance evaluation sample should be submitted as a blind sample so that it receives treatment similar to other routine samples. The sample may be analyzed with an audit team present so that the actual

procedures used and the abilities of specific project personnel can be evaluated. The PEA is conducted as follows:

(1) Submission of performance evaluation sample to the laboratory.

(2) Results are returned to HWERL and subjected to a statistical analysis involving between-laboratory analysis. Results are considered acceptable if they are within defined limits (see Table 2).

(3) If results are rated *Conditionally Acceptable* or *Not Acceptable,* corrective action is required of the subject laboratory. Such corrective action must be documented and submitted to the HWERL Project Officer and QAO for approval.

(4) HWERL then approves the corrective action or makes further recommendations.

A PEA does not provide any information on overall project documentation or implementation of quality assurance because it is very narrow in scope. It can be very complimentary to a TSA because it provides quantitative data to supplement the qualitative data generated during the TSA.

Audit of Data Quality

Due to several major weaknesses observed in the field application of Audits of Data Quality (ADQ), HWERL has not undertaken such audits during FY86 and FY87. Instead, HWERL is involved in development of a different strategy for ADQs. The positive, comprehensive approach developed by HWERL to conduct Audits of Data Quality (ADQ) is a structured two-tiered approach. The first tier consists of a multipart questionnaire and rating scheme that enables the qualitative assessment of the sufficiency of verifiable documentation of data and their associated data quality indicators (e.g., precision, accuracy, representativeness, completeness, comparability, limits of detectability). The second tier consists of a two-part questionnaire and rating scheme that enables quantitative evaluation of data quality and end-user data acceptability. The HWERL ADQ approach combines many of the advantages of other approaches, including:

- The use of three-valued logic (*Yes/no/not applicable*), to minimize subjectivity.

- The use of weighted ratings, to emphasize the most critical evaluators of data quality.

- well-defined point-scoring and rating schemes, to provide unambiguous and comparable audit results.

- Well-defined acceptance criteria, to establish clear reference points from which corrective action decisions or other administrative judgment calls can be made.

- Independent rating of typical subsections of the questionnaires, to enable detailed evaluation of project strengths and localized identification of problem areas.

Management Systems Audit

The Management Systems Audit (MSA) is not presently performed by HWERL; rather, it has historically been performed by either EPA's Quality Assurance Management Staff (QAMS) or Office of Environmental Engineering and Technology Demonstration (OEETD). The audit is to investigate HWERL QA procedures. An evaluation of the adequacy of the internal management systems necessary for the successful implementation of a quality assurance program is made. Since HWERL does not conduct these audits, detailed procedures are not described here.

RESULTS OF FY86 AND FY87 AUDITS

Following the completion of a TSA or PEA, an evaluation rating will be assigned. These ratings and the corrective actions required are given in Tables 1 and 2. It should be noted that HWERL policy dictates that measurement work should not proceed for projects given *Conditionally Acceptable* or *Not Acceptable* review or audit ratings. Only deficient measurement systems may be stopped where other measurement systems within a project are acceptable. Also, work may not be stopped at all if data quality would further suffer through this action and corrective action can be quickly and easily implemented.

Table 3 gives a summary of the types of audits conducted in FY86 and FY87 and the ratings given.

Table 1. HWERL Rating System for TSA

Rating	Explanation/Action Required by the Technical Project Officer	Status of Measurements
Acceptable	None	Work Proceeds
Acceptable with Qualifications	Minor deficiencies are revealed by the audit. Minimum criteria are satisfied and good data quality seems likely; qualifications on the possible limitations of the data are noted and some corrective actions may be recommended. The recommendations may be implemented at the Technical Project Officer's discretion.	Work Proceeds
Conditionally Acceptable	Major concerns are identified by the audit. Corrective action* is required by the Technical Project Officer to ensure quality results	Measurement work should not proceed for Category I or II Projects.**
Not Acceptable	Critical deficiencies are revealed by the audit that require the Technical Project Officer to take substantial corrective action* before measurement work proceeds.	Measurement work should not proceed until deficiencies are resolved.

* Part II of the Corrective Action Recommendation Form is to be used by the Technical Project Officer in documenting the resolution of cited deficiencies.

** Category III and IV Projects: Measurement work may proceed, but the deficiencies that were cited in the audit report must be resolved within thirty (30) days. If the deficiencies are not resolved during the 30-day grace period, then the measurement work should not proceed.

Table 2. HWERL Rating System for PEA

Rating	Explanation/Action Required by Technical Project Officer
Acceptable	All critical measurements are within a 99 percent confidence interval calculated from available performance evaluation data of EPA and State laboratories.
Conditionally Acceptable	Eighty percent or more of the critical measurements are within the above-cited 99 percent confidence interval. Those critical measurements which are outside of the confidence interval are identified for corrective action at the direction of the Technical Project Officer.
Not Acceptable	Less than 80 percent of the critical measurements are within the above-cited 99 percent confidence interval. The project, itself, is flagged and those critical measurements which are outside of the confidence interval are identified for corrective action at the direction of the Technical Project Officer.

Note: Measurements which are not critical to meeting the project's QA objectives and which are not within the 99 percent confidence interval are flagged, but do not affect the rating.

Table 3. HWERL Audits in FY86 and FY87[1]

Audit Type	Number Conducted	Rating[2]			
		A	A/Q	C/A	N/A
TSA	14	4	3	5	2
PEA	30	7	-	21	2

[1]Through June 1987

[2] A - Acceptable
A/Q - Acceptable with Qualifications
C/A - Conditionally Acceptable
N/A - Not Acceptable

REVIEW OF AUDITS AND ANALYSES IN NEW JERSEY'S LABORATORY CERTIFICATION PROGRAM

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ABSTRACT

The New Jersey Department of Environmental Protection administers a regulatory structure based on data of documented quality. One of the means by which the State controls and administers quality assurance activities is through the use of a State Laboratory Certification Program.

Analytical data submitted to the State by permit holders must be provided by Certified Labs. The current program registers 462 labs, certifies by categories (e.g. microbiology, organics, inorganics, wet/limited chemistry, radiation and bioassay), and covers activities under NPDES, RCRA, Safe Drinking Water Act and various State programs. Within categories, labs are also certified by instrument where appropriate (e.g. GC, GC/MS). The Certification program functions by use of audits and performance evaluation (PE) samples, and through data review and complaint procedures from permit bureaus.

The certification program currently registers 232 labs for drinking water analyses and 381 labs for water pollution work with approximately 147 labs using GC or GC/MS, 202 labs using AA, 27 labs ICAP and 10 labs using HPLC. Many of the labs tend to provide multiple services, and over 200 labs in the program offer microbiological services.

Evaluation of PE samples has indicated that labs have the most difficulty analyzing drinking water for Hg, $CHCl_3$, silvex, dibromochloromethane, 2, 4-D, fluoride, Ag and Ba, while for water pollution they met MeCL, Chlorobonzene, Total Residual Chloride and 1, 2-Dichloroethane. Auditing has revealed that the most common lab deficiencies are inadequate records, inadequate instrument tuning, errors in identification, problems with spikes, surrogates, recoveries and minimum detection limit, and blank contamination and inadequate standards.

INTRODUCTION

The New Jersey Department of Environmental Protection (DEP) administers numerous regulatory programs to protect the environment and public health. Effective administration of these programs is based on data of documented quality. The Department annually prepares a State Quality Assurance Program Plan which identifies the

processes which the Department quality assurance and quality control activities will follow to achieve this goal. This Program Plan and attendant work plan applies to all Department activities in environmental monitoring and clean-up under the Safe Drinking Water Act (SDWA), the Clear Water Act, RCRA, CERCLA, the Clean Air Act, etc. The state QA program uses several elements to control QA activities. These elements include the use of specialized QA/QC requirements in permits, use of QA Program Plans and Work Plans, administration of State analytical services contracts, use of lab and field audits and performance evaluation (PE) samples, and a State Laboratory Certification Program.

According to DEP's regulations, analytical data submitted to the State by permit holders must be provided by Certified Labs. This laboratory certification program was established in 1981 (1) and will be revised during 1987-88. The current certification program registers 462 labs, and covers activities under NJPDES, RCRA, SDWA and various State programs (e.g. A280 drinking water, ECRA). Specific areas of RCRA programs currently requiring certification include issues involving potable water, groundwater and NJPDES permits. The new laboratory certification regulations under promulgation will provide additional support for the RCRA program.

The laboratory certification program certifies by categories: microbiology, organics, inorganics, wet/limited chemistry, radiation and bioassays. Within categories, labs are also certified by instrument (e.g. GC, GC/MS, HPLC) and by method regulations will include several novel areas including: ames testing, sludge analyses, several areas in microbiology (beach and pool monitoring), potable water and RCRA programs (2).

Approximately 462 laboratories are in the program (Table 1) with approximately 147 labs providing GC data, 91 labs providing GC/MS data, 202 labs using AA, 27 labs using ICAP and 10 labs using HPLC. Over 200 labs in the program provide microbiological services with many labs providing multiple services. The certification program includes approximately 100 out of state labs including Canada. The certification program functions by use of audits and PE samples, with permit bureaus receiving QA data submitted within permit requirements. Typically, results from more than 28,000 organics analyses and 11,000 inorganics analyses are submitted annually through permitting, compliance and monitoring activities.

TABLE 1

CURRENT NUMBER OF LABORATORIES IN THE NEW JERSEY LABORATORY CERTIFICATION PROGRAM

Category	Number of Certified Labs
Micro	201
Ltd. Chemistry	411
Atomic Absorpt.	202
Gas Chromatography	147
Radiochemistry	7
Bioassay	18
Program	
Drinking Water	232
A280	46
Water Pollution	381
Radiochem	7
Bioassay	18

Laboratories entering the certification program submit a fee and application which is reviewed for credentials, qualifications, etc. Once the application is approved, a set of performance evaluation (PE) samples are sent. After a lab has correctly analyzed the set of PE samples, an on-site audit is conducted. When a lab has passed these procedures, it is then certified.

Once in the program, laboratories are audited (announced and unannounced) approximately once per year with emphasis placed on labs with inconsistent records, those handling high volume and/or sensitive work, and those for which we receive complaints or faulty data. These audits include verification of personnel, materials, adherence to regulations, and includes tracking of randomly picked actual sample numbers and data submitted by the lab to DEP, to verify results. Depending on the certification category, labs must also successfully analyze PE samples each year. Enforcement of the lab certification regulations include the use of fines, suspensions, decertification or combinations of them.

The lab certification regulations stipulate the procedures and/or methods to be used for analyses. For most analyses, including organics and inorganics, these methods are incorporated by reference from the Federal procedures in 40 CFR part 136 and 141. Within the context of the certification program methodologies, specific quality control items are required. These include the maintenance of control charts, spikes, duplicates, blanks, establishing a minimum detection limit, calibrations, correcting baselines, linearity checks of standards (and analyzing within the correct portions of

the curve) and analysis of PE's and standards. These and other items described below are some of the items routinely evaluated in auditing lab performance.

The Certification Program uses several quality control enforcement mechanisms, routine and semi-routine, to enforce the program and compliance of the laboratories in following prescribed methods and procedures. The routine part of the program consists of monitoring the analysis of PE samples for drinking water (SDWA and A280) and water pollution (NJPDES). In addition, labs and permittees participate in EPA's periodic assessment of matrix blank samples in DMR studies. Routine on-site audits are conducted to verify adherence to methods and regulations and to evaluate analytical QA/QC records. The credentials of responsible individuals and analysts are also reviewed and cross checked to be sure education is appropriate and degrees are from accredited schools. Part of the semi-routine enforcement involves investigating complaints from personnel outside DEP and from inside DEP from permit bureaus and/or data reviewers. These semi-routine procedures generally culminate in an extensive on-site investigation to verify adherence to the regulations and verify analytical results. Verification of analytical results involves taking sample data submitted to DEP and tracking this data through all the steps from when the sample entered the lab and was analyzed to when the data was forwarded. The audits are extremely thorough and labs must support the data generated.

The enforcement of provisions of these audits can culminate in a variety of actions ranging from administrative consent orders (ACO), fines, suspension and/or decertification depending on the severity of the findings. The most common problems encountered with labs are ranked in order of frequency: 1) failed PE's; 2) audit discrepancies (failures in adhering to methods and regulations); 3) and credentials/personnel problems. Occasionally, fraudulent activities are identified concerning falsification of data, analyses and records which will result in vigorous prosecution by the State.

The current number of laboratories applied or certified in the program are listed in Table 2 by instrumental parameter. This represents most of the analytical chemical work performed in the program. The monitoring of performance evaluation samples for drinking water and water pollution parameters has identified some characteristics of performance and discrepancies. Table 3 presents a summary of results of PE sample evaluation for drinking water parameters from 1982 to 1985. Although the number of labs in the studies increased over four years, the percent of labs with acceptable results remained relatively constant from 1983-1985. An example of some of the PE samples missed by laboratories is represented in Table 4. Although some of the water study analytes differ, two analytes (Bromodichloroethane - BCDM and Bromoform -

$CHBr_3$) appear to be commonly missed in both studies. The rationale for why analytes are not acceptably analyzed varies and ranges from solvent contamination (e.g., methylene chloride) to inadequate laboratory analyses in determining MDLs, linear ranges, following prescribed procedures, etc. Typical PE sample water study results are provided in Table 5. This represents the percent of laboratories achieving acceptable results for each analyte in drinking water. In this study $\geq$ 75% of the analyses conducted by labs were acceptable of almost 50% of the analytes. In Water Study 15 for water pollution PE analytes, $\geq$ 75% of the analytical results were acceptable from 31 out of 46 analytes (67%). Although the analytes, MDLS, procedures etc. vary between the PE water studies and analytes, the number of laboratories generally performing acceptably seems to average approximately 75-85%.

TABLE 2

CURRENT NUMBER OF LABORATORIES APPLIED OR CERTIFIED TO SUBMIT ANALYSIS TO DEP PER INSTRUMENTAL PARAMETER

GC/MS	91
GC	147
AA	202
ICAP	27
Ion Chromatography	91
HPLC	10

TABLE 3

SUMMARY OF DRINKING WATER STUDY PE RESULTS

	WS-010	WS-012	WS-014	WS-016
Study Year	1982	1983	1984	1985
Total Samples Run	1830	1830	2292	1964
% Acceptable	70	79	81	81
% With Error > 50%	15	19	13	6
% With Error > 25%	41	41	28	30
% With Error > 1%	57	74	72	78
Labs in Study	77	93	95	94

TABLE 4

EXAMPLES OF "PROBLEM" ANALYSIS IDENTIFIED IN PE SAMPLE STUDIES DURING 1985

Drinking Water (WS016)	% Acceptable	Water Pollution (WS015)	% Acceptable
Hg	55	MeCl	53
$CHCl_3$	55	Chlorobenzene	53
Silvex	58	Total Residual Chloride	55
DBCM	58	1,2-Dichloroethane	55
2,4-D	61	TCN	65
F	61	1,1,1-Trichloroethane	65
$CHBr_3$	63	$CHBr_3$	65
BDCM	68	Oil & Grease	68
Ag	72	BDCM	70
Ba	73	CCL_4	70

TABLE 5

NEW JERSEY WS016 RESULTS BY PARAMETER (1985 DRINKING WATER)

PARAMETER	% ACCEPTABLE
As	74
Ba	73
Cd	88
Cr	79
Pb	84
Hg	55
Se	76
Ag	72
NO_3	75
F	61
ENDRIN	86
LINRANE	83
MEXTHOXYCHLOR	89
TOXAPHENE	78
2,4-D	61
SILVEX	58
$CHCl_3$	55
$CHBr_3$	63
BROMODICHLOROMETHANE	68
DIBROMOCHLOROMETHANE	58

On-site audits constitute an important part of the compliance program. Discrepancies identified in on-site audits fall into several broad categories which include: lack of documentation, improper records, incorrect lab practices, sample storage and holding time excursion, inappropriate methods, equipment, lack of experienced personnel and inadequate accredited credentials.Table 6 lists some of the common on-site audit discrepancies found in auditing. The types and frequency of discrepancies found in audits can be ranked in order of frequency from 1 (most common) to 7. These are:

1. MDL - use of incorrect approach or failure to determine.
2. Incorrect adherence to method.
3 Calibration - failure to calibrate, maintain, verify purity and concentration.
4. Control Charts - failure to establish, maintain, take corrective actions.
5. Spike/recovery - inappropriate values or ranges relative to analytical range.
6. Standards - lack of/or inadequate.
7. Linearity - failure to establish or work within linear regions.

TABLE 6.
COMMON PROBLEMS ENCOUNTERED AUDITING

GC/MS not tuned, libraries & compounds mistakenly identified
Problems with spikes, surrogates, recoveries, MDL
Sample preparation/extraction problems
GC columns incorrect or not monitored
Inadequate documentation
Standards not run
Inadequate personnel/lack of experience & credentials

Illustrations of some of the poorly analyzed or inappropriate quality control data are provided in Figures 1-4. In Figure 1, the lab submitted a quadratic fit calibration curve when a linear curve and linear regression was required. The chromatograms in Figures 2, 3 and 4 all illustrate poor resolution, peaks off-scale and elevated baselines. Yet these chromatagrams were submitted as laboratory standards.

Although most of the laboratories in the certification program are in compliance in adhering to regulations and methodologies, results of on-site audits and evaluation of PE samples indicates that some are not or have periodic problems. The reasons why all laboratories aren't in full compliance vary and obviously may ultimately depend on the individual laboratory, equipment, lab practices, type of analysis, method, analyte and analyst. However, based on our

findings, some consistent general categorization can be made. Many of the labs in noncompliance simply fail to adequately follow prescribed methodologies, either ignoring or short cutting various analytical requirements, steps and quality control procedures. This has been observed in issues concerning use of appropriate equipment, materials, standards and establishing documented routine lab quality control procedures. Problems in quality control procedures generally involve failure to establish standards, calibration checks, cross checks and control charts as required per method. Those labs issuing questionable data or failing PE samples have generally suffered from errors in dilution and data transcription as well as contaminated standards, failure to establish an adequate MDL and quantifying in an inappropriate part of the calibration range.

Administering the New Jersey State Laboratory Certification Program has demonstrated that three components are necessary to monitor laboratory performance. These are the use of PE samples, audits and review of data. On-site audits in which actual data packages submitted to the State are fully validated are extremely effective. The NJDEP is currently revising its Laboratory Certification Regulations (N.J.A.C. 7:18) which will include new areas for certification including analyses for RCRA programs. These new regulations will be based on clear definition of methods and quality control procedures required.

Please note that the interpretations and opinions expressed in this paper are those of the authors and should not be construed as official policy of the New Jersey Department of Environmental Protection.

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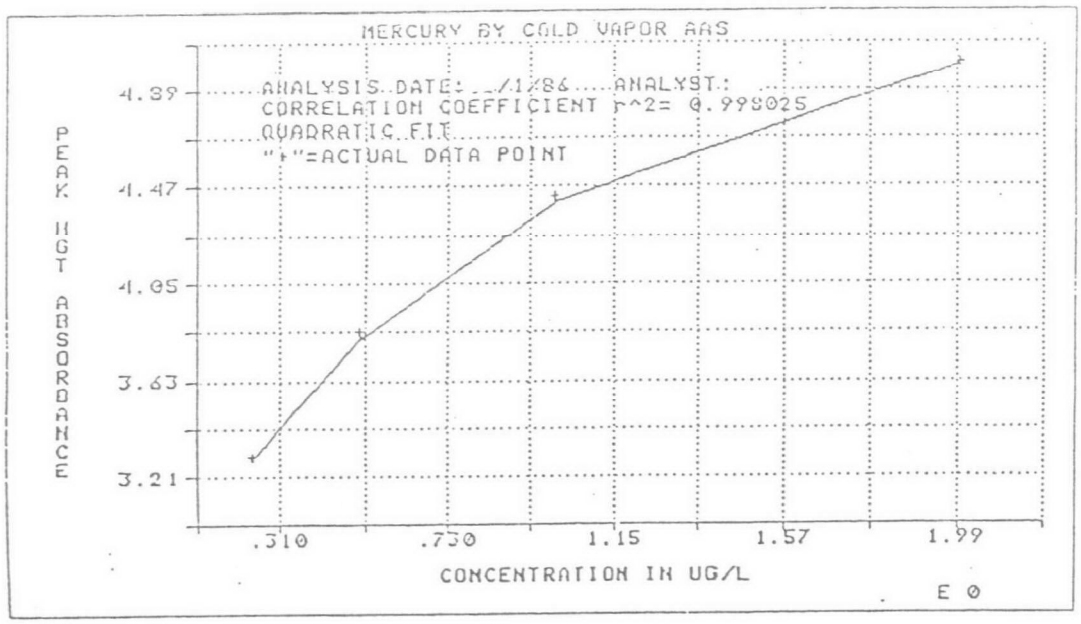

Figure 1. Example of Incorrect Linear Calibration

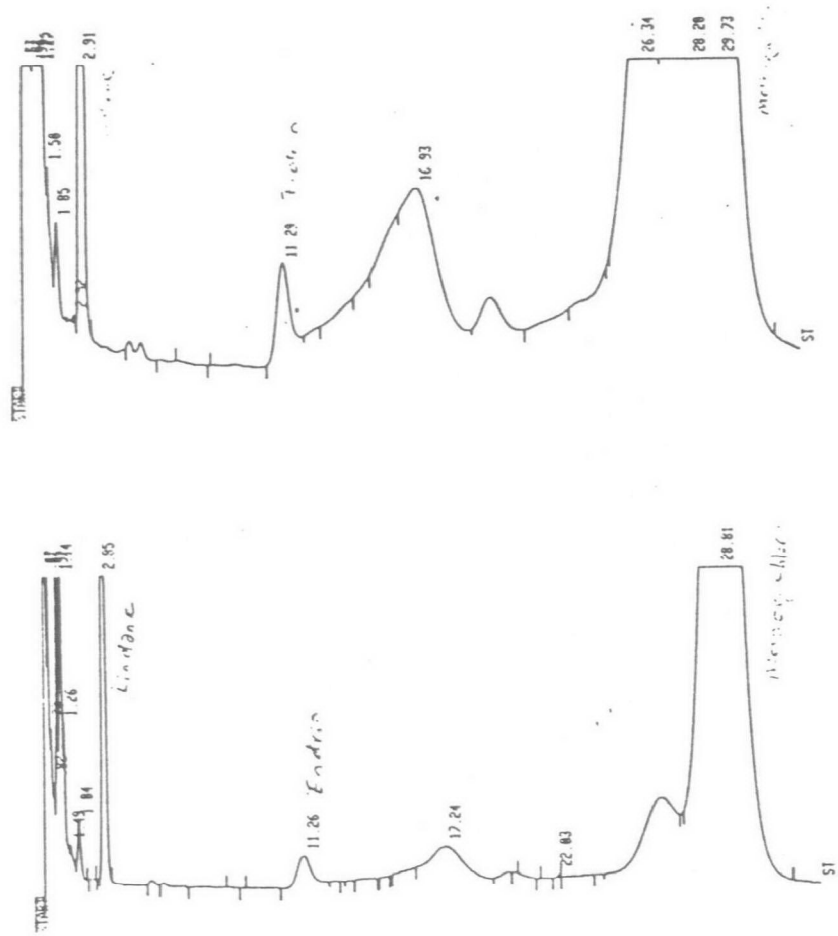

Figure 2. Examples of Poorly Resolved Mirex Standard Chromatograms

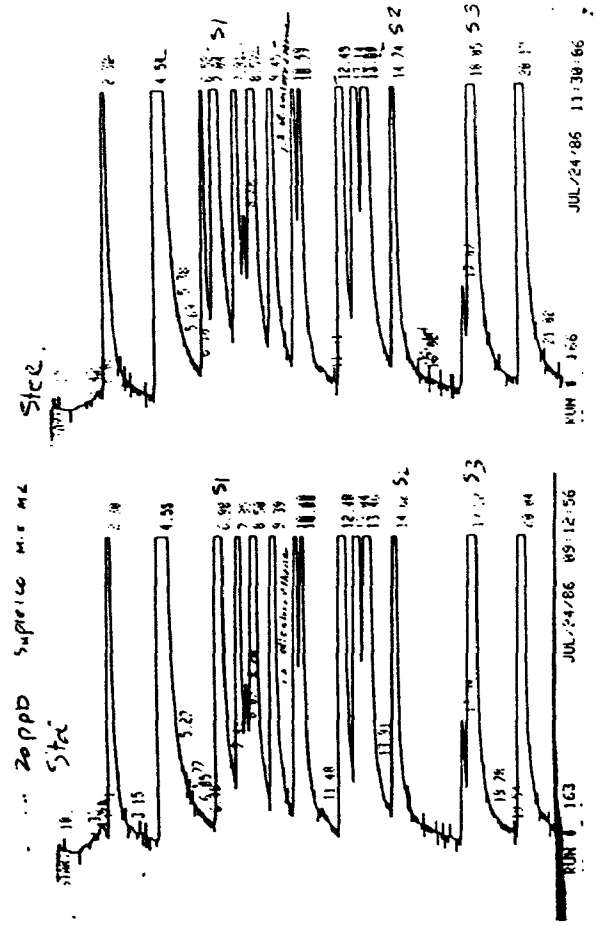

Figure 3. Examples of Poorly Resolved Standard Chromatograms for VOA's

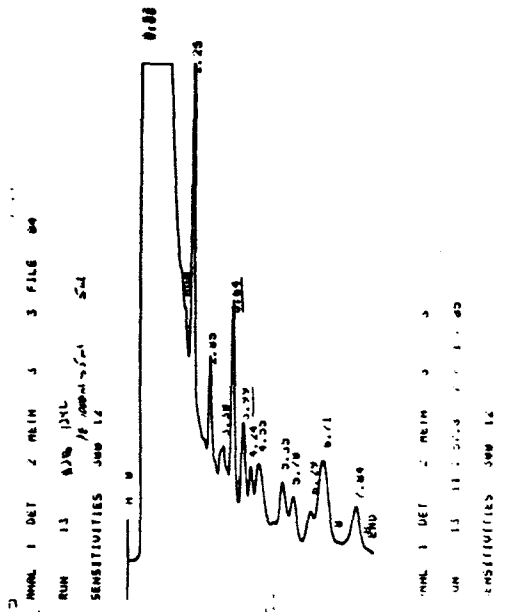

Figure 4. Example of Poorly Resolved PCB (1242) Standard

LANDFILL CONSTRUCTION--QUALITY ASSURANCE BEYOND TESTING

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ABSTRACT

Prerequisites for quality assurance during construction of any landfill are selection of an appropriate site and provision of a high-quality design. This discussion of quality assurance assumes that these prerequisites are met, and is limited to the construction phase of a landfill project. The most quantifiable portion of a construction quality assurance program is the physical testing of construction materials and completed work, in the laboratory and onsite. This paper addresses the other aspects of quality assurance that are less quantifiable, but are nonetheless essential to the construction of a functional and safe landfill. Geomembrane construction is stressed because it presents the most difficult quality assurance challenges.

INTRODUCTION

The reason that geomembrane construction has been receiving so much attention, is that, unlike most other types of heavy construction, the smallest flaw or oversight can result in failure (leakage) of the installation [1]. This makes quality assurance of paramount importance to successful construction. In addition, geomembranes are frequently at greater risk of damage during installation than during their service life, due to stresses caused by equipment handling during layout, backfilling of trenches, movement of equipment over the surface, temperature changes, and other temporary stresses. Vigilance during construction is essential to assure the completion of every detail of work, to prevent practices that may cause damage to the geomembrane, and to expedite the repair of any damage that occurs. To this end, EPA requires a construction quality assurance (CQA) plan for projects under its authority [2]. A CQA plan should be prepared and followed for the construction of every landfill regardless of whether it is required by permitting agencies.

Testing of geomembrane material and seams, by both destructive and nondestructive methods, must form a significant part of every CQA plan, but testing alone cannot provide quality assurance. While the strength of seams can be tested effectively in the laboratory on samples cut out of installed geomembranes [3], these tests can only be representative. Each time a sample is removed for testing the lining must be repaired. Commonly used nondestructive test methods, such as the vacuum box, test the continuity rather than the strength of seams and cannot be used in all locations [4].

Geomembrane testing onsite is typically performed as part of the contractor's quality control program. While the contractor bears responsibility for constructing the landfill as designed, quality assurance personnel should be under the direction of the engineer, representing the owner of a project. This is because quality assurance is inseparable from other responsibilities of the engineer such as preparation of specifications, understanding of design requirements as they relate to site conditions, and taking action to remedy observed noncompliance by the contractor. Quality assurance personnel should observe tests performed by the contractor and perform any additional tests required.

In addition to testing, quality assurance requires good project specifications, full-time observation of construction, and harmonious communication between the contractor and the engineer. Proper specifications provide the basis for avoiding construction problems and for correcting them when they occur by making clear to the contractor what is expected. Full-time observation is essential for quality assurance of work that cannot be tested or will be covered, and to provide correlation for representative results of destructive seam tests. Observation must go far beyond occasional checks on completed work to include close observation of each step of the work as it is done. Related to these tasks is the development of a good relationship between the resident engineer (the observer) and the contractor. This relationship should be pursued and, though not measurable, may at times provide more quality assurance than do other factors. These three aspects of construction quality assurance are discussed below.

SPECIFICATIONS

The primary purpose of specifications is to list material requirements and method of payment. However, many other conditions of the work should also be set forth in the specifications. Current landfill designs typically include at least one geomembrane lining in addition to a clay or clay substitute secondary lining, and the geomembrane material most frequently selected is high-density polyethylene (HDPE) because of its chemical and biological resistance to many types of leachate [4]. Some of the following suggestions for conditions to be included in the specifications reflect these common design features, while others are general requirements useful for many work elements, such as earthwork and leachate collection.

Geomembrane Specifications

In addition to listing detailed requirements for the geomembrane material, the specifications should clearly state other basic requirements. The intent of the work--to provide a watertight facility--should be stated along with a definition of the word watertight as, for example, "no leakage of solid or liquid waste through the material." The geomembrane installer should be the material manufacturer, or a company licensed by the manufacturer, in order to secure the most experienced and knowledgeable crew of installers with direct access to the manufacturer's testing facilities

and technical expertise. If the installer and manufacturer are not the same entity, a manufacturer's representative should be onsite to provide technical supervision and assistance at all times during installation of the geomembrane and overlying materials. If a leakage problem develops after construction, two-party responsibility could easily lead to significant delays in repair work while the two parties debate the source of the problem.

The specifications should also cover as many incidental requirements as can be anticipated, such as protection of the geomembrane during storage, from sunlight, soil, and other substances. Even if only a short construction season is intended, conditions may change following contract award, and material may be exposed to the elements longer than expected. Even material with ultraviolet resistance should be protected from long-term exposure. Allowable methods of temporarily anchoring the geomembrane during layout before panels are seamed, should also be specified to protect the material. If this is not included the contractor may choose, for example, to use burlap bags of gravel to hold the sheets in place; if one of these bags breaks, one unrecovered piece of gravel could later cause a puncture in the geomembrane when an overburden is applied. Old tires used as anchors may have protrusions that could cause scratches or punctures. Tightly woven bags filled with sand are acceptable anchors.

The specification for seaming the geomembrane is critical to integrity of the completed lining. Field seams on geomembranes vary for different types of material; the most common seams are adhesive and thermal [5]. HDPE is seamed by thermal methods, with heat and pressure applied to the overlap (hot wedge method) or by the addition of extruded HDPE along the overlap in addition to heat and pressure. The latter type of seaming is called extrusion fusion welding and is the recommended method because (a) the weld is visible to observers (unlike the hot wedge seam), (b) the added resin increases the strength of the seam, and (c) vacuum-box testing can be done in planar areas without cutting through overlapped surfaces. Specifications for adhesive seams, required for PVC material, should specify the appropriate amount of adhesive to add because too much can be damaging to the material.

Seam specifications should also list appropriate overlap widths, and should require that the welding equipment for HDPE seams be capable of continuously monitoring and controlling temperature in the fusion zone.

For locations where pipes within the lined area penetrate through the perimeter membrane, special requirements should be specified to prevent leakage. Such pipe penetrations typically occur where leachate collection pipes exit the landfill. Specifications should require that pipe boots be fabricated with the same quality seams as elsewhere and dimensions should be shown on a drawing. Figure 1 is an example of a pipe penetration through a single geomembrane and soil-bentonite lining composite, which met the requirements for conditions at one site. Other sites and project requirements would

entail different design considerations. To obtain a tight seal where the geomembrane is connected to the concrete transition block beneath the pipe boot, specifications should indicate that the surface of the concrete and both surfaces of the geomembrane be cleaned just prior to the work and that neoprene adhesive be applied to both the concrete and the underside of the membrane. The correct amount of tightening of the nuts on the anchor bolts should also be specified. Nuts should be tightened sufficiently to deform the neoprene pad uniformly along its length but not to compress the neoprene more than to 90 percent of its original thickness. (See Figure 1.)

Poor weather conditions during seaming can greatly impair the integrity of seams. Precipitation can create voids in both adhesive and thermal seams. Even small drops of water prevent adhesion or lower the equipment temperature. No seaming should be performed during adverse weather conditions. Adverse weather includes any amount of precipitation, low temperatures (varies for different materials), and high winds.

While quality assurance should be the engineer's responsibility (on behalf of the owner), quality control (QC) should be the contractor's responsibility. The contractor should control the quality of work through whatever means are necessary, including inspection and testing, and regardless of the amount of additional testing and observation performed by the engineer's quality assurance personnel. The specifications should state this clearly to eliminate any assumption on the part of the contractor that a portion of work is of acceptable quality simply because it has not been questioned by the engineer. Defects found in completed work indicate a deficiency in the contractor's QC program.

The contractor's quality control of the geomembrane installation can be presumed to include a minimum amount of testing, such as nondestructive tests of all seams (required by EPA) and strength tests of sample seams made at the start of each shift [2]. The minimum testing required to be done by the contractor should be specified, along with the requirement to notifying the engineer prior to performing the tests so that quality assurance personnel can observe them.

Additional tests to be performed by quality assurance personnel should also be described in the specifications. The contractor must know the type and frequency of required testing programs and of tests by others in order to price the work.

Specifications should state that all defects found during inspection and testing of the seams by either the contractor or the quality assurance personnel should be marked immediately for repair. Patches required for these repairs, and for repairs to the lining where samples have been removed, should be large enough to provide the minimum overlap and should have rounded corners.

General Requirements (Common to Many Work Elements)

The specifications should list experience requirements for work requiring special skills, such as geomembrane installation. Experience should be required of both the installing company and the personnel assigned to the given project. This will avoid the problem of a project becoming the experimental arena for a contractor or subcontractor new to the business. A lack of knowledge about the properties of geomembranes and the equipment and seaming methods required for installation would make leak-proof installation virtually impossible.

A schedule of work should be required to provide evidence that the work has been planned and is proceeding as planned and to enable the engineer to plan the quality assurance work. Different phases of construction will affect the number and the experience of quality assurance personnel required. A construction schedule will aid in providing sufficient staff and equipment for this work. The contractor should be required to update the schedule daily, if necessary.

The contractor should also be required to submit shop drawings for layout of the work not detailed in the plans. This forces the contractor to plan the work and may allow the engineer to detect potential problems in the execution of the work. For example, geomembrane seams perpendicular to the direction of slope should be avoided. Unacceptable drawings should be corrected and resubmitted.

Provide specifications for each material required even when only a small quantity may be needed, such as neoprene adhesive, mastic tape, and stainless steel bands. If product brands or requirements are not known, specify "as recommended by geomembrane manufacturer."

A dimension should be listed for the measurable tolerance for every pertinent item of construction, such as for thickness of material, width of overlap, performance test results, and elevations. For example, a clay lining 0.5 meters thick may have an allowable deviation in thickness of 2 centimeters. This provision may prevent disagreements during construction and will define the work for quality assurance personnel and the contractor.

When materials arrive on the site, each separate item should be labeled showing brand, dimensions, date of manufacture, and placement (if appropriate).

Problems that may come up should be anticipated and the specifications should provide an avenue for resolution, if possible. The words, "or as approved," should be inserted where appropriate to give the contractor the opportunity to apply better ideas.

The method of work should be the contractor's option, except when it affects the quality of work, as described above. The contractor should be able to plan and execute the work with as much freedom as

allowable in order to do the work at the least cost and so that the contractor, rather than the owner, will bear responsibility for unsuccessful methods of work. For these reasons, the specifications should generally avoid listing methods.

CONSTRUCTION OBSERVATION

During landfill construction, particularly when a geomembrane is installed, construction quality cannot be assured without observation of the work. This is because much of the work is covered, and test methods for geomembranes are insufficiently developed to enable quality assurance through testing alone. The staff assigned to the task of observation should be knowledgeable about the reasons for design and about the products used; should be sufficient in number to observe work at different locations as it occurs [4]; and should be knowledgeable about the problems created by the use of marginal materials and inappropriate construction methods. This section describes many examples of construction tasks that must be observed during landfill construction to provide quality assurance.

The material beneath the geomembrane, usually clay or a low-permeability substitute, should be checked for full depth and for continuous protection of the surface from dessication and precipitation [6]. The surface should be smooth and free of protrusions of gravel. The backfill around concrete pipe-penetration blocks should blend with the surface of the concrete to provide a compacted, uniform surface. Transitions for changes in slope must be smooth and rounded.

Installation of the geomembrane seams and pipe penetrations must be carefully observed. Grinding of seam edges in an HDPE lining and cleaning of seam surfaces in any geomembrane must be done just prior to seaming. The alignment of the weld area on an extrusion-welded seam should not vary more than approximately 0.5 centimeters in either direction. Any variation in excess of this amount, in the shininess of the surface, or in the apparent thickness of the weld area should be given particular attention during nondestructive testing and perhaps tested destructively. Quality assurance personnel must be familiar with the appearance of seams that have been tested with positive results in order to more easily detect even the most minor deviations that may indicate a potential problem. If copper wires are inserted in seams for later spark tests, the placement of the wires must be observed.

Poorly constructed pipe penetrations are one of the common causes of leaks in geomembranes. The surface of the concrete supporting block must be smooth and clean in order to protect the lining and to provide a good seal, and corners should be chamfered. As shown in Figure 1, the neoprene adhesive should be placed on both the concrete surface and the geomembrane surface continuously around the perimeter of area to be connected, and the butyl mastic tape should also be placed on both adjacent, clean surfaces. The nuts on the adhesive anchors should be carefully tightened as described above in the

section SPECIFICATIONS. The pipe boot should fit snugly over the pipe and surrounding area without folds or gaps, and all seams should be made against a firm subgrade.

Thermal expansion and contraction of HDPE is a common installation problem, even in moderate climates, producing folds of expanded material during warm hours and bridging over bends and trenches in the subgrade during cool hours [6]. This can create stress in the seams, can pull overlapped edges apart, and can make backfilling difficult because folds and bridging cannot be allowed beneath the overburden. Because of this problem placement of both the lining material and the sand cover (or trench backfill) should be done when the lining is at neither temperature extreme. If the lining is placed during cool weather numerous wrinkles are likely to appear during the warmer times of the day. To remove the folds during placement of the overlying sand layer, some folds will probably have to be cut, overlapped, and seamed. Similarly, bridging due to contraction may require repair by cutting the lining, adding material, and seaming each edge.

Granular drain material typically placed over the geomembrane, sometimes with a geonet between, must be at least 1 meter deep in areas where equipment will travel in order to protect the geomembrane. Prior to placement of the sand layer, all stray gravel and other debris must be removed from the lining. Damage may occur due to stresses caused by the equipment traveling on steep access roads, and sharp turns and stops of equipment [6].

The backfill in the geomembrane anchor trench must be carefully compacted. Trench backfill more permeable than the surrounding material may allow liquid to seep beneath the liner [7].

Leachate collection pipes must be cleared of all obstructions prior to final placement.

Edges of nonwoven geotextiles placed over the granular drain material should be overlapped sufficiently to prevent the occurrence of any uncovered area through which the sand might be contaminated with overlying fine material. The contractor should not be allowed to heat tack the geotextile because heating can burn holes in it.

Quality assurance personnel must be alert to practices that may cause damage to the geomembrane, such as careless operation of equipment and placing sharp tools on the lining surface. All gouges, scratches, and punctures must be marked immediately and repaired in a timely manner.

CONTRACTOR RELATIONS

Because of the exacting nature of many portions of landfill construction work and to the high degree of quality assurance required, the working relationship between the engineer and the contractor is a factor that can greatly affect the performance and quality of the

work. A good relationship between these parties can be deliberately developed on any project, beginning with specifications that clearly state the requirements of the work.

At the prebid meeting for a project, the engineer should make sure bidders understand the purpose of the job, the potential problem areas, and the importance of close coordination between various operations, such as between geomembrane installation and earthwork. The general contractor should be aware before bidding of the impact that geomembrane construction requirements may have on other work. An example of this would be placement of drain materials over the geomembrane during weather conditions most favorable to the geomembrane to avoid expansion and shrinkage problems.

At the preconstruction meeting these issues should be addressed in greater detail, including the issue of coordination between the quality assurance personnel and the contractor. The contractor should be told whom to contact when the resident engineer is not available. The resident engineer should have a detailed understanding of the project and be capable of making decisions in a timely manner. In turn, the contractor must also designate primary and backup personnel to provide communication at any time. The contractor must clearly understand that he is expected to provide current schedules (updated daily).

After construction begins, the following practices may alleviate potential problems:

1. The engineer/quality assurance personnel should ask questions of the contractor during observation to ascertain the intended methods and sequence of work. Information gained might enable necessary changes in procedure to be made earlier, thus avoiding delays that may otherwise be unavoidable. Contractors and engineers are both more amendable to revisions when they can be made before the work in question is performed.

2. Mutual respect between the engineer and the contractor is essential to maintaining good communication. An attitude of superiority on the part of the engineer may cause a reluctance by the contractor to performing any item of work not expressly defined in the plans. The engineer should listen to suggestions made by the contractor and be open to implementing them if, upon analysis, they are more efficient or effective than the specified item.

3. The engineer should explain the logic behind the design and specifications. Problems of nonconformance during construction are frequently the result of contractors not understanding the reasons for certain requirements they may perceive to be impractical. For example, a contractor may tack a geotextile overlap using heat if it has not been explained why this is not allowed.

4. Use appropriate language (i.e., diplomacy) in handling perceived problems. A polite question or reminder by the engineer may motivate remedial action by the contractor and avoid a contest of wills. Written directives are necessary and are always preferable to verbal threats and accusations when nonconformance becomes a problem. An example of diplomatic communication would be, "I noticed the liner is not resting on the subgrade in some places around the pipe boot. When were you going to work on that?" Serious contractual problems may result from careless verbal directives.

CONCLUSION

Testing programs of construction materials and workmanship are fundamental to quality assurance but they must be combined with good specifications, observation of the work, and good contractor relations for the achievement of the highest quality landfill construction. Specifications should be thorough but also must be clear and provide avenues for unexpected changes. Construction must be closely observed to avoid the small errors that may later cause serious problems. Attention to the development of good communication between engineer and contractor can prevent construction problems and will help to assure the superior workmanship essential to landfill construction.

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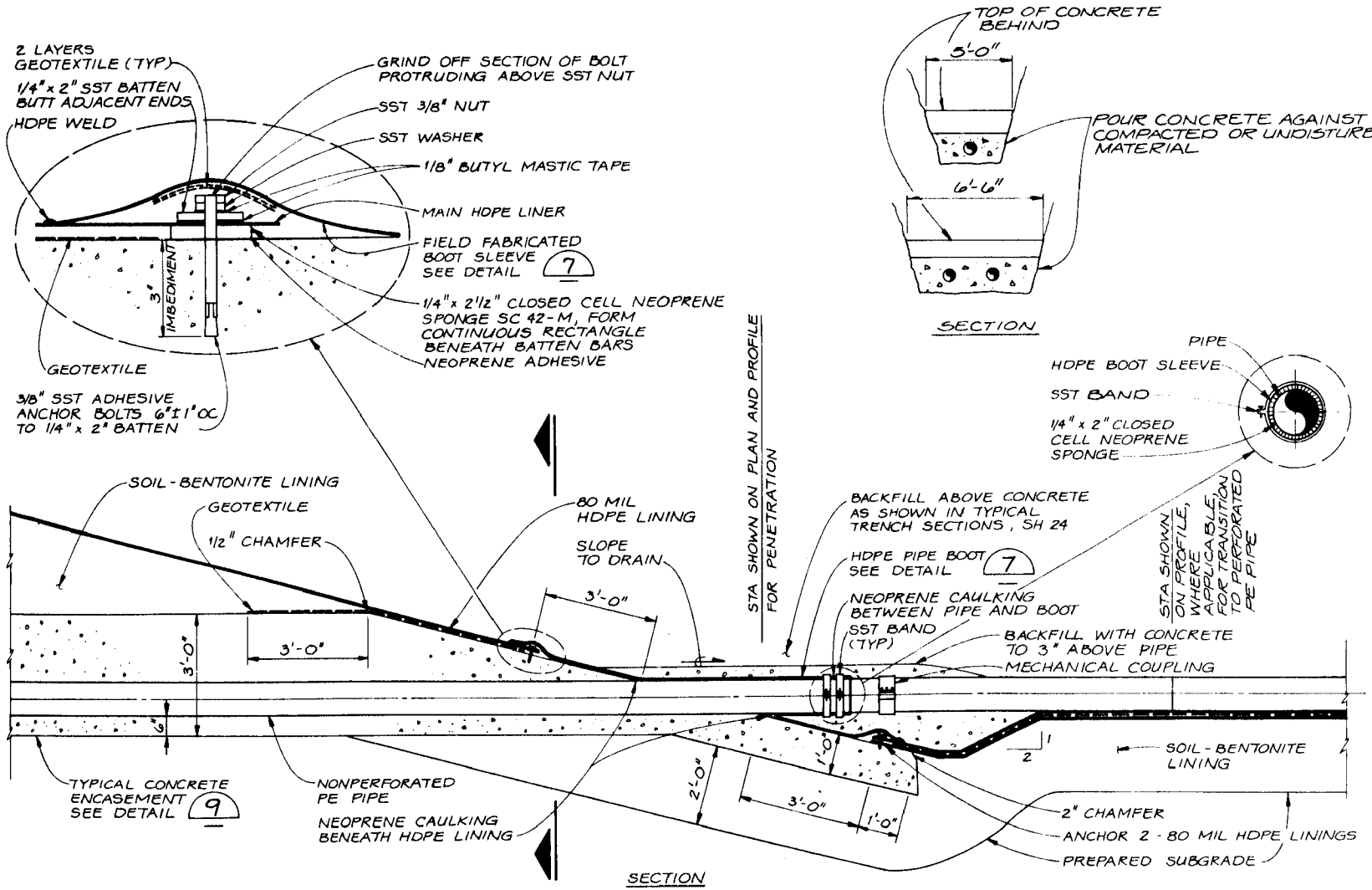

Figure 1

EXAMPLE OF PIPE PENETRATION THROUGH SINGLE GEOMEMBRANE

DEVELOPMENT OF A SPECIAL ANALYTICAL SERVICES (SAS) SOP FOR LABORATORY PERFORMANCE ON VOLATILE METHOD AND TRIP (FIELD) BLANKS ASSOCIATED WITH POTABLE AND LOW LEVEL MONITORING WELL SAMPLES

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ABSTRACT

The objective of this presentation is to suggest that volatile organic analysis of potable and low level monitoring well water can be improved by a Special Analytical Services (SAS) defined algorithm. The SAS includes an initial demonstration and continuing achievement in method blank and trip blank controls for methylene chloride (this study) and any other desired target volatile analytes(s). The SAS has been shown to lessen false positives for reported data than that being routinely reported by Regular Analytical Services (RAS). The SAS was used for four sampling episodes at three Superfund Sites and was found to give MB and TB control wherein data could be reviewed by a modified Quality Assurance, Data Validation- Standard Operating Procedures within the SAS. For Superfund Sites I-CFS and II-FL, the SAS was able to produce data, via modified EPA Method 601, which could be validated by means of successful control of Method Blanks and Trip Blanks to less than, or equal to, 1.0 ug/L. The sample data for Sites I and II suggests that previously run Regular (Routine) Analytical Services analyses were suspect (yielding false positives).

The SAS evolved during developmental research for HSL analytes by Cryofocus Capillary GC/MS. The research was performed on a low level monitoring well, A-1, at Superfund Site III-PR. The data suggested that previous and the currently RAS split samples generally were with flawed in the methylene chloride analytical results for this low level monitoring well.

The SAS was shown to be instrumentation independent and successful for the analysis of both potable and low level monitoring well samples. In New Jersey, the Department of Environmental Protection has defined Level II Action for 4.8ug/Lto 48ug/L methylene chloride. Decisions involving alternate water supplies to residences is possible for those potables having this level of contamination. Current practice of RAS for MB and TB control is inadequate.

FIRST USE OF SAS FOR CONFIRMATION OR NEGATION OF METHYLENE CHLORIDE PRESENCE IN RESIDENTIAL WELLS ADJACENT TO SUPERFUND SITE I. [5,6,7,8,9]

A request to begin an initial laboratory demonstration, sampling and monitoring analysis for Methylene Chloride for low level

presence equal to or greater than 5 μg/L in potable samples from residence wells adjacent to the Superfund Site I-CFS landfill. [6]

BACKGROUND INFORMATION

Within written Personal Correspondence: Genicola to Morris, dated October 21, 1986 [8], a procedure for the determination of methylene chloride as a single monitoring analyte needing confirmation was developed. The basis for the testing is that data generated heretofore at this site could not be confirmed nor negation of methylene chloride presence in drinking water samples. The SAS, Special Analytical Services, procedure has evolved emphasizing control of VOA glassware, special control of reagent water used for method blanks, regular trip blanks and special trip blanks, TBO and TBO' [fully under laboratory control and the basis point for regular TB evaluation when validated]. Included in the laboratory demonstration with is deliverable records of analytical quality of reagent water before filling the TB for the field and the extra trip blank basis points TBO and TBO'. The TBO and TBO' are stop/go decision laboratory quality control previous to sample analyses (Figure 1 and Logic Diagrams I and II).

The Department's Bureau of Environmental Laboratories was selected because an earlier study [13] had shown that Method Blanks used in Cryofocus Capillary GC/MS of HSLs had Methylene Chloride control at 0.2 to 0.3 ug/L on a regular basis. Additionally, the BEL had the desire to successfully attempt and complete this study.

AUTHORIZATION TO PROCEED WITH SAS TASKS

The dates for the Initial Demonstration were December 8, 1986 in which a 90 vial lot of 40ml VOA vials was made available by BEL, an initial demonstration of reagent water in Rm 109 [Room contains GC and GC/MS instrumentation and Charcoal Filter for Preparation of Reagent Water for Method Blanks]. The reagent water shall have 1.0 ug/L level of Methylene Chloride background or less, three Trip Blanks including TB1, TBO(1) and TBO'(1) shall be filled and analyzed as described in the above cited correspondence [8] except that TBO shall be analyzed on December 12, 1986. All TBs are to show 1.0 or less ug/L Methylene Chloride contamination in order to proceed with samples from Superfund Site I-CFS drinking water wells[8].

Samples to be run shall include thirty-three (33) potable wells which are to be sampled in duplicate and iced, no synthetic refrigerant, and stored in special small approximate 2.5 gal volume potable shuttles (must only be used for potable water samples).

Analytical considerations shall include that the monitoring shall be performed under EPA Method 601 but only for one analyte Methylene

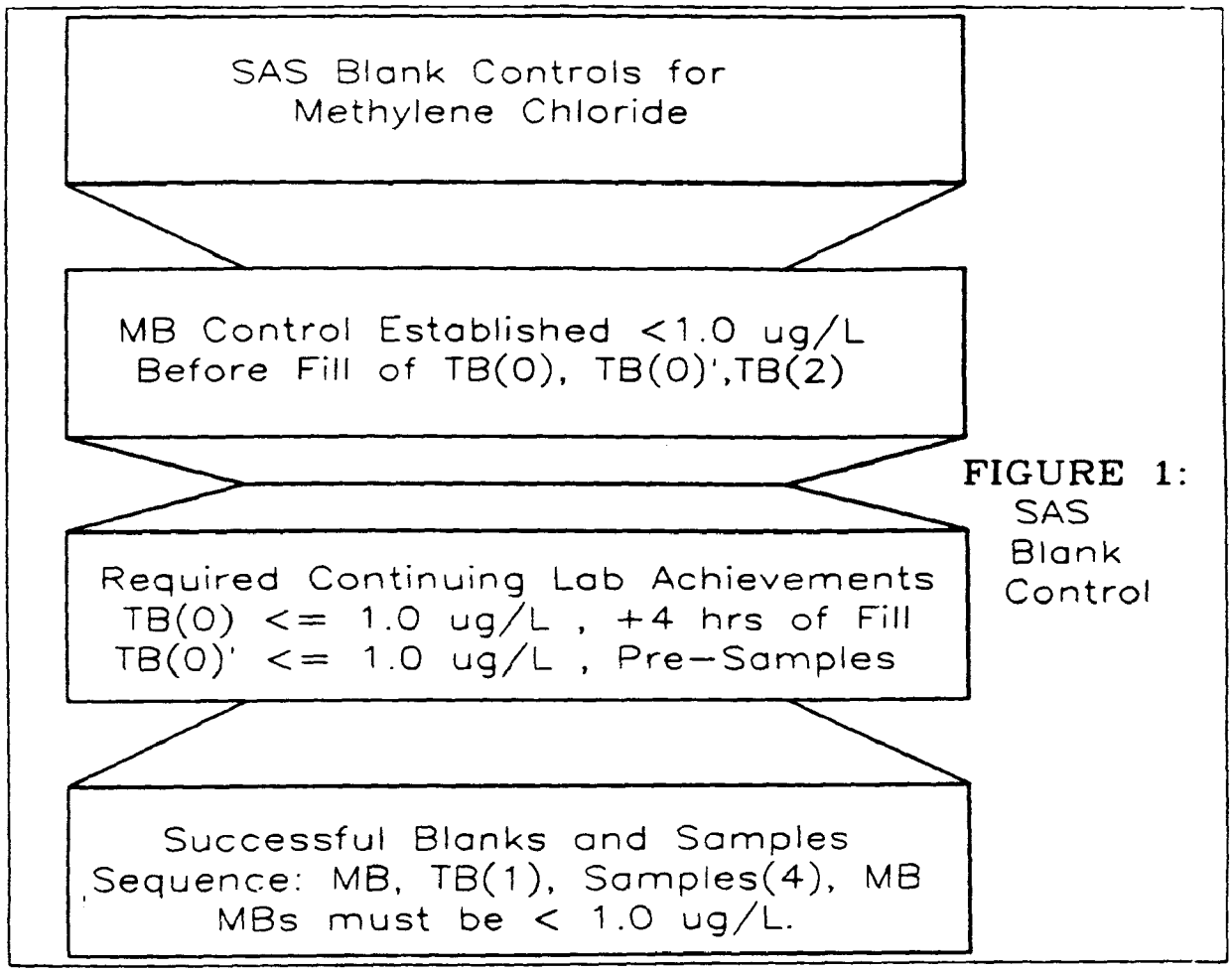
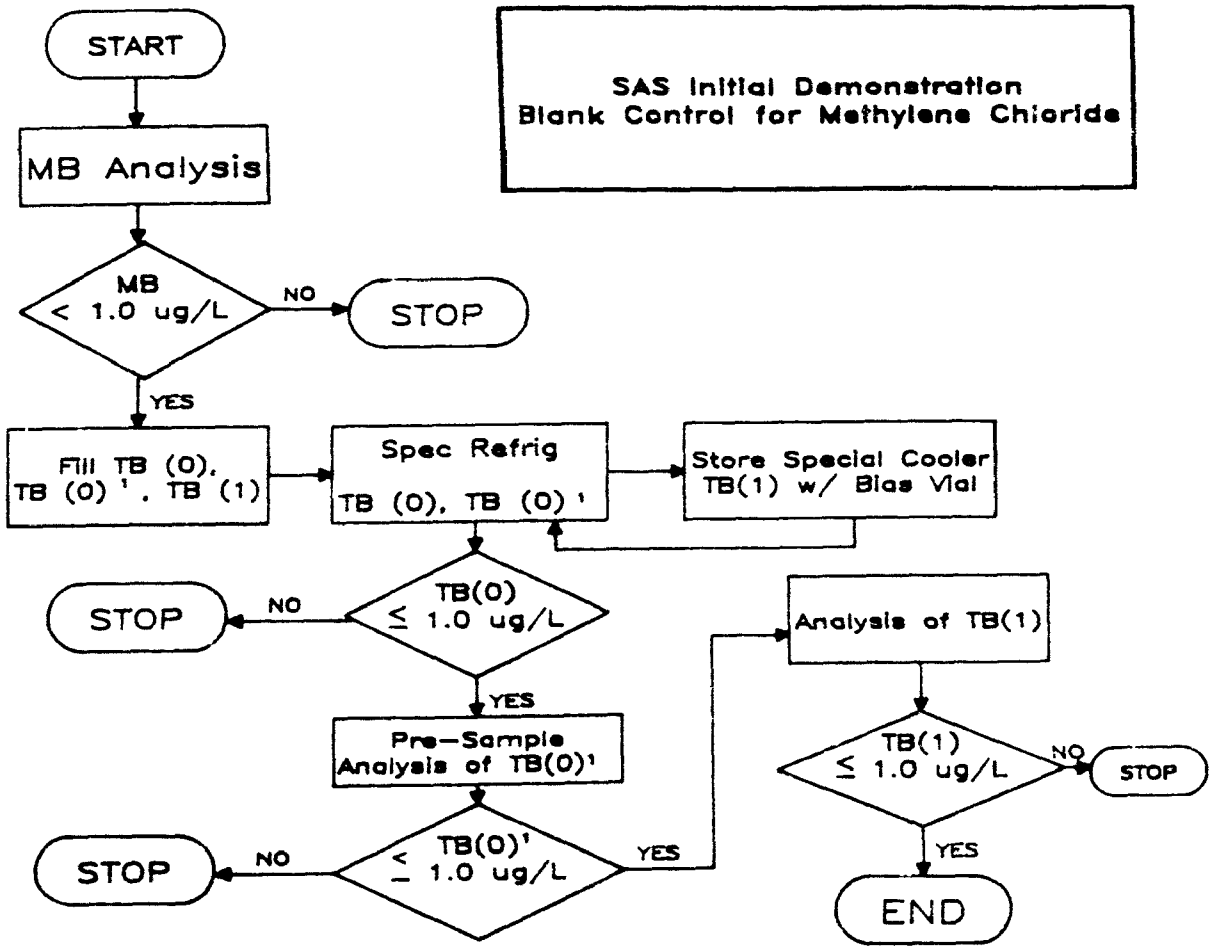
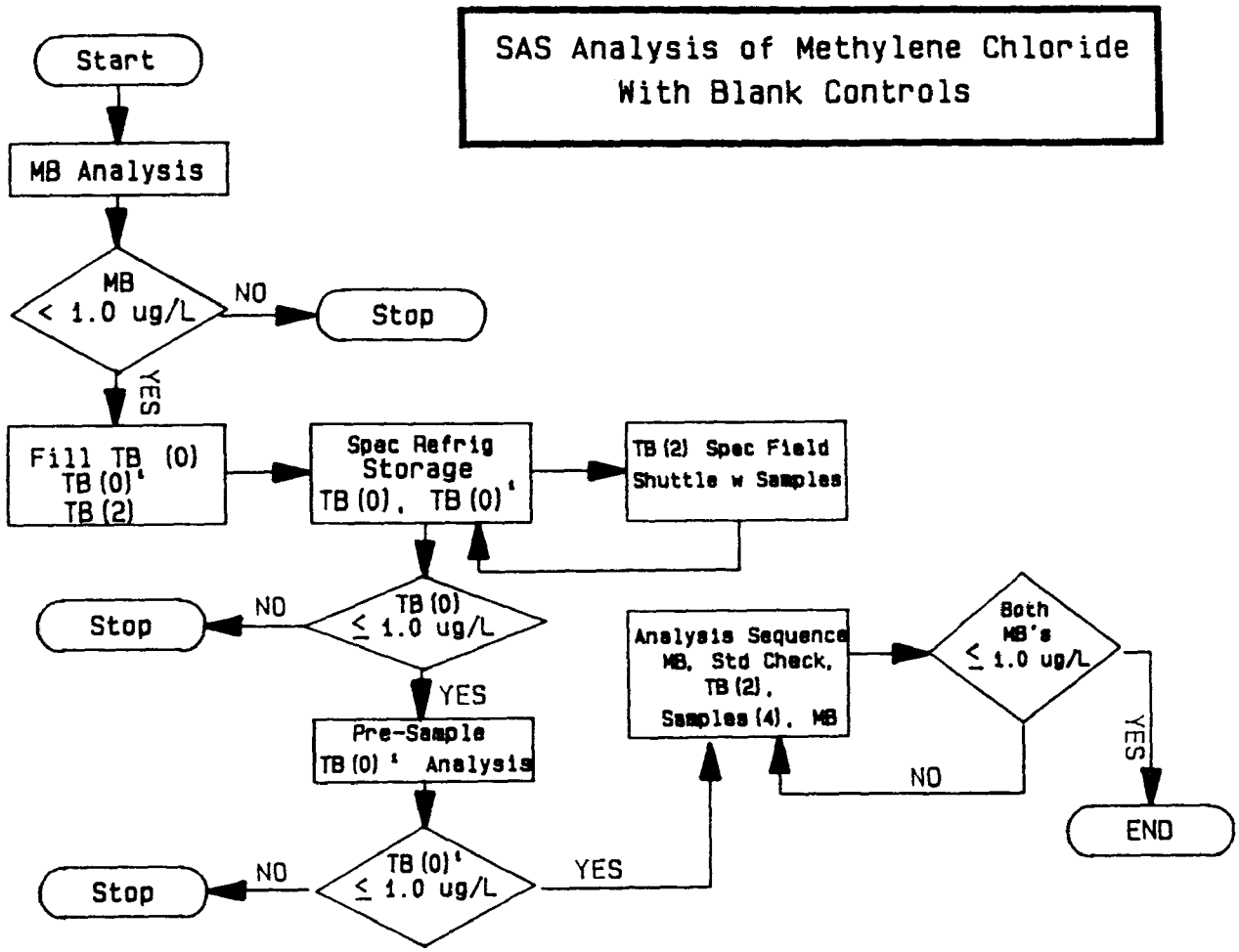


FIGURE 1: SAS Blank Control

Logic Diagram I: Initial Laboratory Demonstration of Special Analytical Services for the Analysis of Methylene Chloride. The Method Blank (MB), Trip Blank Basis Points (TB0 and TB0') and Trip Blank (TB) Controls. TBs are Fully under the Laboratory Quality Control for the Initial Demonstration.



Logic Diagram II: Special Analytical Services for the Analysis of Methylene Chloride with Method Blank (MB), Trip Blank Basis Points (TBO and TBO') and Trip Blank (TB). TBO and TBO' are fully under the Laboratory Control and as such are Stop/Go Decisions after filling with Reagent Water (MB analyzed). TBO is analyzed after four (4) hrs. of filling. TBO' is analyzed just previous to beginning sample analysis.



Chloride. Only one surrogate shall be employed and recovery versus laboratory generated limits of acceptance must be met or repeated successfully at laboratory expense. All data relating to standards, method blanks and trip/field blanks must be presented in acceptable deliverables format. Data reporting shall be presented in IFB/CLP deliverable form with CLP data qualifiers by the laboratory.

If possible sampling should be undertaken on Monday December 15, 1986 and Thursday December 18, 1986. Sample bottles for December 15, 1986 must be picked up on Friday December 12, 1986 and TB2, TBO(2) and TBO'(2) filled with preanalyzed (less than 1.0 ug/L methylene and chloride) reagent water . . . Sample bottles for the December 18, 1986 sampling must be picked up at BEL on Wednesday December 17, 1986 and TB3, TBO(3) and TBO'(3) filled with preanalyzed reagent water (less than 1.0 ug/L Methylene Chloride). TBO (2 or 3) respectively must show a less than, equal to 1.0 ug/L methylene chloride contamination level as a stop/go situation. Thus analysis must be completed before sampling is to begin (within 4 hours of filling the TBO (2 or 3). If unsatisfactory, the laboratory must contact the SMO through whom the sampling team shall be told not to proceed with continuing taking samples.

Sample analysis shall be rated against the individual shift method blank (less than 1.0 ug/L) and the TBO' (2 or 3) being under control at 1.0 or less ug/L Methylene Chloride before proceeding as a stop/go decision point. If unsatisfactory, the laboratory must contact the SMO before proceeding with the analysis.

The laboratory shall run an appropriate number of method blanks to ensure that during sample analysis, the methylene chloride contamination is kept under 1.0 ug/L. Suggested frequency for this study is every 5 samples; these blanks are billable. Standard checks at 2.0 ug/ml shall be after every five samples and method blank check. The laboratory shall reanalyze at its own expense those samples affected by loss of control for method blanks or standard checks.

PROTOCOL CONTROL OF METHOD BLANKS - METHYLENE CHLORIDE [1,2,3,4]

EPA Methods [1,2,3] and OERR CLP-IFB Contracts have a MDL defined limit for the contamination allowable in a method blank with no reporting suggestions for levels below the MDL for the former, and 5 X the CRDL(CRQL) limit (Figure 0-a) for contamination but with defined reporting requirements below the CRDL, the "J" qualifier to any found analyte "above zero".

EPA guidance for validation in the CLP is that a "common laboratory contaminant" can not be confirmed for a sample unless the sample has 10 x that found in any associated blank.[4]

The EPA Methods have no reporting requirements below the MDL and therefore the EPA CLP guidance document is ineffective for low level samples and method blanks.

SAS CONTROL OF METHOD BLANKS [7,8]

The NJDEP SAS requires laboratory reporting for methylene chloride to a CRDL(CRQL) of 1.0 U with the "J" qualifier for value one order of magnitude lower, 0.1 to 0.9. Additionally, any sample having an associated found in the method blank would be reported by the laboratory with a "B" qualifier. [Multiple qualifiers to numerical data are allowed].

Quality Assurance, Data Validation would "negate" as present any methylene chloride in a sample with an associated method blank wherein the sample was under 3 X MB. Negated values are raised to the value in the sample and becomes "UB" qualified. Sample values greater than, equal to 3 X MB are "JB"(qualitatively possible). Sample values equal to, greater than 5 X MB are validated as Value B (i.e. 15B).

Assuming Method Blank is contaminated to just under the CRDL of 5ug/L for CLP, to the MDL of 0.5 ug/L and 2.8 ug/L for the EPA 601,624 and to the CRDL of 1.0 ug/L for the SAS, Figure 0-b gives the data validation possible.

RESULTS OF THE SAS FOR SUPERFUND SITE I-CFS [9,10]

The SAS analysis of thirty-three (33) residential wells adjoining the Superfund Site I-CFS were performed on sampling episodes of December 15, 1986 and December 18, 1986. Each sampling episode required its own set of MB, TBO, TBO' and TB which were designated as TBO(2), TBO'(2) and TB(2) for the former and TBO(3) and TB(3) for the latter.

All MBs and TBs, including the associated TB basis points, were kept under 1.0 ug/L Methylene Chloride. The resulting sample data had thirty samples data validated as 1.0U or 1.0UB. Two samples were validated as "qualified" present at 2JB each. Only one "suspect" residence had a methylene chloride result at 5.5B. Solvents were evident in residence via Chain-of-Custody notations.

Alternately, RAS analysis was performed on 15 of residence wells on a "split" sample basis. The results of the CLP laboratory yielded unacceptable MB and TB values for validation purposes versus the NJDEP Level II Action for Methylene Chloride (Figures 1a, 1b and Tables 1a, 1b).

Note should be made that for residence PA at Superfund Sites I-CFS, the value reported by RAS was 180 ug/L where both split and

Figure O-a, Comparison of Method Blank Controls and the QA Data Validation for Methylene Chloride in the EPA CLP.

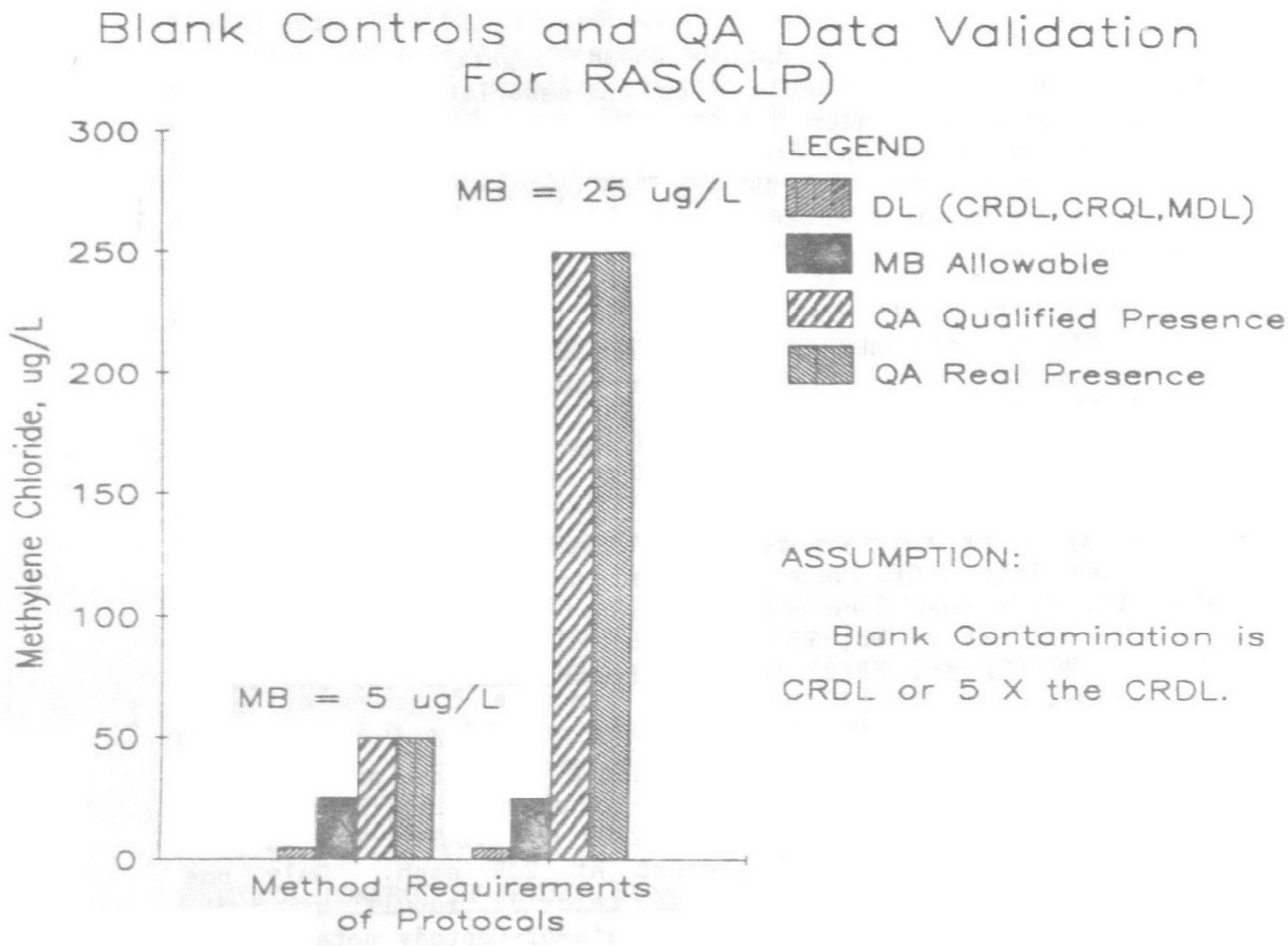


Figure 0-b. Comparison of Method Blank Controls and the QA Data Validation for Methylene Chloride in Three EPA Protocols and the NJDEP SAS.

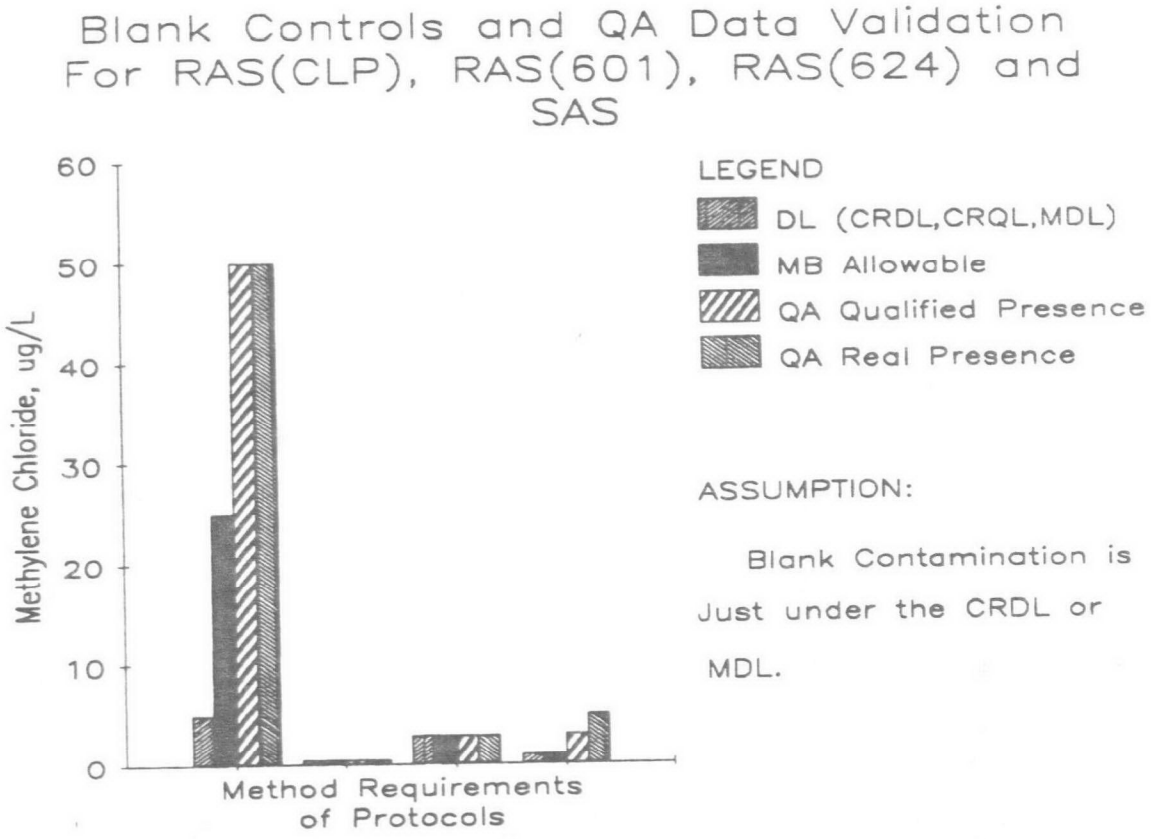


Figure 1a: Methylene Chloride Results, Method Blank Control and Trip Blank Results using RAS versus Split Sample SAS for Superfund Site I-CFS. Special Attention should be Noted on the TB2 Results for RAS Versus SAS. The Latter has little or no Control Versus Validation Control for the Former.

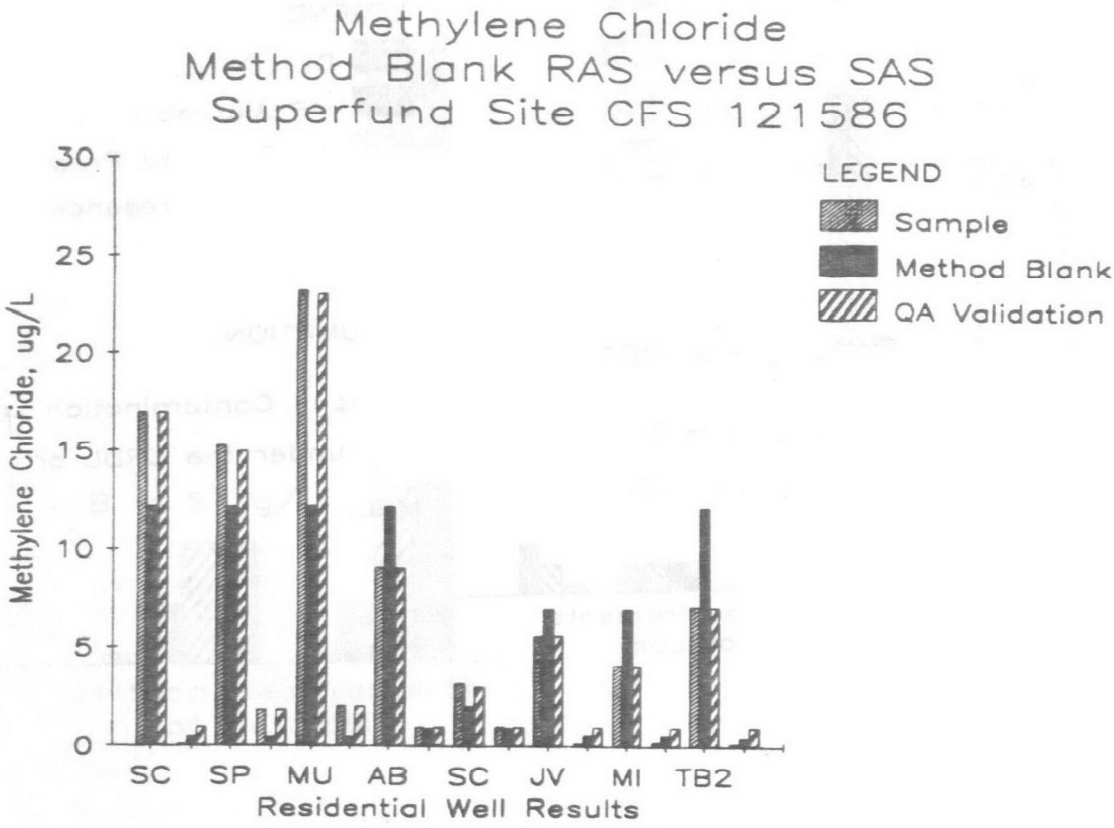
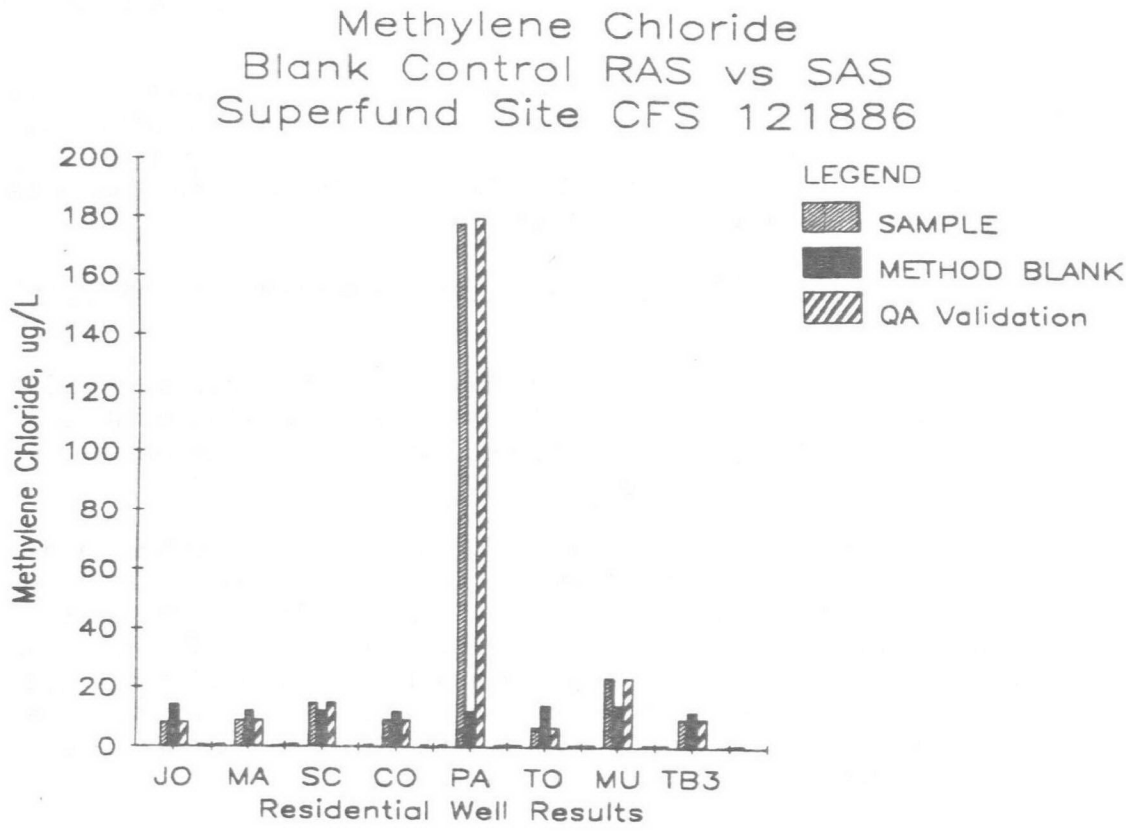


Figure 1b: Second Sampling Episode Results for the RAS Versus SAS Split Samples at Superfund Site I-CFS. Special Attention should be Noted on the PA Residential Well Results which is a Level III Action Site, if Verifiable. Refer to Figure 1c for Invalidation by SAS.



subsequent SAS reported 1.0 UB and 1.0U, respectively. The PA sampling site has never seen excessive (NJDEP Level III-more severe than Level II) methylene chloride. The results of the RAS were quality assured as being "probably flawed" but could not be negated as present since the 180 ug/L was more than 10 x MB and TB values. Only through the MB being in excess of the EPA Method 624, could the QA review question the PA Residence results (Figure 1c).

Additionally, previously obtained data for the potable samples: SC and AB was compared to the December 1986 sampling episodes. RAS data is shown to either be issuing "false positive" or ineffective data for quality insurance for low level samples. (Figure 2 and Table 2)

SAS USE IN POTABLE AND MONITORING WELLS AT SUPERFUND SITE II-FL [11]

Results of the SAS for sample taken in April 1987 were 1.0U or 1.0UB for all confirmation samples. Previous RAS results with uncontrolled MB AND TBs were not expected to be contaminated environmentally with Methylene Chloride. Validation on RAS data was not possible for the NJDEP Action Level II.

SAS DEVELOPMENT FROM RESEARCH IN HSL VOLATILE ANALYSIS BY CRYOFOCUS CAPILLARY GC/MS [13]

Monitoring Well A-1 (Lower Cohansey Aquifer) RAS Results in 1984 for the Superfund Site III-PR yielded Methylene Chloride at 89 ug/L and 1,2-Dichloroethane at 50 ug/L. The RI/FS excluded the Methylene Chloride for all samples.

Monitoring Well A-1 was analyzed in 1986 using split samples to one CLP (New England), one nonCLP (Mid-Atlantic), and the NJDEP-BEL. The former reported Methylene Chloride at 7B along with Acetone 6JB, Benzene 2JB. The nonCLP laboratory found "ND" for all HSL analytes. The Cryofocus Capillary results found 6.2 ug/L trans-1,2-Dichloroethene (a known contaminant for the PR site); no other compound above 1 ug/L was found. Methylene Chloride was present in the MBs at 0.2 ug/L (Figures 3a, 3b and 3c).

Most HSL analytes had five level standardization calibration from 0.5 ug/L to 20 ug/L (Figure 3d).

CONCLUSIONS

The analysis of low level analytes including, and in particular Methylene Chloride, can be controlled through SAS laboratory practice on a confirmational basis. It is possible to integrate the SAS within an RAS method or in tandem for QA purposes. The results from three Superfund Sites for potable and low level monitoring well samples can be satisfactorily analyzed and data

Table 1a

SPLIT SAMPLE ANALYSIS

Comparison of Methylene Chloride Results, ug/L, using Regular Analytical Services and Special Analytical Services for CFS 121586:

Residence		Lab	Sample Results	Method Blank	QA Decision
SC	2	RAS SAS	17.0 0.13UB	12.2 0.48	Negate, 17UB Negate, 1.0UB
SP	3	RAS SAS	15.3 1.8	12.2 0.48	Negate, 15UB 1.8JB
MU	4	RAS SAS	23.2 2.0JB	12.2 0.48	Negate, 23UB 2.0JB
AB	8	RAS SAS	9.14 1.0UB (0.05)	12.2 0.92	Negate, 9.1UB 1.0UB
Trip Blank TB (2)		RAS SAS	7.14 0.2JB	12.2 0.48	Negate, 7.1UB Negate, 1.0UB

Figure 1b: Expanded View with PA results removed.

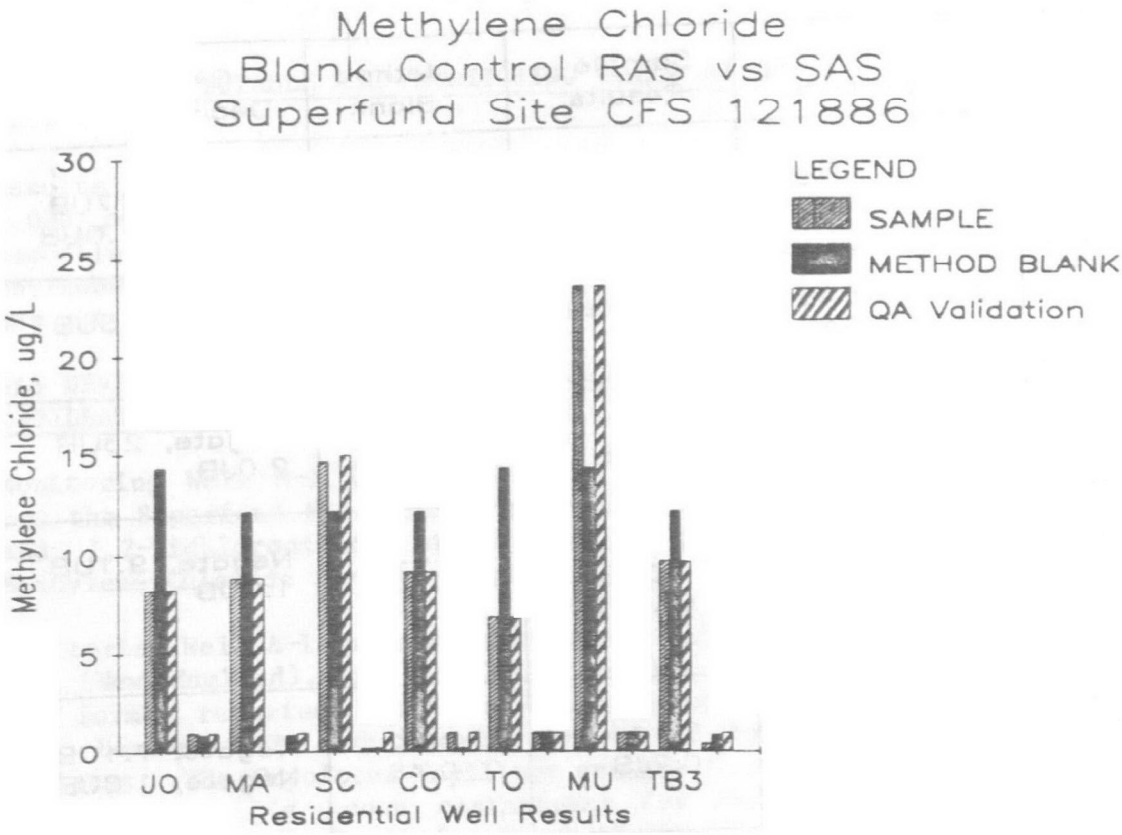


Table 1b

SPLIT SAMPLE ANALYSIS

Comparison of Methylene Chloride Results, ug/L, using Regular Analytical Services and Special Analytical Services for CFS 121886:

Residence		Lab	Sample Results	Method Blank	QA Decision
JO	19	RAS SAS	8.27 1.0UB (0.09)	14.4 0.87	Negate, 8.3UB 1.0UB
MA	20	RAS SAS	8.90 0.10JB	12.2 0.87	Negate, 8.9UB Negate, 1.0UB
PA	26	RAS SAS	178 1.0U	12.2 1.0U	180B 1.0U
MU	32	RAS SAS	23.6 1.0U (0.08)	14.4 1.0U	Negate, 23.6UB 1.0U
Trip Blank TB (3)		RAS SAS	9.72 0.45JB	12.2 0.87	Negate, 9.7UB Negate, 1.0UB

Figure 1c: Superfund Site I-CFS. Results of Split RAS/SAS Samples and Confirmational Sample for the PA Residence. SAS Results for 121886 and 040787 were 1.0UB and 1.0U, Respectively. The 180 ug/L would have involved A NJDEP Action Level III, if confirmed. Decision was made to invalidate the RAS result.

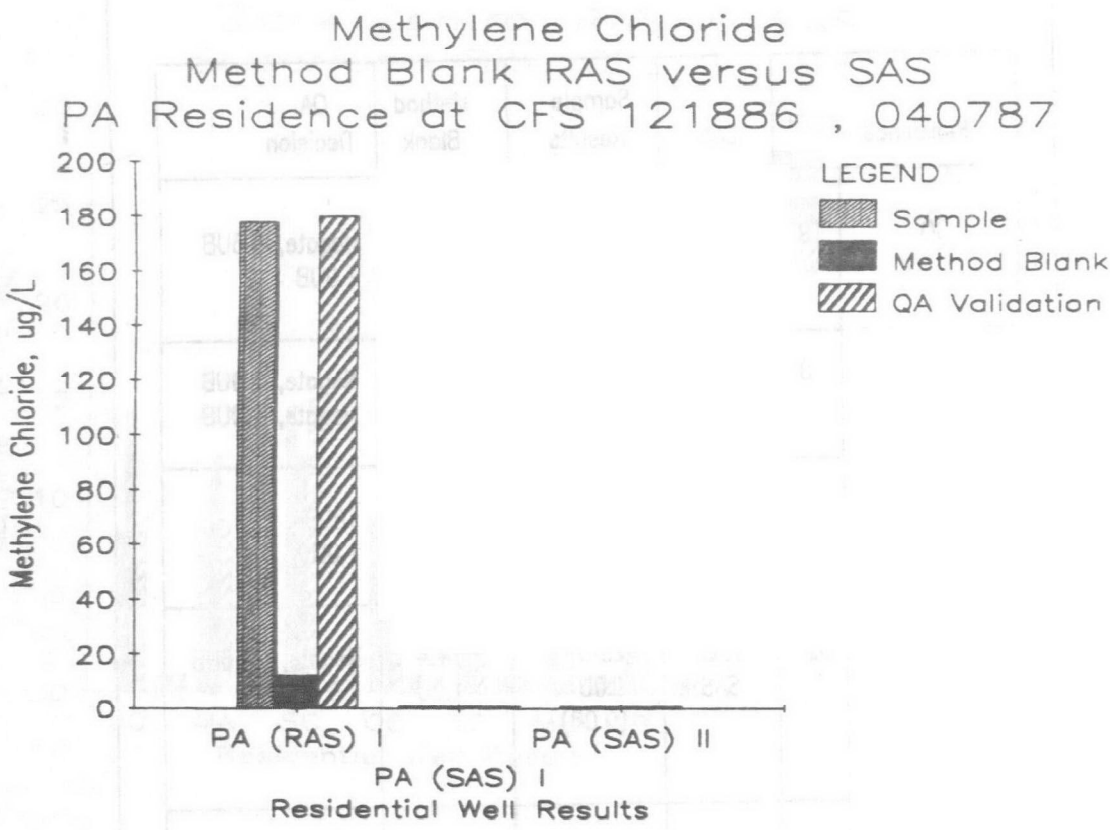


Figure 2: Comparison of RAS/SAS Split Results with Previous RAS Data for Residences SC and AB At Superfund Site I-CFS.

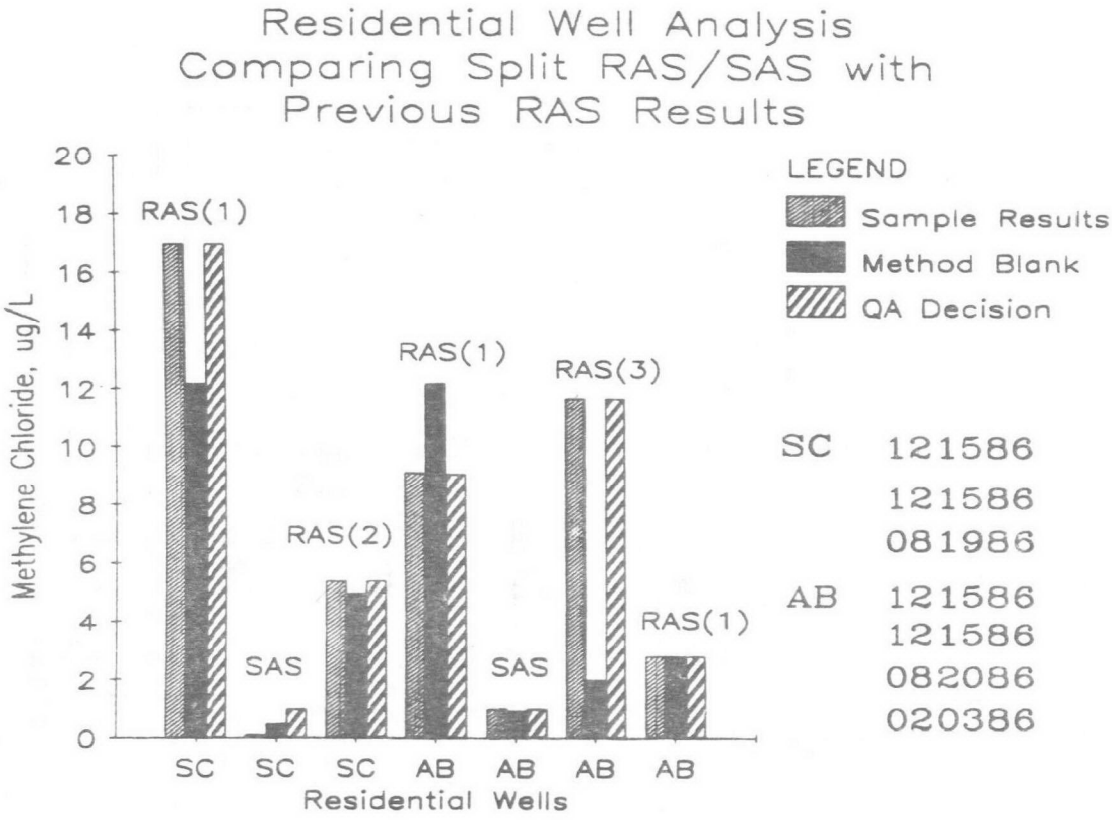


Table 2

RESIDENTIAL WELL ANALYSIS

Comparison of Methylene Chloride Results, ug/L, using Regular Analytical Services and Special Analytical Services for CFS 121586 with previous site sampling episodes using RAS:

Residence		Lab	Sample Results	Method Blank	QA Decision
SC	121586	RAS [1]	17.0	12.2	Negate, 17UB
		SAS	0.13UB	0.48	Negate, 1.0UB
	081986	RAS [2]	5.4	4.96	Negate, 5.4UB
AB	121586	RAS [1]	9.14	12.2	Negate, 9.1UB
		SAS	1.0UB (0.05)	0.92	1.0UB
	082086	RAS [3]	11.7	2.0	11.7B
	020386	RAS [1]	<2.8	<2.8	NA
Trip Blank (Associated)	121586	RAS [1]	7.14	12.2	Negate, 7.1UB
		SAS	0.2JB	0.48	Negate, 1.0UB
	081986	RAS [2]	5.3	4.96	Negate, 5.3UB
	082086	RAS [3]	11	1.9	11B
	020386	RAS [1]	<2.8	<2.8	NA

RAS [1] Mid-Atlantic CLP Laboratory, GC/MS (624)

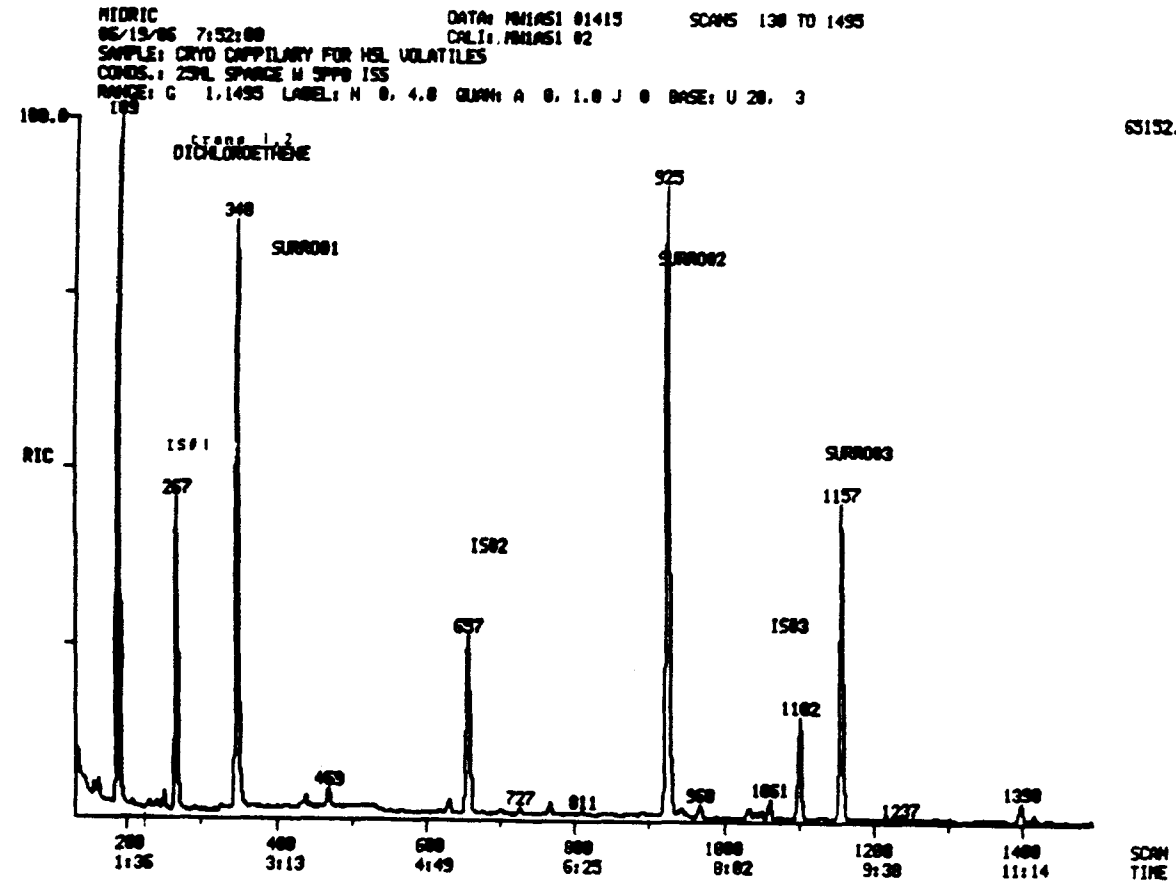
RAS [2] Southeastern CLP Laboratory, GC/MS (624)

RAS [3] New England CLP Laboratory, GC/MS (624)

SAS New Jersey State Laboratory, Hall (Modified 601)

FIGURE 3a:

Superfund Site III (PR) Results by Cryofocus Capillary GC/MS.



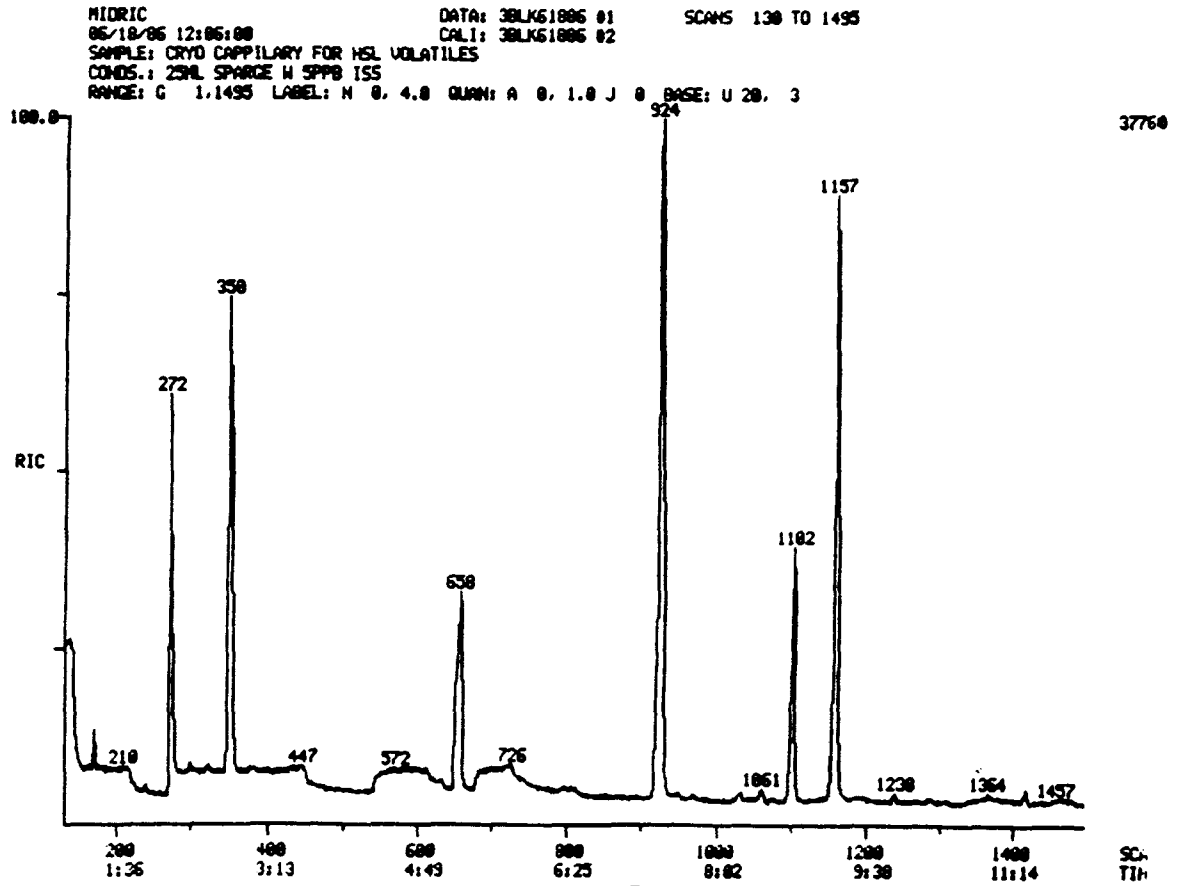
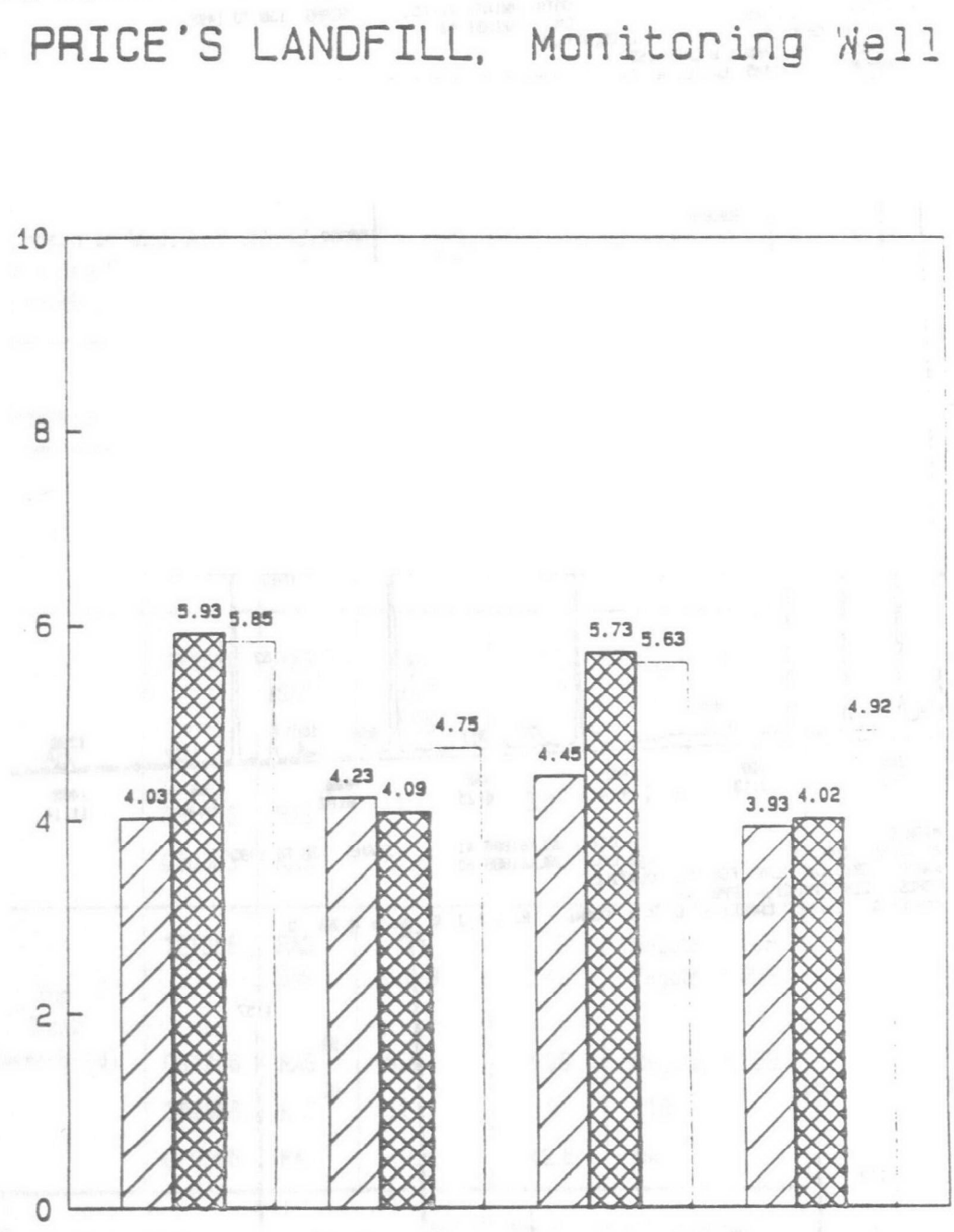


FIGURE 3b:

Surrogate Recoveries for 5 ug/L Spiking Level
Using Cryofocus Capillary GC/MS.



"Surrogate Recoveries from 5 ug/L Spike Levels and Analyzed by Cryofocus Capillary GC/MS for CLP Target Volatile Analytes, the HSLs".

FIGURE 3c: Monitoring Well A 1 of the Lower Cohansey Aquifer at Superfund Site III (PR).

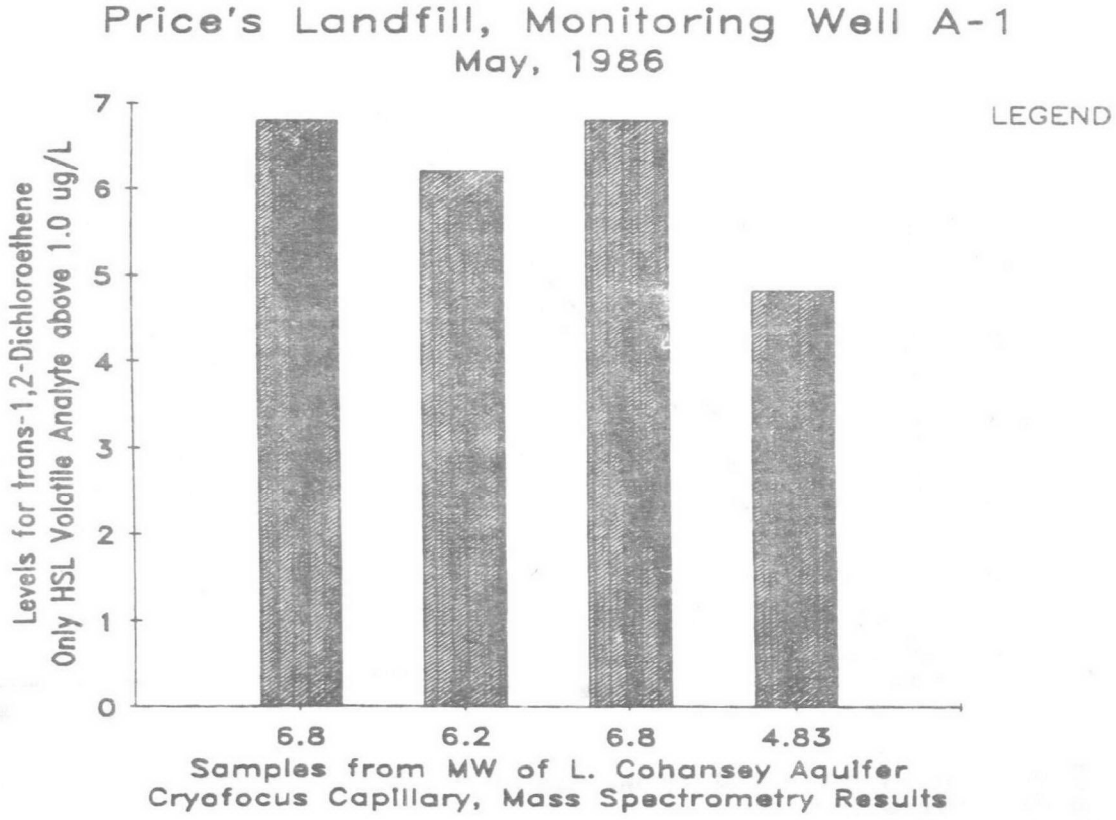
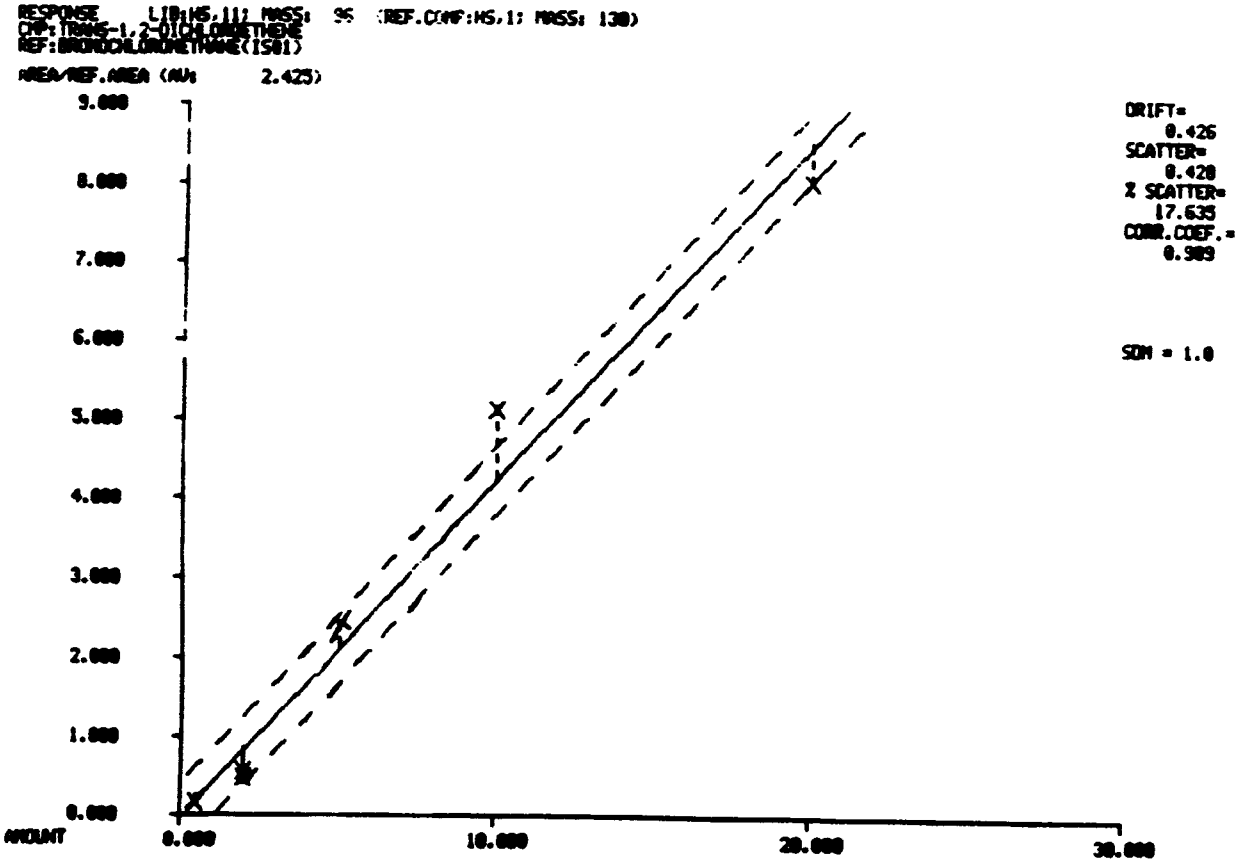
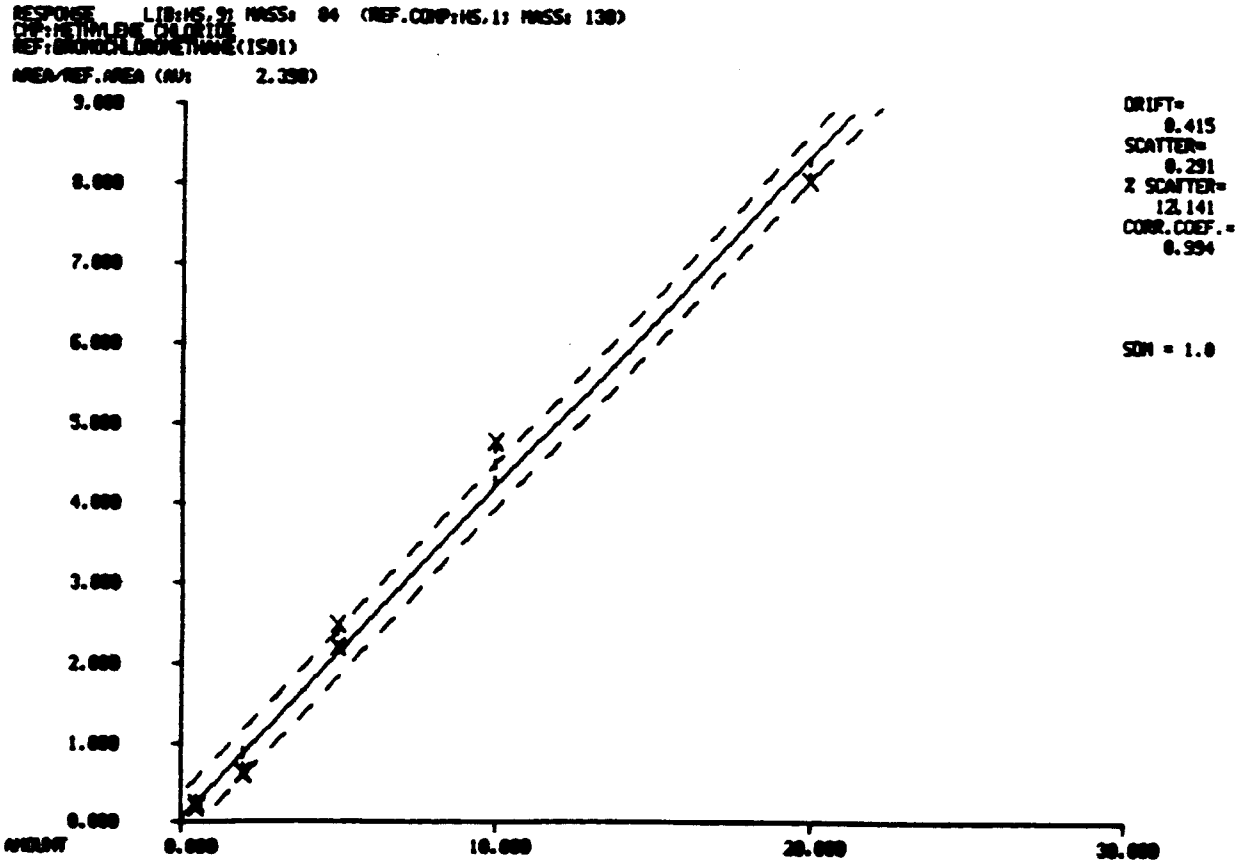


FIGURE 3d: Response curves showing five point low level Standardization used by SAS, Cryofocus Capillary GC/MS.





validated if MB and TB controls and proofs are achieved by the laboratory and documented.

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Fed. Reg., 49, No. 209, p. 141 (EPA Method 624, Purgeables), October 26, 1984.

"Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography/Mass Spectrometry" (EPA Method 524.2), August 1986.

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"Guidelines for the Professional Quality Assurance Data Validation of Analytical Sample Deliverables", DHSM (OQA), NJDEP, February, 1986.

"Drinking Water Guidance, Interim Action Levels and Recommendations of Responses for Selected Organics in Drinking Water", Division of Water Resources, NJDEP, January 1986.

Level II . . . Confirmation of Level II concentrations wherein Methylene Chloride is listed as = 4.8 ug/L and 48 ug/L) the Department shall require "recommend alternative water sources and/or appropriate treatment techniques.]

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"The Quality Assurance, Data Validation Results for the Special Analytical Services Determination of Methylene Chloride: for the PA Potable Water Taken April 7, 1987", April 1987, Personal communication: F. Genicola to R. Kaiserman.

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F. Genicola, "Volatile Organics Analysis of Hazardous Substance List Compounds in Monitoring Well A-1 for the Lower Cohansey Aquifer by Purge and Trap/Cryofocus Precapillary/Capillary Chromatography/Mass Spectrometry using a Modified Target Compound Analysis", May 1987 [Unpublished Study Submitted to Rutgers University's Cook College, Department of Environmental Science].

DEVELOPMENT OF STANDARDS FOR EPA HAZARDOUS WASTE METHODOLOGIES

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ABSTRACT

Every laboratory involved in environmental testing must maintain appropriate standards for the various methods generated by the US Environmental Protection Agency (EPA). It is impractical for each laboratory to develop and test all the necessary standards, or for the EPA to provide all standards to every laboratory. Therefore, commercial standards are a necessity for any environmental analysis program. This presentation will cover the steps involved in developing high quality, readily available standards for many EPA analyses.

To ensure that standards are of the highest possible quality, the quality assurance program must combine thorough testing with verification against EPA standard materials. The ideal multi-step quality assurance procedure includes testing all raw materials by several independent methods, determining the appropriate solvent for each component and its compatibility with other potential components, and verifying each compound against internal reference standards and (whenever possible) external reference materials.

The methods used to evaluate raw materials will be described, with data for selected compounds used as examples. Data from an independent laboratory study will show the traceability of commercial standards to standards from the EPA repository. Development of new standards for the growing list of EPA test methods also will be discussed.

INTRODUCTION

Recently the EPA has developed several new methods that require capillary gas chromatography as the analytical technique. The Superfund Contract Lab Program (CLP) analytical protocol for semi-volatile priority pollutants, which was the basis for EPA Method 8270, is an example of these methods. The CLP protocol calls for combining the acid and base-neutral fractions, prior to injection, and calibrating the capillary GC/MS system at a minimum of five different concentrations over a wide calibration range. Two additional new EPA methods, 502.2 and 524.2, describe capillary GC analysis of volatile organic compounds in water. Methods 502.2 and 524.2 extend purge and trap-based analysis to more than 50 compounds, covering a range of volatility from dichlorodifluoromethane to trichlorobenzene.

QUALITY CONTROL

To fill a need these new methods have created, Supelco has developed a series of analytical standards specifically designed for capillary analysis. In developing these standards, efforts were made

to ensure the highest quality by employing a multi-step quality assurance program. Table I shows the steps involved in this program.

SEMI-VOLATILE POLLUTANTS

The standards for the semi-volatile priority pollutants, introduced in December 1984, differed significantly from previously developed standards in their formulation and testing. Because many of the semi-volatile priority pollutants are unstable or insoluble, when combined in the same mixture, we grouped the compounds into eight stable mixtures containing two to sixteen compatible components. Table II shows the make-up of these mixtures. The new standards contained higher concentrations of each component (2000 µg/ml each for the pollutants, 4000 µg/ml each for the internal standards). This ensures that the concentration of each component will be sufficient for calibrations, even if all eight standards are combined.

The final step in the quality assurance program was a comparison of these standards, by an independent laboratory, to standards from the EPA standards repository. As an added check, 51 isotopically labeled compounds and 2,2'-difluorobiphenyl were used as internal standards. The first comparison was done in July 1984. The results indicated that for 12 of the 66 compounds evaluated, the discrepancy between the commercial standard and the EPA repository standard exceeded 25%. Because this comparison was made against repository standards that were several years old, a second comparison was made in November 1986 against recently prepared repository standards. In addition, the newer repository standards more closely matched the commercial standards in composition and solvent matrix.

In the second comparison, only 2 compounds showed a difference that exceeded 25% between the commercially available standards and the EPA repository standards. Table III shows the results of the second comparison using the isotope dilution technique. Table IV shows the same comparison, but using the six internal standard method used by the Contract Lab Program (CLP). The compounds are listed in decreasing order from the highest to the lowest percent difference. The two compounds with the highest percent difference (benzoic acid and 4-nitroaniline) also have the lowest response factors and are the most difficult of the compounds to monitor.

VOLATILE POLLUTANTS

In the past few months we have completed work on a series of five standard mixtures, each containing 8 to 16 volatile organic compounds. Included are all 58 compounds currently required in EPA methods 502.2 and 524.2. Table V shows the composition of the five mixtures. These standards were developed through a quality control program similar to that for the semi-volatile pollutants. The volatile pollutant standards, however, have not been compared to EPA standards, because not all components are yet available from the repository.

CONCLUSION

Commercial standards have been developed for several new EPA methods for semi-volatile and volatile organic compounds. These standards have undergone a multi-step quality assurance program, including purity determinations for raw materials, lot to lot comparisons and, when possible, comparison to EPA standard materials. Comparison of the commercial semi-volatile pollutant standards to standards from the EPA standards repository show there is excellent agreement between these standards. Work is continuing at Supelco to develop new standards for additional EPA methods, including Appendix IX compounds and nitrogen and phosphorus pesticides.

TABLE I

1) Purity Determination for Raw Materials

   a) Melting point for all solids
   b) Refractive index for all liquids
   c) IR spectra for all compounds
   d) Capillary GC/FID for all compounds

2) Gravimetric Determinations

   a) Accuracy to ± 0.5%
   b) Recording balances used for all weighings

3) Evaluation of Standard Mixtures

   a) Comparison of two independently produced lots
   b) GC or HPLC techniques used for evaluations
   c) Six months stability determined for mixtures

4) Capillary GC/MS Comparison to EPA Repository Standards

   a) Analysis done by an EPA approved independent laboratory
   b) All analyses done in triplicate
   c) Isotope dilution techniques used for quantitation

TABLE II

BASE-NEUTRALS MIX 1	BASE-NEUTRALS MIX 2
Bis(2-chloroethoxy)methane	2-Chloronaphthalene
Bis(2-chloroethyl)ether	1,2-Dichlorobenzene
Bis(2-chloroisopropyl)ether	1,3-Dichlorobenzene
4-Bromophenyl phenyl ether	1,4-Dichlorobenzene
4-Chlorophenyl phenyl ether	Hexachlorobenzene
Bis(2-ethylhexyl)phthalate	Hexachlorobutadiene

TABLE II (continued)

Butyl benzyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
N-Nitrosodimethylamine
N-Nitrosodi-n-propylamine
N-Nitrosodiphenylamine

POLYNUCLEAR AROMATICS MIX

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

PHENOLS MIX

4-Chloro-3-methyl phenol
2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
2,4,6-Trichlorophenol

HAZARDOUS SUBSTANCES MIX 1

Benzoic acid
2-Methylphenol
4-Methylphenol
2,4,5-Trichlorophenol

Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene
Azobenzene
Nitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone

CHLORINATED PESTICIDES MIX

Aldrin
α-BHC
ß-BHC
γ-BHC (Lindane)
δ-BHC
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide

BENZIDINES MIX

Benzidine
3,3'-Dichlorobenzidine

INTERNAL STANDARDS MIX
Acenaphthene-d10
Chrysene-d12
1,4-Dichlorobenzene-d4
Naphthalene-d8
Perylene-d12
Phenanthrene-d10

HAZARDOUS SUBSTANCES MIX 2

Aniline
Benzyl alcohol
4-Chloroaniline
Dibenzofuran
2-Methylnaphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline

TABLE III

SIMILARITIES BETWEEN EPA REPOSITORY AND COMMERCIAL STANDARDS
(ISOTOPE DILTUION METHOD)

Compound		Relative Response EPA	Relative Response Supelco	Relative Percent Difference (%)
Benzoic acid	*	0.10	0.13	30.49
4-Nitroaniline	*	0.06	0.05	-25.92
4-Nitrophenol		0.90	1.11	23.93
4,6-Dinitro-o-cresol		0.82	1.00	21.39
Bis(2-chloroethyl)ether		3.95	4.64	17.42
Benzo(b)fluoranthene		1.04	1.22	17.34
Phenol		3.07	3.55	15.70
Dibenzofuran		0.95	1.08	14.59
Phenanthrene		1.02	1.17	14.46
2-Chlorophenol		0.97	1.11	14.34
4-Bromophenyl phenyl ether	*	0.22	0.24	13.63
Dimethylphthalate		0.89	1.01	13.41
2,4,5-Trichlorophenol	*	0.20	0.22	13.11
Chrysene		1.09	1.23	12.86
Benzyl alcohol	*	0.26	0.29	12.48
Di-n-butylphthalate		0.94	1.05	12.27
Benzo(a)pyrene		1.04	1.17	12.26
Hexachlorobenzene		1.24	1.39	12.21
2,4-Dinitrotoluene		0.92	0.80	-12.20
2-Nitroaniline	*	0.28	0.32	12.16
Benzo(ghi)perylene		1.23	1.37	11.87
Naphthalene		1.00	1.12	11.76
1,2-Dichlorobenzene		1.54	1.71	11.40
2,6-Dinitrotoluene		0.89	1.00	11.38
4-Chloro-m-cresol		1.00	1.11	11.24
1,2,4-Trichlorobenzene		0.88	0.98	11.23
1,4-Dichlorobenzene		1.49	1.65	11.00
Anthracene		1.06	1.17	10.88
2-Nitrophenol		0.96	1.07	10.87
Nitrobenzene		0.91	1.01	10.55
Benzo(a)anthracene		1.06	1.17	10.47
Acenaphthene		1.04	1.14	10.13
Pentachlorophenol		0.89	0.98	10.08
Pyrene		1.01	1.11	10.00
Di-n-octylphthalate		1.01	1.11	9.85
N-Nitrosodi-n-propylamine	*	0.38	0.42	9.83
Diethylphthalate		0.98	1.08	9.61
Bis(2-chloroisopropyl)ether		0.89	0.98	9.47
Hexachlorobutadiene		1.59	1.74	9.46
Acenaphthylene		1.99	2.17	9.11
Fluorene		1.15	1.25	8.84

TABLE III (continued)

SIMILARITIES BETWEEN EPA REPOSITORY AND COMMERCIAL STANDARDS
(ISOTOPE DILTUION METHOD)

Compound		Relative Response EPA	Relative Response Supelco	Relative Percent Difference (%)
4-Chloroaniline	*	0.52	0.56	8.56
Butyl benzylphthalate	*	0.41	0.45	8.49
1,3-Dichlorobenzene		1.52	1.65	8.46
Bis(2-chloroethoxy)methane	*	0.56	0.60	8.19
Fluoranthene		1.00	1.07	7.84
2-Methylnaphthalene	*	0.88	0.95	7.73
2-Chloronaphthalene		1.38	1.48	7.10
Hexachloroethane		1.81	1.94	7.04
2,4-Dichlorophenol		1.57	1.68	6.67
Benzo(k)fluoranthene		0.96	1.02	6.51
Isophorone		1.05	1.12	6.41
Bis(2-ethylhexyl)phthalate		1.05	1.11	5.87
2,4-Dimethylphenol		2.03	2.15	5.80
N-Nitrosodimethylamine	*	0.32	0.34	5.75
Hexachlorocyclopentadiene		4.15	3.94	-4.91
2,4,6-Trichlorophenol		0.77	0.81	4.79
4-Methylphenol	*	0.42	0.44	4.51
2-Methylphenol	*	0.41	0.43	4.00
Dibenzo(ah)anthracene	*	0.39	0.40	2.32
4-Chlorophenyl phenyl ether		1.07	1.10	2.26
Indeno(1,2,3-cd)pyrene	*	0.40	0.41	2.10
2,4-Dinitrophenol		0.96	0.95	-1.38
3-Nitroaniline	*	0.17	0.17	0.10
Difluorobiphenyl (int. std.)	*	1	1	0
Aniline	*	ND	0.76	---
Benzidine		ND	1.69	---
3,3'-Dichlorobenzidine		ND	1.01	---
N-Nitrosodiphenylamine		ND	0.21	---
Azobenzene		ND	1.11	---

*No isotopically labeled analog
ND - Not determined

TABLE IV

SIMILARITIES BETWEEN EPA REPOSITORY AND COMMERCIAL STANDARDS
(SIX INTERNAL STANDARDS METHOD)

Compound	Relative Response		Relative Percent Difference (%)
	EPA	Supelco	
Benzoic acid	0.08	0.11	28.49
4-Nitroaniline	0.09	0.07	-23.43
4,6-Dinitro-o-cresol	0.08	0.10	20.90
2,6-Dinitrotoluene	0.22	0.26	17.80
Benzo(b)fluoranthene	1.27	1.49	17.73
Di-n-butylphthalate	1.06	1.25	17.66
2,4,5-Trichlorophenol	0.27	0.32	17.57
Benzyl alcohol	0.77	0.90	17.50
2-Nitroaniline	0.39	0.46	16.43
4-Bromophenyl phenyl ether	0.20	0.23	15.57
N-Nitrosodi-n-propylamine	1.15	1.33	14.79
Anthracene	0.89	1.02	14.70
Bis(2-chloroethyl)ether	1.58	1.82	14.68
Phenanthrene	1.02	1.17	14.46
Benzo(k)fluoranthene	1.31	1.50	14.03
Dibenzofuran	1.46	1.66	13.81
2-Chlorophenol	1.30	1.47	13.49
Chrysene	1.09	1.23	12.86
Phenol	1.65	1.86	12.69
Benzo(a)pyrene	1.04	1.17	12.26
2,4-Dinitrotoluene	0.33	0.29	-11.89
Naphthalene	1.00	1.12	11.76
Dimethylphthalate	1.15	1.28	11.61
Diethylphthalate	1.16	1.29	11.54
Di-n-octylphthalate	2.00	2.22	11.25
1,2-Dichlorobenzene	1.39	1.54	11.13
1,4-Dichlorobenzene	1.49	1.65	11.00
N-Nitrosodimethylamine	0.97	1.08	10.54
4-Nitrophenol	0.06	0.06	10.16
Acenaphthene	1.04	1.14	10.13
Bis(2-chloroisopropyl)ether	0.45	0.49	10.13
Hexachlorocyclopentadiene	0.26	0.24	-10.06
Hexachlorobenzene	0.21	0.23	10.01
4-Methylphenol	1.27	1.39	9.22
Hexachloroethane	0.48	0.52	9.21
2-Methylphenol	1.24	1.34	8.74
Dibenzo(ah)anthracene	0.88	0.95	8.15
Butyl benzylphthalate	0.75	0.81	8.11
2-Chloronaphthalene	1.48	1.59	7.84
Benzo(ghi)perylene	0.92	0.99	7.70

TABLE IV (continued)

SIMILARITIES BETWEEN EPA REPOSITORY AND COMMERCIAL STANDARDS
(SIX INTERNAL STANDARDS METHOD)

Compound	Relative Response		Relative Percent Difference (%)
	EPA	Supelco	
Indeno(1,2,3-cd)pyrene	0.90	0.97	7.69
1,3-Dichlorobenzene	1.43	1.53	7.48
Fluorene	1.21	1.31	7.47
Pentachlorophenol	0.07	0.07	7.37
Pyrene	1.54	1.65	7.26
Fluoranthene	0.79	0.84	6.98
Acenaphthylene	1.65	1.75	6.67
Benzo(a)anthracene	1.18	1.26	6.56
4-Chloroaniline	0.43	0.46	6.12
Bis(2-chloroethoxy)methane	0.47	0.49	5.73
1,2,4-Trichlorobenzene	0.31	0.32	5.49
2,4-Dinitrophenol	0.09	0.08	-5.29
2-Methylnaphthalene	0.74	0.78	5.22
Difluorobiphenyl (int. std.)	1.38	1.44	3.93
3-Nitroaniline	0.24	0.25	3.79
2-Nitrophenol	0.20	0.20	3.41
Nitrobenzene	0.19	0.20	3.30
Isophorone	0.87	0.89	1.66
4-Chlorophenyl phenyl ether	0.60	0.61	1.62
2,4,6-Trichlorophenol	0.39	0.39	1.61
2,4-Dichlorophenol	0.28	0.27	-1.60
2,4-Dimethylphenol	0.34	0.34	-1.57
Hexachlorobutadiene	0.17	0.17	1.56
4-Chloro-m-cresol	0.32	0.32	1.54
Bis(2-ethylhexyl)phthalate	1.10	1.12	1.21
Benzidine	ND	0.16	---
Azobenzene	ND	1.12	---
Aniline	ND	2.37	---
3,3'-Dichlorobenzidine	ND	0.33	---
N-Nitrosodiphenylamine	ND	0.13	---

TABLE V

VOLATILES MIX 1

tert-Butylbenzene
sec-Butylbenzene
Chlorobenzene
2-Chlorotoluene
4-Chlorotoluene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Isopropylbenzene
n-Propylbenzene
o-Xylene
p-Xylene

VOLATILES MIX 2

Benzene
Bromobenzene
n-Butylbenzene
Ethylbenzene
p-Isopropyltoluene
Naphthalene
Styrene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
m-Xylene

VOLATILES MIX 3

1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,1-Dichloroethane
1,2-Dichloroethane
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropylene
Hexachlorobutadiene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene
1,2,3-Trichloropropane

VOLATLIES MIX 4

Bromochloromethane
Bromodichloromethane
Bromomethane
Carbon tetrachloride
Chloromethane
Dibromochloromethane
cis-1,2-Dichloroethylene
trans-1,2-Dichloroethylene
Trichlorofluoromethane

VOLATILES MIX 5

Bromoform
Chloroethane
Chloroform
Dibromomethane
Dichlorodifluoromethane
1,1-Dichloroethylene
Methylene chloride
Vinyl chloride

Quality Assurance of Analytical Chemistry Through Auditing

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ABSTRACT

Hazardous waste is an extremely complex and variable material. In general, the waste generator is not concerned with the homogeneity or the consistency of the waste. Therefore, the material which is submitted to Chemical Waste Management for waste disposal evaluation offers the analytical chemist a challenge not found in other industries. Manufacturers of chemicals are concerned with the yield and quality of their product. Product specifications must be met. The waste resulting from the process or material which is "out of spec" is set aside for proper disposal without regard for the "quality" of these materials. Because the composition of the waste cannot be controlled, it became essential to develop a stringent program to control and assess the analysis of the waste. The guidelines set forth by the Association of Official Analytical Chemists were used as the basis for developing the Chemical Waste Management Qaulity Assurance Policy.

The major concern of Chemical Waste Management is to provide valid, defensible data in a timely manner. The terms used in this statement require further explanation. Valid means that the precision and accuracy of the analytical data are maintained for all parameters being tested at our laboratories. To be defensible, the data and the records of the data must be able to withstand scrutiny, of the highest degree. The records must be completely traceable from the start of the analytical process to the final report. There are many factors which will be described later that also contribute to defensibility. Briefly, these include: qualified personnel, appropriate analytical methods, and proper equipment and facilities. The demands of chemical processing hazardous waste and the costs resulting from delaying transportation equipment were critical in evaluating which quality assurance and quality control procedures would be included in the overall plan. The processing of hazardous waste like most other industrial processes requires a short turnaround time for analysis. Therefore, generation of the data must be done in a timely manner.

The Chemical Waste Management Quality Assurance Policy includes the following principles:

(1) Defensible Documentation
(2) Analytical Methods
(3) Sampling and Sample Control Methodology
(4) Facility Adequacy
(5) Equipment Maintenance and Calibration
(6) Personnel Training

(7) External and Internal Assessment
(8) Quality Control Policy and Procedures

These principles are briefly described as follows:

(1) Defensible Documentation

This principle requires the use of accountable documents, standard operating procedures (SOP) for recording data, chain-of-custody requirements, instrument parameters, and analytical methods. The procedures for loss or destruction of data and archiving are also included.

(2) Analytical Methods

A site specific methods manual must be in place and include all methods described in the Waste Analysis Plan. Standard methods are used when applicable. A methods review committee submits new methods or modifications of existing methods to the Director of Analytical programs for approval. The Chemical Waste Management nine-point format is required.

(3) Sampling and Sample Control Methodology

Standard operating procedures are used to describe the appropriate sampling techniques and equipment. The sample chain of custody must remain inviolate. Test samples are properly prepared and test portions are properly taken for analysis. The written procedures include labeling, sample containers, holding times, documentation requirements, and safety concerns for the sampler.

(4) Facility Adequacy

Adequate space, proper safety equipment, appropriate laboratory furnishings, and sufficient instruments and supplies are maintained at all laboratories. Sufficient hood space in proper working condition is provided to protect all laboratory employees. Housekeeping guidelines are used to maintain a proper environment for performing analysis.

(5) Equipment Maintenance and Calibration

All maintenance and daily performance checks must be documented as permanent laboratory records. Instruments which require calibration are scheduled for service on a regular basis. Equipment may be sent out or have the proper service performed in the laboratory as required. All calibration curves and printouts must be properly documented and stored.

(6) Personnel Training

Written training protocols must be documented. New employees as well as current employees shall be kept informed of methods and new technologies. Attendance at symposia, training courses, and further

formal education is encouraged. Training which has been completed must be documented for each employee and kept as part of the training records.

(7) External and Internal Assessment

The Manager of Quality Assurance/Quality Control and the Qaulity Assurance Unit, which consists of several quality assurance and quality control auditors, are responsible for external assessment through the use of audits. The performance of the laboratory is evaluated and reported to management. The site laboratory manager internally assesses compliance to the QA/QC policies and procedures on a regular basis. Review of documentation, use of blind duplcates and quarterly reference materials are used to evaluate individual performance in the laboratory.

The use of audits and their results will be described below in more detail. The external assessment of the Chemical Waste Management laboratories has had the greatest effect on the quality assurance of the analytical chemistry within those laboratories.

(8) Quality Control Policy and Procedures

The Quality Control Policy and Procedures apply to the data generation processes which occur within the laboratories. Typical quality control concepts deal with a product manufactured with "zero defects" or with a service provided with "every customer satisfied." In the analysis of hazardous waste, the product is valid, defensible data. The precision and accuracy of that data are a result of the quality control principles that follow.

(a) Instrument Performance Paramenters

A daily check must be performed on all equipment and instrumentation to verify that performance is within a set of criteria statistically pre-established. The time spent to perform this check must be reasonably short. The data is recorded in bound notebooks to substantiate instrument performance.

(b) Contamination Evaluation

The analyses of method blanks for each parameter tested are performed with each batch of samples. The results are documented to show that cross-contamination of samples and contamination of the reagents have not occurred. The method detection limits and the resulting limit of quantification are used as criteria for the acceptability of the blank results.

(c) Quality Control Check Samples

Each analytical test performed in the labortory is required to have a quality control check sample which is analyzed daily. Statistical process control charts are generated from the data for the check samples. The control charts are used to maintain precision of the

analytical process. After reference laboratory analysis of the quality control check sample, the accuracy of the analysis can also be monitored. Control limits of plus or minus three standard deviations of the mean are established as acceptability criteria.

(d) Dupliction

Every tenth sample for each parameter is analyzed in duplicate. Two test portions are taken and carried through the analytical procedure. The acceptance criterion for the relative percent error hs been set at a maximum of twenty percent. Control charts are generated from this data.

(e) Fortification

Every tenth sample for each parameter is fortified with a known amount of the analyte being tested. The fortifcation is made to the sample which was duplicated. The accuracy of the anlytical test is determined by calculating the percent recovery of the fortification. The acceptance criteria have been set at 80% to 120% recovery. Control charts for each parameter are generated from the recovery data.

(f) Reference Materials

Each quarter, standard reference materials from the EPA, NBS, or standard service organizations are analyzed for each parameter available. The performance must be within the acceptance range stated on the standard material.

(g) Round Robin Analysis

Each quarter, a set of samples are submitted to the laboratories for anlaysis. These round robin samples are formulated by the quality assurance unit and the results are compiled and distributed to the laboratory managers. All results must be within two standard deviations of the mean to be acceptable.

(h) Reference Laboratory Evaluation

Each month, the labortory must submit a sample which has already been analyzed to the Technical Center for interlaboratory duplicate analysis. The quality assurance unit serves as the mediator between the laboratories to address any discrepancies and to compile the data to determine any systematic bias in analysis.

Evaluation of laboratory performance is determined through a rigorous audit program. Two specific audits have been developed; namely, the Quality Assurance Audit and the Quality Control Audit.

Quality Control Audit

The quality control audit is in the format of a matrix. The paramenters tested by the labortory form one coordinate of the

matrix. A section of the QC policy is reviewed through a series of questions which form the other coordinate. Each question is answered with a numerical score. If all of the details are in place, then a five is awarded. When some portion of the required information is missing, a three is awarded. If the procedure is not in place, then a score of one is given. Some questions may be answered as "not applicable." The total number of questions answered are summed, and the average is determined by dividing the sum by the number answered. When all of the parameter columns are completed, then the overall average of the columns is determined by summing the average scores for each column and dividing by the number of columns. This process is completed for each part of the quality control policy described earlier. The score for the audit is derived by summing the overall average for all of the parts (a) through (h).

The individual sections of the quality control audit (a through h) can be averaged for all laboratories audited to determine which areas need further attention. The quality assurance unit will then provide additional training and technical assistance to improve the specific areas of concern. The overall progress of the program is monitored by plotting the average scores for each section through time.

The scores for the audits are compiled and evaluated semi-annually. When the data for the last year and a half are plotted together, the progress is clearly shown.

Quality Assurance Audit

The quality assurance audit consists of a series of questions covering each of the major principles of the Quality Assurance Policy. The questions are all written in a form for which the correct answer is "yes." The other choices for each questions are "no" and "not applicable." The number of questions answered "yes" is divided by the number of questions answered as applicable. This result expressed as a percentage becomes the score of the audit. Acceptance criteria have been established to determine if a particular laboratory is performing up to company standards.

The quality assurance audit is summarized. From this summary, action items are established and discussed with the laboratory manager and appropriate facility management personnel. Resolution of these items moves the laboratory toward the objective of the program. The quality assurance practices improve through time as the audit process is repeated. The auditor will review the preceding action items to be sure that all of them have been addressed since the last audit.

The quality assurance audit scores are plotted in descending numerical order. Each succeeding round of scores is added to the same graph. The average score has increased and the slope of the line has decreased. The positive impact that auditing has on the quality assurance of analytical chemistry is most significant.

PREPARATION OF NATURAL MATRIX TYPE SAMPLES FOR PERFORMANCE EVALUATION OF RESOURCE CONSERVATION AND RECOVERY ACT (RCRA) CONTRACT LABORATORIES

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ABSTRACT

The Quality Assurance (QA) Branch develops, analyzes, and distributes natural matrix samples to evaluate the performance of laboratories conducting analyses for the Office of Solid Waste (OSW). In these studies, each laboratory is requested to analyze an organic sample and an inorganic sample using the analytical methods specified by OSW.

The sample designs and reference values are established by multiple analyses in the QA Branch laboratory and contract referee laboratories. These data are evaluated statistically and must be judged acceptable before samples are distributed to the 50-60 RCRA contract laboratories. These data are also furnished to OSW for use in evaluating the results reported by the contract laboratories.

INTRODUCTION

The Quality Assurance (QA) Branch of the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cincinnati) provides QA support for the quality control efforts of laboratories within the United States which conduct water and waste analyses under the Safe Drinking Water Act (SDWA), the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), and Comprehensive Environmental Response Compensation and Liability Act (CERCLA) and regulations.

Under RCRA, the QA Branch develops, analyzes, and distributes solid matrix samples quarterly to evaluate the performance of laboratories conducting solid waste analyses. In these studies, each laboratory is sent two samples, one each for organic and inorganic analyses using the methods specified in Office of Solid Waste (OSW) Method Manual 846, Test Methods for Evaluating Solid Waste, 1982. The methods for trace element analysis includes an acid extraction (1310), followed by measurement using the Inductively Coupled Plasma Method (6010). The extraction procedure simulates the leaching of waste in a sanitary land fill. The recovery of the metals at the extraction pH 5 $\pm$ 0.2 is comparable to conditions in a sanitary land fill. Because the samples are natural matrix samples and

theoretical values are not calculable, their reference values are established by multiple analyses in the QA Branch laboratory and contract referee laboratories. These data are then evaluated statistically and must be judged acceptable by the QA Branch before the samples are approved for distribution in a formal study to the 50-60 RCRA contract laboratories. The reference values and statistical estimates are then furnished to OSW for use in evaluating the results reported by the participating laboratories.

SAMPLE DESIGN AND PREPARATION

Base materials for preparation of the organic and inorganic samples are industrial wastes or soils such as electroplating waste, wire-coating waste or creosote-contaminated soil added to infusorial earth, kaolin or garden soil. Stock solutions of analytes prepared from reagent-grade chemicals are added to the base materials (called spikes) to produce the desired levels for each contaminant.

PREPARATION OF INORGANIC SAMPLE

Approximately 75 lbs. of relatively dry base material are passed through a 4 mm mesh screen and transferred to a 3.5 cu. foot cement mixer. Use of the small cement mixer is ideal; it is open at the top for easy access and is tilted at a 45° angle for tumbling and mixing. Stock solutions of chemicals are spiked into the base material to adjust analyte levels. Spikes are first dissolved in hot or cold reagent water before being slowly mixed with the tumbling base material. The amount of spike is based on the desired "analyzed" target value and experience gained in previous use of the matrix. Note that the RCRA method for metals incorporates a weak extraction using acetic acid which may not recover 100% of a metal. For example, an analyzed value of 230 mg/L barium required an initial spike of 846 grams of $BaCl_2$ with 75 lbs. of base material and a total of 8 liters of water. Furthermore, analyses for some metals exhibit a "threshold" point before detection. In these cases (i.e., Ba, Cr, Pb), doubling or tripling the spike may yield little or no response until the threshold is reached. On the other hand, compounds like sodium arsenate, cadmium nitrate, mercuric nitrate, and sodium selenite show the effect of addition immediately without building to a "threshold" level.

In preparing the samples, the chemist needs information on the concentration of various compounds. This is obtained by analyzing spiking, mixing and analyzing again. The target concentrations are generally the desired levels set by Office of Solid Waste and Emergency Response (OSWER), i.e., barium at a level of 100 mg/L. Table 1 summarizes the final composition and analyses of a single batch of an inorganic solid matrix sample for RCRA.

TABLE 1: INORGANIC SOLID MATRIX SAMPLE

ELEMENT	ADDED AS COMPOUND	COMPOUND ADDED, g	WATER ADDED, mL	FOUND mg/L*
As	$Na_2HAsO_4 \cdot 7H_2O$	300.	2000	7.
Ba	$BaCl_2$	846.	3000	107.
Cd	$Cd(NO_3)_2 \cdot 4H_2O$	34.	1000	3.
Cr	$K_2Cr_2O_7$	367.	3600	0.1
Hg	$Hg(NO_3)_2 \cdot H_2O$	21.	400	0.5
Pb	$Pb(NO_3)_2$	582.	3000	1.5
Se	Na_2SeO_3	167.	1000	9.

*Results of analyses by inductively-coupled plasma after spike.

Experience in preparing this type sample indicates that the pH generally stays above 5.0 units. The process of adding more base material and water to reduce an overspiked value and/or adding more of a compound to raise an analyte value is continued until the target values are reached. If the sample is too viscous for good mixing, water is added and mixing continues. Dry solids adhering to the bottom or sides are broken up and mixed into the slurry.

Once the analyses confirm that the desired range of concentrations has been reached, a small subsample is taken to verify that the pH remains above 5.0 units. If a pH adjustment is necessary, a small amount of ammonium hydroxide is added.

When the analyzed values are on target, the consistency is not too viscous, the sample appears well mixed, and the pH is acceptable, mixing is continued at least overnight. While the mixer is still rotating, a long handled scoop is used to remove approximately 200 grams of solid sample and then to place it in each of a series of 8 oz. glass jars. About an inch of air space is left to facilitate mixing prior to removal for analysis. The spillage is wiped off the outside, the cap is placed on tightly, and plastic tape is then wrapped tightly around the cap to prevent loosening.

About 65 samples (200 ± 50 grams) are prepared from each batch, and labeled. The order in which the samples are filled is noted on the labels and analyses of the 1st and last sample serve as an indications of batch homogeneity.

PREPARATION OF ORGANIC SAMPLE

Industrial wastes and soils are also used as base materials for the organic sample. Some samples contain adequate organics without spiking, such as creosote-contaminated soil. Industrial waste or soil may be diluted with infusorial earth if necessary. Organic compounds from the Appendix VIII list are added to the base material to obtain the desired levels.

The key steps required in the preparation of a typical organic sample are described below:

The amount shown for each of the compounds in Table 2 is weighed out and dissolved in methylene chloride and added to the base material.

TABLE 2: PREPARATION OF AN ORGANIC SOLID MATRIX SAMPLE

ANALYTE	AMOUNT ADDED, mg	ANALYTE FOUND ug/g
acenaphthene	229	97
2,4-dimethylphenol	583	70
p-chlorophenol	938	104
2,4,6-trichlorophenol	344	120
4-bromo-phenyl phenyl ether	476	132
p,p'DDD	345	98
bis (2-ethyl hexyl) phthalate	350	121
isophorone	470	150

The selected volumes of analytes are added to 1500 grams of a 50/50 mix of infusorial earth and kaolin. Water and additional base material are added to bring the total weight of the sample to 1775 grams.

The sample is placed in a 3 liter ceramic container, sealed, and mixed on a ball mill for three to four hours. The container is opened periodically and the solids cleared from the sides of the container. Mixing continues for approximately 4 hours. At this point, at least 2 subsamples are withdrawn and analyzed to verify homogeneity. When the analyses indicates a homogeneous mix, approximately 20 grams are dispensed into each of seventy 2-oz. bottles with teflon lined caps, and sealed.

ANALYSES OF PREPARED SAMPLES

The QA Branch analyzes the samples at time zero, two weeks and six weeks. Concurrently, samples are sent to three referee laboratories for analyses as unknowns. The OSW specified methods are used to analyze the inorganic and organic samples. The data are compiled and the mean recoveries and standard deviations of each analyte determined. These statistical results are then provided to OSW for use in establishing acceptance limits for data from the 50-60 participating RCRA laboratories. The calibration standards required in the organic analyses are provided from the USEPA Repository of Toxic and Hazardous Materials to ensure comparable standards among all laboratories.

STUDY DESIGN

The samples are mailed to the RCRA laboratories with instructions for sample handling and specifying the OSW methods to be used for the analyses. Since some organic methods permit use of more than one solvent for the extraction, the instructions specify one solvent for use in the study. The instructions also include a listing of the compounds to be measured in this sample. The complete package of organic and inorganic samples with instructions for handling and analyses, and the calibration standards are mailed to the laboratories specified by OSW. In about four weeks, data from these laboratories are returned to OSW for evaluation of laboratory performance.

A FIELD AUDIT PROGRAM TO ENSURE THE QUALITY OF ENVIRONMENTAL MEASUREMENTS

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ABSTRACT

The word audit, by definition, means to examine with intent to verify. In recent years, field audits at hazardous waste sites have become a tool which may be used to insure quality control at a site under remediation. A Quality Control Field Audit is the primary method utilized by the State to insure contractor compliance with the terms and conditions of the contract and also to determine the adequacy of field operations in generating data representative of environmental conditions. NJDEP/DHSM has developed stringent guidelines for contractors either working directly for the Department or planning to submit data to the Department for review and validation. NJDEP/DHSM has been operating a Field Audit Program for over four (4) years with audits being conducted at over five hundred sampling events. The Field Audit Program has taken a very aggressive approach to Remedial Investigations (RI) at Superfund Sites since New Jersey has initiated RI's at over ninety NPL sites.

By use of a detailed field auditing form, the auditor can highlight certain deficiencies which may affect data quality and usefulness. Conversely, the forms may be used to indicate complete compliance by the contractor. In most cases, the auditor and contractor will be able to develop altered field procedures as necessary, to ensure the quality of the samples and subsequent data generated.

If deficiencies noted in the field are deemed major by the auditor, and no satisfactory alternative can be arranged between the auditor and the contractor, the power to stop work until the problem is mitigated is invested in the auditor. Should the contractor choose to continue with field activities, he is informed it is at his own risk.

Typically, an auditor is present on the first or second day of sampling conducted for environmental analysis. The auditor may return to the site further into the project to witness sampling of various media. If an incidence of non-conformance is noted early in field activities, he may return at a later date, unannounced, to insure the contractor is in compliance with the revised protocol.

Contractor non-compliance falls into two categories: (1) minor infractions, and (2) major infractions. Minor infractions are those problems brought immediately to the contractor's attention in the

field. The impact to data generated is greatly minimized if the improper procedure can be quickly corrected. Major infractions are those procedures which substantially deviate from the approved work plan or DHSM Field Procedures. A major infraction would be something that potentially causes data critical to the evaluation of a project to become qualified or suspect.

Hence, the Field Audit program is a valuable mechanism by which the State can assess contractor compliance with approved field methods and to minimize the need for resampling at sites or data qualification due to contractor non-compliance.

INTRODUCTION

The word audit, by definition, means to examine with intent to verify. In recent years field audits have become an essential mechanism for ensuring that quality control requirements and procedures are strictly adhered to during the collection of environmental measurements. The New Jersey Department of Environmental Protection (NJDEP) has operated a Field Audit Program for the past four (4) years with over five hundred (500) sampling episodes having been audited by trained personnel. The justification for allocating resources to operate such a program is derived from NJDEP's aggressive commitment to insuring the validity of analytical data resulting from the collection of environmental measurements at various hazardous waste sites. The audit program is based upon the premise that one must insure the quality and representativeness of samples generated in the field in order to certify that corresponding analytical data is in fact representative of site conditions. A second important premise is that sampling techniques utilized during several sampling events must be consistent for the duration of a project to ensure that data from one event is comparable to another in terms of how samples are collected, handled, and packaged prior to shipment to the laboratory for analysis. An audit program also provides oversight in the field to insure contractor compliance with the terms and conditions of NJDEP approved site specific documents which may include Quality Assurance Project Management Plans, Field Sampling Plans, and Health and Safety Plans. These documents provide a bench mark for trained auditors upon which contractor performance is evaluated. Thus, review and familiarity with these documents by the auditor is a prerequisite to conducting a Quality Control Field Audit.

This paper will describe the primary components of NJDEP's Quality Control Field Audit Program and focus on the application of field audits to Remedial Investigations at Superfund sites conducted in accordance with the provision of CERCLA.

PROGRAM ORGANIZATION

NJDEP'S Quality Control Field Audit Program operates out of the Bureau of Environmental Measurements and Quality Assurance (BEMQA) within the Division of Hazardous Site Mitigation. BEMQA is responsible for all aspects of data collection, handling and validation. The Bureau is charged with assuring that all data collected by and presented to the NJDEP Hazardous Waste Programs is of a known and verifiable quality and is representative of actual environmental conditions under investigation. The Bureau is further organized into two major groups; the Environmental Measurements Section and the Quality Assurance Section. A primary component of the Environmental Measurement Section (EMS) is the Quality Control Field Audit Program and Technical Review Service.

At present this program consists of one full time program manager and four full time auditors to oversee sampling activities at New Jersey Superfund sites. An additional pool of trained personnel is available within EMS when temporary increases in field activities occur. Program personnel work in concert with NJDEP Site Managers and Technical Coordinators with respect to review of technical documents, approval of specific sampling procedures, and also recommend changes in procedures to incorporate the most current QA/QC protocol into the site evaluation/remediation strategy. The auditor also interacts with the Quality Assurance Section staff to provide valuable information that may be used to answer questions or clarify issues related to analytical data quality and validation.

PERSONNEL TRAINING AND QUALIFICATIONS

Members of the EMS audit team should possess the appropriate education, training and field experience prior to conducting field audits individually. Each member of the audit team should satisfy the following requirements.

1. A minimum of one year field experience in the collection of environmental measurements following NJDEP methodologies and use of approved sampling equipment.

2. A minimum of one year experience performing technical document reviews and preparation of comment memorandums.

3. At least six months field training with an experienced auditor in conducting field audits, and preparing QC Field Audit Reports.

4. Demonstrated ability to accurately identify problems with a contractor's performance and maintain a professional and objective attitude when interacting with contractor personnel to mitigate observed problems.

5. Enrollment in the NJDEP Medical Surveillance Program.

It is important to ensure that auditors are familiar with problems that routinely occur in the field and that they are able to recommend the appropriate corrective measures. This ability is essential to prevent unnecessary delays and prevent actions from occurring which are out of compliance with the approved project plans.

ADMINISTRATIVE AND OPERATIONAL PROCEDURES

To properly manage an audit program day to day operations must be organized and set forth in writing. To meet this objective NJDEPs audit program has developed several procedures and administrative requirements to promote efficient operations.

All NJDEP Site Managers and Technical Coordinators must provide the Audit Program Manager with the applicable technical documents for review at least two weeks prior to scheduled field activities. This allows the auditor sufficient time to become familiar with the objectives of a particular sampling event and an opportunity to recommend changes in sampling procedures if deemed necessary.

These documents are reviewed for individual technical merit and evaluated against those procedures found in the NJDEP Field Sampling Procedures Manual, July 1986 Edition. These plans are also reviewed in terms of their applicability to site specific conditions and are evaluated to determine if the specific objectives of the sampling episode will be met through implementation of the various documents as written.

Copies of the final revised documents are also reviewed to determine if comments from the auditor were incorporated. Participation in the review process is an important quality control function designed to prevent plans of questionable integrity from being implemented which may result in the generation of less than acceptable analytical data.

All requests for document reviews and field audits are received via a one page Work Request Form which specifies who the requester is, the nature of the task, and other relevant information including the due date. All work requests are then entered into a tracking system to maintain up to date information on current work load, staff assignments, and project status. This tracking system is also used to plan weekly field schedules, record outputs (Field Audit Reports, Document Review Memorandums, etc.) and as a source of information for preparation of monthly reports on program activities. Additional procedures with corresponding flow charts have also been developed to display the flow of information, personnel

responsibilities, and documentation required for completing all document reviews, field audits and audit reports.

Another important element of the program is the actual format used to document contractor performance in the field. Detailed reporting forms are utilized by the auditor to record information related to a particular sampling event. These contractor evaluation forms consist of the following.

1. Cover Sheet Page

   This form asks for a brief synopsis of the actual audit in terms of the site name and location, the contractor's name, who requested the audit, what the relevant plan and documents are, highlights of problems encountered if any, matrices witnessed and a recommendation for qualification of analytical data due to collection procedures if warranted.

2. General Information Page

   Here the names of personnel on site, their affiliation and phone number are recorded. Also included are spaces to record the regulatory program being applied to the project, the project phase, weather conditions, level of personnel protection utilized and any other comments the auditor feels are warranted.

3. QA/QC Information Page

   On this page the auditor is asked to record the name of the laboratory performing the analysis, specific analytical parameters requested, and indicate if Chain-of-Custody was initiated properly for all samples.

   Other items requested include specifies on sample preservation technique, decontamination of sampling equipment, use of QA/QC samples (duplicate field blanks, trip blanks) description of sample shuttles and type, frequency of use and calibration methods used for air monitoring instrumentation.

   The audit forms also include separate pages which must be completed for each sample. Separate forms for aqueous and non-aqueous samples are used providing specific information on sample locations, sampling method, collection time, sample appearance and other relevant details of a specific sample. Another report form is used when observing the installation of monitoring wells as part of a groundwater investigation program.

By using a consistent reporting format and following specific operational procedures, audit personnel are provided basic tools for implementing the program in a timely and efficient manner.

PROCEDURES TO ADDRESS CONTRACTOR NON-CONFORMANCE

When conducting a Quality Control Field Audit, the auditor may witness a situation that may cause the contractor to deviate from the approved sampling plan or the auditor may actually witness sample collection and handling procedures that will potentially compromise the integrity or representativeness of a particular sample or sample shipment. Recognition and mitigation of these problems is perhaps the most important element of a QC Field Audit Program.

NJDEP is committed to immediate identification and subsequent correction of any problems in the field on a real time basis. In this situation the auditor is empowered to request the contractor to stop work immediately, identify the problem observed and recommend specific actions necessary to permit the sampling episode to continue. By recommending immediate corrective action the auditor can ensure that resampling of a particular location is accomplished if the initial procedure witnessed was performed incorrectly. This type of corrective action is preferred over simply recording the deviation in the audit report and allowing a sample of questionable integrity to be submitted for analysis.

Here again specific procedures to guide the auditor with respect to communicating with contractor personnel and NJDEP management staff have been developed to accomplish problem resolution. These procedures are separated into two categories. The first deals with mitigation of minor infractions or non-conformance items. These are problems brought immediately to the attention of the contractor and are easily corrected. Negative impact to samples generated can be readily eliminated and procedures are corrected to achieve the desired result. Examples of minor infractions routinely observed are as follows:

1. Failure to change disposable gloves between procurement of individual samples.
2. Insufficient well evacuation.
3. Incorrect decontamination of sampling equipment.
4. Improper operation of sampling equipment.

The second category addresses major infractions or non-conformance items. These include events or procedures that substantially deviate from approved plans and sampling procedure or will otherwise result in increased project costs not previously approved. A major infraction would be something that causes subsequent analytical data

critical to the environmental evaluation of a project to be qualified or suspect. This type of infraction has the potential to result in the auditor requesting total or partial rejection of samples scheduled for shipment to a laboratory or a recommendation to the Quality Assurance Section Chief that analytical data generated be qualified or rejected.

Examples of major infractions may include:

1. Failure to provide required QA/QC samples.
2. Lack of field equipment decontamination.
3. Substantial changes in sample location, matrix or frequency.
4. Use of non-approved sampling equipment or methodologies.

In addition to monitoring contractor performance the presence of an auditor on site has other benefits.

In the event citizens or media representatives arrive on site these individuals communicate directly with an NJDEP representative who can briefly explain what is happening on site and refer individuals to the Department's Press Office, Office of Community Relations or other appropriate officials for further information. The presence of an auditor during the sampling of residential potable wells also provides an opportunity for homeowners to speak directly with a government official who can answer questions and/or direct them to the appropriate NJDEP office for further information.

Other benefits of the program include the generation of a Quality Control Field Audit Report to NJDEP Site Managers which provides valuable information within two weeks of the sampling event. Without the benefit of the report, management staff might wait substantially longer periods of time until the results of the site investigation are reported formally to NJDEP by the contractor. The audit report can also be used to verify or challenge the findings of the contractor's report with respect to the collection and handling of samples and the evaluation of on site conditions.

The findings contained within the audit report may also be used to assist in the review and validation of analytical data. In addition to laboratory performance, the methods employed to collect, handle, preserve and package environmental samples may have a significant impact on data quality. By monitoring these activities in the field the audit program assists in assuring that remedial decisions are based on data generated from representative samples.

Potential cost savings are also realized by preventing samples of poor quality from being analyzed and preventing subsequent remedial decisions from being based on data of questionable integrity.

PROGRAM SUMMARY AND FUTURE OBJECTIVES

The Quality Control Field Audit Program has gained respect and recognition as an essential component of the Department's Quality Assurance Program. Field audits initially were employed as a tool for evaluating contractor performance in the field when Remedial Investigations were first conducted at Superfund Sites.

Since that time New Jersey has initiated Remedial Investigations (RIs) at over ninety (90) NPL sites and has proposed an aggressive schedule for conducting RIs at many additional sites in fiscal year 1988. The audit program managed by BEMQA has also been utilized by other regulatory programs within NJDEP when collection of environmental measurements by contractors are required to evaluate the known or suspected presence of hazardous materials on site.

The audit program has several program development items on its future agenda. The first is the development of a contractor education program. This program will consist of seminars for professional firms having been awarded contracts by the Department to conduct remediation activities at hazardous waste sites. These seminars will focus on applicable QA/QC requirements associated with the collection of environmental measurements and generation of analytical data. The intent of these seminars is to provide an opportunity for DEP and contractor personnel to discuss current policies and requirements prior to the preparation of site specific proposals. Since QA/QC policies are frequently revised as new technical approaches are developed, it is important for all contractors working for the Department to be familiar with up to date requirements.

A second important objective is the continuance of a cooperative working relationship with the USEPA Region II Monitoring Management Branch. For the past year BEMQA staff have been meeting regularly with our EPA counterparts to discuss various QA/QC issues involving both field and laboratory performance standards. Our mutual goal is to establish consistent policies between the two agencies and to maintain a forum for policy review and evaluation.

Finally, the audit program is committed to the continued objective and consistent evaluation of professional firms contracted by the Department to conduct hazardous waste site Remedial Investigations. Through these efforts we will continue to assist in assuring that the Department is provided with accurate, measurable data which provides an important basis for responsible decision making.

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The authors of this paper are staff members of New Jersey Department of Environment Protection, Division of Hazardous Site Mitigation.

Note: These procedures are representative of the types of controls which are in effect as of May 1987. These controls are subject to revision and expansion.

PERFORMANCE AUDITS RECOMMENDED FOR VOLATILE AND SEMI-VOLATILE ORGANIC MEASUREMENTS DURING HAZARDOUS WASTE TRIAL BURNS

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ABSTRACT

The measurement of air toxic organics requires sophisticated sampling and analysis systems. Agency personnel responsible for the use of air toxic measurements need to be concerned about the accuracy of such measurements. The application of quality assurance practices is important to the generation of high quality measurement data. One such practice is the performance audit, which involves providing "unknown" or "blind" samples for measurement. When conducted simultaneously, during a hazardous trial burn test, the performance audit provides an assessment of the measurement accuracy.

The Quality Assurance Division of USEPA's Environmental Monitoring Systems Laboratory has a program to develop selected volatile and semi-volatile organic audit materials to federal, state, and local agencies or their contractors for use in performance audits to assess the accuracy of measurement methods during hazardous waste trial burn tests. Research Triangle Institute (RTI), under contract to the USEPA, has responded to this need through development of gas cylinders containing 27 gaseous volatile organic compounds in five, six, seven and nine component mixtures at ppb levels and 5 semi-volatile organics spiked on XAD-2 cartridges.

Studies of all organic compounds (both volatiles and semi-volatiles) were performed to determine the stability of the compounds and their feasibility as performance audit materials. Results indicate that all of the selected organic compounds are adequately stable as reliable audit materials.

Performance audits have been conducted using the audit materials to assess the accuracy of the measurement methods. To date, 110 performance audits have been initiated using ppb level audit gases. The audit results obtained with audit gases during hazardous waste trial burn tests were generally within $\pm$ 50 percent of the audit concentrations. A limited number of audit results were obtained with the spiked cartridges. Results were generally within $\pm$ 35 percent of the audit concentrations. The list of volatile and semi-volatile organics, RTI measurement procedures, stability data, audit procedures and results of representative performance audits will be presented.

INTRODUCTION

The measurement of air toxic organics requires sophisticated sampling and analysis systems. Agency personnel responsible for the use of air toxic measurements need to be concerned about the accuracy of such measurements. The application of quality assurance practices is important to the generation of high quality measurement data. One such practice is the performance audit, which involves providing "unknown" or "blind" samples to laboratories for analysis. When conducted simultaneously during a hazardous waste trial burn test, the performance audit provides an assessment of the measurement accuracy.

The Quality Assurance Division of the U. S. Environmental Protection Agency's (EPA's) Environmental Monitoring Systems Laboratory has a program to develop selected volatile and semivolatile organic audit materials and provide them to Federal, State and local agencies or their contractors for use in performance audits to assess the accuracy of measurement methods used during hazardous waste trial burn tests. Research Triangle Institute (RTI), under contract to USEPA, operates a performance audit program through development of gas cylinders containing 27 gaseous volatile organic compounds in five-, six-, seven-, and nine-component mixtures of parts-per-billion (ppb) levels (7 to 10,000 ppb) and 6 semivolatile organic compounds are shown in Tables 1 and 2 respectively.

The gaseous organic compounds in Table 1 are purchased in compressed gas cylinders from commercial suppliers. These cylinders, along with an appropriate delivery system, are used directly without dilution in the performance audits. The semivolatile compounds, shown in Table 2 are spiked onto XAD-2 cartridges at RTI.

Before being used as an audit material, the contents of each cylinder undergo a series of analyses at RTI. The cylinder contents are analyzed after initial receipt from the manufacturer to check the accuracy of the reported concentration of the test compound. The cylinder contents are then analyzed periodically over the course of a year and later on a yearly basis to estimate the compound stability. Similarly, representative samples of spiked cartridges are analyzed initially and then periodically to determine the compound stability. All concentrations are measured by using gas chromatography (GC) with flame ionization detection (FID) and/or electron capture detection (ECD).

TABLE 1. PPB-LEVEL ORGANIC GASES IN REPOSITORY

Group 1: 5 Organics in N_2	Group 2: 9 Organics in N_2	Group 3: 7 Organics in N_2	Group 4: 6 Organics in N_2
Carbon tetrachloride	Trichloroethylene	Vinylidene chloride	Acrylonitrile
Chloroform	1,2-Dichloroethane	F-113	1,3-Butadiene
Perchloroethylene	1,2-Dibromoethane	F-114	Ethylene oxide
Vinyl chloride	F-12	Acetone	Methylene chloride
Benzene	F-11	1,4-Dioxane	Propylene oxide
	Bromomenthane	Toluene	Ortho-xylene
	Methyl ethyl ketone	Chlorobenzene	
	1,1,1-Trichloroethane		
	Acetonitrile		
Ranges cylinders currently available: 7-90 ppb 90-430 ppb 430-10,000 ppb	Ranges cylinders currently available: 7-90 ppb 90-430 ppb	Ranges cylinders currently available: 7-90 ppb 90-430 ppb	Ranges cylinders currently available: 7-90 ppb 430-10,000 ppb

TABLE 2. SEMIVOLATILE ORGANIC COMPOUNDS IN THE AUDIT REPOSITORY

- Chlorobenzene
- Toluene
- O-Xylene
- Pyridine
- 1,1,2,2,-Tetrachloroethane
- Nitrobenzene

EXPERIMENTAL METHODS

Instrumentation

Analysis of Audit Cylinder Gases: Analysis of ppb-level audit mixtures are performed on a Hewlett-Packard 5880A gas chromatograph (GC) equipped with flame ionization and electron capture detectors. The electron capture detector (ECD) is used principally for measurement of all the halogenated organic compounds except vinyl chloride. A fixed volume of each gas in a sample loop is injected onto the GC column through a six-port gas sampling valve mounted near the injection port. After separation of the organic compounds from nitrogen, a GC response is produced and electronically integrated. GC conditions for all analyses of ppb-level audit gases have been previously described(1).

Preparation and Analysis of Spiked Audit Cartridges: The preparation of the cartridges, 50 g of XAD-2 resin is loaded into a glass source assessment sampling system organic vapor trap and the trap is connected to a Nutech Model 201 Method 5 sampler and room air was sampled through the resin at a flow rate of approximately 1 ft. ^{3}/min. During the approximately 30 min. that room air is being drawn through the resin, a known amount of semivolatile standard mix is injected onto the resin via the flash evaporator. As nitrogen flows through it, the flash evaporator is gradually heated to 250°C, and the volatized compounds are absorbed on the resin.

For analysis of the cartridges, the spiked XAD-2 cartridges are soxhlet extracted with 300 mL of methylene chloride over approximately 20 h. A Kuderna-Danish evaporator is then used to concentrate the extract to 10 mL. The concentrated extracts are analyzed on a Perkin-Elmer Model 3920B GC with a flame ionization detector.

Standardization and Measurement

Calibration of the GC involves measurement of known concentrations of gases in nitrogen. Permeation tubes purchased from commercial suppliers or the primary standards that are prepared and analyzed by the National Bureau of Standards (NBS) are generally used as calibration standards for all the ppb-level multicomponent organic mixtures.

The calibration standard mix for the semivolatile compounds is prepared by weighing known amounts of neat liquids into a volumetric flask which is then filled with methylene chloride to the mark.

A multipoint standard curve is generated for those compounds that exhibit a linear FID response. For those which show evidence of non-linearity, at least two calibration standards are prepared each time a sample is analyzed. Both standards are prepared within 20 percent of the expected sample concentration.

RESULTS AND DISCUSSION

Performance Audits

As stated previously, the EPA (through RTI) supplies audit materials for performance audits upon request from Federal, State or local agencies of their contractors. The contractors must, however, be performing hazardous waste trial burn tests on behalf of EPA or one of these public agencies to qualify for the performance audit. The performance audit should be conducted simultaneously with the actual planned test. Performance audits prior to trial burn tests to asses the proficiency of the measurement system (including the sampling and analytical personnel) are also encouraged.

When a request is received for an audit of the volatile organic compounds, the cylinder pressures are measured, and the cylinder and glass manifold delivery system (when volatile organic sampling train is used for sampling) are shipped by overland carrier to the audit site. General instructions for conducting the audit are included with the audit materials. The audit results are reported to the agency (Federal, State, or local) coordinator requesting the audit. There is no charge to the user except the cost of returning the audit cylinders/audit cartridges.

To date (May 1987), 130 performance audits have been initiated with ppb-level audit gases. Of these 130 audits, 65 audits have been conducted to assess the accuracy of measurement methods (both sampling and analysis procedures) used during hazardous waste trial burn tests. The results obtained for some of the performance audits are shown in Table 3. The results of audits for the VOST methods are usually within the $\pm$ 50 percent limit stated in the VOST protocol(2). A limited number of audits were conducted with the spiked XAD-2 cartridges. An example of audit results obtained with the spiked cartridges is shown in Table 4. Results were generally within $\pm$ 35 percent of the audit concentrations measured by RTI.

The principal results of these audits have been to ensure that analyses are performed properly, to detect problems that could be corrected, and to document the accuracy of the measurement systems used during the hazardous waste trial burn tests.

Table 3. Example of Performance Audit Results
(RCRA Testing)

Group No.	Audit No.	Measured system audited	Audit material	RTI-measured concentration (ppb)	Auditee results accuracy (%)[a]
Group 1	5	VOST collection; GC/MS analysis	Carbon tetrachloride	11.0 ± 0.3	-31
			Chloroform	45.0 ± 0.9	+220
			Vinyl chloride	20.5 ± 0.7	+7
Group 2	37	VOST collection; GC/FID analysis	Acetonitrile	7.9 ± 0.6	+380
			Trichloroethylene	9.0 ± 0.4	+40
			Freon-11	9.4 ± 0.3	+3
			1,2-Dibromoethane	10.2 ± 0.4	+1
			1,1,1-Trichloroethane	10.1 ± 0.5	+8
Group 3	81	VOST collection; GC/MS analysis	Freon-114	8.5 ± 1.3	+131
			Vinylidene chloride	10.9 ± 1.0	-16
			Acetone	27.6 ± 5.7	-18
			Toluene	30.8 ± 3.6	+78
			1,4-Dioxane	28.8 ± 8.9	-79
			Chlorobenzene	31.4 ± 3.6	+49

[a]% accuracy = $\frac{\text{Auditee concentration-RTI concentration}}{\text{RTI concentration}} \times 100$

Table 4. Example of Audit Results
(Spiked onto XAD-2 Cartridges)

Sample No.	Compound	RTI audit concentration (µg)	Auditee concentration[a] (µg)	Percent accuracy[b]
1	Toluene	175	121	-31
	Chlorobenzene	168	126	-25
	Tetrachloroethane	162	124	-24
2	Toluene	172	120	-30
	Chlorobenzene	165	126	-24
	Tetrachloroethane	159	123	-23

[a]Uncorrected for recovery efficiency.

[b]% accuracy = $\frac{\text{Auditee concentration-RTI concentration}}{\text{RTI concentration}} \times 100$

Stability Studies

The data collected over a period of time from the measurement of cylinder concentrations are used to estimate the stability of the cylinder gases. Cylinder gas stability data are important for several reasons. First, the gaseous compounds in the cylinders must be stable to be considered by EPA as reliable audit material. Second, if organic gases in the cylinders are stable, other investigators may more readily use cylinder gases as calibration standards and/or quality control check samples. Finally, if cylinder contents are stable, future EPA regulations may include performance audits as a means of assessing the accuracy of the measurement systems.

The term "stability" as it pertains to organic gaseous compounds, is defined here as the absence of detectable changes in concentrations over time for a given cylinder at a specified concentration level. The cylinder gases are analyzed initially by the manufacturer facility before shipment to RTI. The gases are then analyzed at RTI upon receipt from the specialty gas vendor to corroborate the vendor's analysis. The gas mixtures are again analyzed at 2 months, 6 months, 12 months, and annually thereafter following the initial RTI analysis to determine any change in the gas mixtures. The stability data obtained to date for all the ppb-level organics are summarized and published in a separate report(1). An example of stability data for ppb organic gases in compressed gas cylinders is shown in Table 5. An examination of the stability data for many of the organics in the ppb-level cylinder gases show that most varied by less than 10 percent over a two-year period. Ethylene oxide and propylene oxide at low concentrations (10 ppb-levels) were found to be unstable and therefore those compounds are not recommended for audits.

A limited amount of stability data for the XAD-2 spiked cartridges has been obtained. The data obtained for 6 weeks show that the semivolatile compounds spiked onto XAD-2 cartridges were stable over that period. Further stability studies are in progress.

SUMMARY AND RECOMMENDATION

Compressed gas cylinders containing 21 gaseous volatile organic compounds at part-per-billion levels and XAD-2 cartridges spiked with five semivolatile organic mixtures have been used successfully in audits to assess the accuracy of measurement systems, especially those used during the hazardous waste trial burn tests. Audits have not yet been initiated with the six group 4 gaseous volatile organic compounds (acrylonitrile, 1,3-butadiene, ethylene oxide, propylene oxide, methylene chloride, and 0-xylene).

Table 5. Example of Stability Study
(Group I Compounds)

Activity		Compound				
		Carbon tetrachloride	Chloroform	Perchloro-ethylene	Benzene	Vinyl chloride
Manufacturer Analysis						
Theoretical	ppb	(9.5)	(39.6)	(9.4)	(18.9)	(20.0)
1st Analysis Date		11/17/83	11/17/83	11/17/83	12/06/83	12/06/83
	ppb	(7.7)	(42.1)	(9.2)	(15.8)	(18.3)
2nd Analysis Date		12/16/83	12/16/83	12/16/83	12/15/83	12/15/83
	ppb	(7.1)	(41.2)	(7.7)	(19.6)	(19.2)
RTI Analysis						
1st RTI Analysis Date		1/06/84	1/06/84	1/06/84	1/23/84	1/23/84
	ppb	(9.3±0.3)	(40.0±0.8)	(9.4±0.2)	(19.6±0.6)	(20.2±0.6)
2nd RTI Analysis Day*		59	59	59	49	49
	ppb	(9.3±0.3)	(38.7±0.8)	(10.3±0.2)	(20.0±0.6)	(19.0±0.6)
3rd RTI Analysis Day*		238	238	238	226	226
	ppb	(9.5±0.3)	(40.6±0.9)	(9.5±0.2)	(19.4±0.6)	(20.6±0.7)
4th RTI Analysis Day*		404	404	404	375	375
	ppb	(9.6±0.3)	(37.1±0.8)	(9.1±0.2)	(19.4±0.6)	(20.4±0.7)
5th RTI Analysis Day*		872	872	872	850	850
	ppb	(10.5±0.3)	(40.5±0.9)	(11.2±0.3)	(21.7±0.7)	(19.4±0.6)

*Number of days after 1st RTI analysis date.

Stability studies for all 27 volatile organics and 6 semivolatile organics have been performed to determine the feasibility of using them as audit materials. Results indicate that all of the organic compounds tested (except ethylene oxide and propylene oxide at the 10 ppb-level) are stable enough to be used as reliable audit materials. One hundred thirty performance audits to date (May 1987) have been performed using ppb-level audit gases and the results have generally been within ± 50 percent of the audit concentrations measured by RTI.

It is recommended that a performance audit using these organic mixtures be conducted during each hazardous waste trial burn test as a routine quality assurance procedure. Any federal, state and local agencies and their contractors planning hazardous waste trial burn test may request a performance audit by contacting Mr. Robert L. Lampe (for cylinder gases) and Ms. Ellen Streib (for semivolatile organics) of the EPA, Environmental Monitoring Systems Laboratory Quality Assurance Division, Research Triangle Park, North Carolina 27711.

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DESIGN AND USE OF LABORATORY QC PROGRAMS TO SATISFY DQOS FOR ENVIRONMENTAL MEASUREMENT SYSTEMS

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ABSTRACT

A protocol has been developed for design of laboratory QC programs for use in environmental measurement systems whose purpose is to test compliance with regulatory standards. The data quality objectives (DQO's) which are the basis for evaluating the overall measurement program are bounds on error rates in determining compliance or noncompliance with the standard. The QC program can be tailored to the individual laboratory according to its own bias and precision. In addition to their use for system performance checks, QC data are used to correct measurements for recovery and to estimate false positive and false negative rates associated with the compliance/noncompliance determinations. This process is adaptive: error rate estimates are periodically updated, and the QC program reevaluated and revised (intensified or relaxed) as appropriate.

The use of the protocol is envisioned for GC/MS and other analytical chemistry measurement systems used by OSW. The protocol will be described in more detail and illustrated in specific contexts.

RCRA EXPERIENCE IN SOUTHEAST FLORIDA

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ABSTRACT

The paper highlights some of the areas where refinements or changes, both regulatory and technical, appear needed in the nation's current program of managing Hazardous Wastes. Based on our experience in implementing the federal hazardous waste program at the State level, some of the difficulties encountered are highlighted in order to demonstrate the need for refinements or changes in the existing hazardous waste regulations. Some areas of the hazardous waste regulations, as they currently exist are likely to be inappropriately applied and thereby not meeting the intent of the law. Such areas include test methods, sampling, regulatory interpretation, and enforcement. Some of the paradoxical situations encountered during the past five (5) years of field experience in managing the Federal hazardous waste program in Southeast Florida are illustrated with actual case histories (without naming the companies).

INTRODUCTION

To ensure proper management of HWs, Congress passed in 1976 the first landmark piece of federal legislation known as RCRA. It was amended once in 1980 and recently in November 8, 1984. The 1984 HSWA significantly expanded the scope and detailed requirements of RCRA with approximately 87 deadlines (up to November 8, 1992). A number of "hammer" provisions are included as statutory requirements to go into effect automatically in case EPA fails to issue the required regulations by certain dates. Because of the hammer provisions, EPA often had to move fast to complete the rule making process and to come out with the regulations that will satisfy the critical concerns of both the environment and the industry.

The materials presented here are limited to those regulations finalized by EPA under RCRA Subtitle C: Sections 3001-3019 as codified in Volume 40 of the CFR, Parts 261 through 265. Now that both the regulators and industry have used these new and old regulations for a period, it is time to reflect on whether these regulations together accomplish the congressional intent, or do they need refinements, especially to address situations perhaps not anticipated when they were written. It is in this frame of reference that I have attempted to summarize both my RCRA experience in Southeast Florida and what I learned working with industry and other real life situations in trying to do the best I can to meet the intent of the regulations. The views expressed here are strictly the author's own and are not necessarily those of the Florida Department of Environmental Regulation.

HAZARDOUS WASTE FROM NON-SPECIFIC SOURCES (§ 261.31)
[FR Vol. 50, December 31, 1985, p. 53315-20]

Spent cleaning fluids containing ≥ 10% (by volume) of one or more of the listed solvents (F001 to F005) have to be managed as a listed hazardous waste and any spill has to be cleaned up in accordance with RCRA regulations. But the same cleaning fluid as raw material when spilled is considered a non-hazardous waste spill, and therefore unless the spilled material is characteristically hazardous, RCRA regulations do not apply. Obviously, this is not the intent of the law. Also, there is no way the inspector can distinguish between the two spills even with laboratory testing.

Conversely, there is a spent cleaning fluid containing < 10% (by volume) of one or more of the listed solvents F001 to F005. It is not a hazardous waste unless shown to be characteristically hazardous. If there is a spill of this material, the clean-up doesn't have to meet RCRA standards, and sometimes no clean-up is required. Yet a spill involving far less quantity of a listed waste solvent (because of the application of the mixture rule § 261.3(b)(2)) requires extensive clean up of both soil and affected ground water to background levels (which often means no detection) or requires delisting (§ 260.22). Clearly such a scenario doesn't meet the intent of the law. The inspector as before, has little choice but to accept the operator's statements.

SATELLITE ACCUMULATION RULE [§ 262.34 (c)]

If a 55 gallon and a one gallon container are full at the same satellite area, the rule says that the 1 gallon container (representing the amount in excess of 55 gallons) becomes subject to full regulation within three days of accumulating the excess amount. However, I feel that the larger quantity posing the greater threat should be regulated.

In case of accidents involving satellite areas, the rule doesn't require notification under § 265.56(d) or (j). The rule also exempts satellite areas from such things as no smoking signs, spill control measures, personnel training involving use of emergency equipment as well as implementation of preparedness and prevention procedures.

I feel that a 55 gallon spill in a satellite area can pose a serious threat to human health, and therefore personnel should be knowledgeable in HW handling as well as in proper fire and spill control measures. One way to accomplish these objectives would be to have the existing contingency plan include remedial actions to be taken in case of spills or fires at satellite areas.

In accordance with § 262.34(c), all wastes in excess of 55 gallons (or in excess of 1 quart of acute HW) are to be marked with the date the

excess amount began accumulating and this excess amount must be removed within three days. For the inspector, verification of compliance here is not very practical.

WASTEWATER TREATMENT UNIT EXEMPTION

In accordance with § 264.1(g)(6), TSD standards do not apply to "wastewater treatment units" as defined in § 260.10. To retain this exempt status, the tank must be part of a wastewater treatment facility regulated under section 402 (for industrial wastewater discharges) or 307(b) (for POTW discharges) of the Clean Water Act. It must (a) treat or store an influent hazardous waste or (b) generate, accumulate, treat or store a hazardous wastewater treatment sludge. Also, any mixture of sewage and other wastes passing through POTW is not regulated as hazardous wastes [§ 264.4(1)].

An interesting scenario here is that there are privately owned sewage treatment works operating as efficiently as any POTWs, and yet, these privately owned works unlike POTWs are not exempt from RCRA.

NOTICE IN THE PROPERTY DEED [§ 264.116 & 119]:
[FR Vol. 51, May 2, 1986, p. 16433-34]

Prior to the 5/2/86 FR changes (p. 16422-59) regarding closure, 264.120 required a notice in the property deed once on-site contamination due to past HW disposal has been established. The law also provided deletion of such notation once contamination is cleaned-up.

The regulatory changes (effective 10/29/86) appears to have modified this process. § 264.116 states that a survey plat must be submitted "no later than the submission of the certification of closure." "No later than" implies that the survey plat must be submitted on or before the submission of certification of closure. It is the owner/operator (o/o) who decides when to file the plat, and if so, the o/o could wait until the last minute before filing the plat with local land use authorities. Often closures take several months and sometimes years to complete the closure. During this long interval, potential property buyers cannot be made aware of hazardous waste contamination if such information is not in the survey plat and/or notice in the deed.

If the regulatory agency cannot require evidence of significant contamination entered into the title deed, then how can the government reasonably assure that potential buyers are notified in advance (and before a violator "skips town")?

Subpart G (§ 264.119) seems to provide such notices and plats only after closure and assumes that a disposal facility will always complete

closure prior to selling the property. While most companies will complete cleanup, we have encountered some that attempt to evade the law, delay notifying potential buyers, sell before (or in lieu of) cleanup, etc.

If a facility is certified closed, chances are that such facilities are the "good guys" operating under the law, and for the most part, contaminants at levels of concern may have been already removed. If that is so, as in the case of clean closure, then why bother to have an entry in the title deed or plat? Once HW concerns are established, it is prudent to have entry as soon as possible in the title deed or property plat for protecting the innocent buyers from the polluters who are eager to sell and leave town. The whole concept seems to suggest that perhaps the closure may not be clean and so be correspondingly forewarned.

EXTRACTION PROCEDURE (§ 261 Appendix II)

Based on the prescribed test procedure under RCRA, the EP toxicity result is expressed in units of mg/l. But actually, the EP leached quantity is milligrams per 50 grams of test sample. But the results from contaminated soil, sediment, or sludge sample when analyzed for total metals or pesticides are customarily expressed as mgs/kg. If the total numbers are high enough to be of environmental concern, the next question is "how much of it is leachable"? Therefore, to get a proper perception of leachability against the background of their corresponding totals present, the EP test data has to be multiplied by 20. Otherwise the EP test data is a watered down number for leachability, and this may give a false sense of security.

Examples:

(a) I have a sludge sample with a total lead content of 100 mg/kg. If I am told that it is 50% leachable or soluble, it means 50 mg lead/kg sludge is leachable. Yet the EP number under RCRA will be approximately 2.5 mg/l and I have observed "informed" people concluding that 97.5% is not leachable and tied up in the soil by their cation exchange capacity!

(b) We had one facility with a closed out drainfield where the EP toxic values for all cored soil samples showed levels at or below the GW standard for chromium. Yet the on-site GW consistently showed high levels of chromium (by as much as 100 - 400% above GW standard) even after a year. The problem had to be corrected by removing soil from the drainfield.

Another intrinsic problem with the EP test procedure is that it doesn't take into account the amount of water or other liquids present in the test sample. It is suspected that samples collected on behalf of the

PRP are in such a way to deliberately include a greater proportion of liquid in sediment or sludge samples in an effort to bring down the EP values. Even when sludge samples from a wastewater tank or sediments from a canal bottom are collected and analyzed independently by two chemists, the EP test data can show significant differences depending on how the samples were collected. Similarly, when contaminated soil samples are collected, one during dry season and another immediately after a heavy rain, the EP test data between the two test samples would show significant variation.

Another limitation of the procedure is limiting the pH during extraction to a rigid value of 5 which may be a conservative value for the EP study most of the time. I have come across at least 3 sites in Southeast Florida where the natural GW pH was observed to be around 4±. A proper pH for EP study pertaining to those sites should approximate the natural GW value. But the EP procedure under RCRA doesn't give that flexibility to change the prescribed pH from 5 in order to reflect the non-typical field conditions.

Despite the little problems described above, the EP test procedure is a very useful tool in evaluating the environmental threats posed by various hazardous wastes. It is my opinion that the usefulness as well as precision and accuracy of EP test data for samples (such as sludge and contaminated soil) can be enhanced by expressing leachability as mgs/kg of dry solid.

NEW SMALL QUANTITY GENERATOR RULES
[FR Vol. 51, March 24, 1986, p. 10146-78]

Based on one year of past experience in implementing the new SQG rules, following are some thoughts on bottlenecks as I have observed.

(1) MANIFEST EXEMPTION PURSUANT TO RECLAMATION CONTRACT [p. 10155-8; § 262 Subpart B]:

> The "tolling arrangement" exemption (e.g., absence of a TSD "sign-off" manifest copy) does not provide a means for ensuring the generator that the wastes were actually received at the recycling facility. The mere presence of a contract does not guarantee that the wastes will be properly managed. The transporter/recycler could mis-manage or even not deliver the waste and the generator would not be aware of the fact. In addition, the presence of a contract does not necessarily mean the generator is still using that service. The generator could also be mis-managing the wastes, but could tell an inspector that the waste is being handled in accordance with the contract. Since the generator would not be required to keep even a log (only the transporter/recycler must keep a log), an inspector would not be able to verify the pickup of waste and the inspector

would also be unable to verify that the waste actually reached the designated facility without inspecting the TSD facility (which is not feasible for every shipment even if the TSDF is located in the district, and certainly not very practical if the TSDF is located out-of-state). I believe that the "tolling" exemption should be modified, at a minimum, to include a requirement for:

(a) the generator to keep a log showing the same information required of the transporter's log; or
(b) the transporter providing the generator a receipt for having picked up so much of a certain waste.

In summary, the "tolling" exemption needs to be improved to eliminate the possibility of abuses, and to make it easier for an inspector to verify proper waste management. It should also be noted that implementation of above suggestion would not place a burden on small companies, but rather would protect them.

(2) ACCUMULATION LIMIT
[p. 10161; § 261.34(d)]

The greatest paradox in implementing the new RCRA program exists here. For example company "A", a SQG producing on the average 4 drums a month, has on site about 25-30 drums for about 200 days, and meets only very minimal requirements (which doesn't even include a written contingency plan) to protect human health and environment. Across the street company "B" producing on the average 6 drums a month is being cited for storing without a permit about 6-8 drums for about 100 days, even though this facility is better operated and meets more regulatory requirements (including an elaborate and government approved contingency plan) to protect both the environment and human health. Obviously company "A" with four times the amount of waste sitting twice as long than company "B" (coupled with the fact that company "A" meets only very minimal requirements in terms of personnel training, contingency plan, etc.) poses much greater risk. It makes the inspector very uncomfortable to cite violations on company "B" when company "A" goes free.

The new rules would also be a departure from previous accumulation strategy in which exceeding a limit would subject the company to the next higher level of regulation. For example, a SQG would be subjected first to generator requirements, and then only to possible TSDF requirements. The new rules would subject an SQG to a storage permit if > 6000 kg or 180/270 days is exceeded, without going through a generator phase. CESQG who accumulates > 100 kg HW, instead of meeting the SQG requirements, is simply being exempted from regulation until the 1000 kg limit is exceeded. In the case of acute HW, it is either a CESQG (< 1 kg/mo.) or a generator (> 1 kg/mo.), but can never be SQG. In other words, an incremental, step-wise level of regulation is not maintained, and the absence of this simple logic makes the inspector's job more difficult.

It should be noted that it is the 6000 kg quantity, (and not the 180/270 day time) that is crucial in considering risk. On p. 10161, EPA states that "the Agency could see no substantive difference in potential risk" when comparing 180 versus 270 days. If so, some of the small companies are losing out on the regulatory breaks. The legislative intent of HSWA clearly was to give certain regulatory relief to small companys for their survival while enhancing the

protection of the environment. EPA appears to identify small companies as those generating < 1000 kgs/month and this alone can hardly be a criteria to define "small companys". Some small companies by the very nature of business they are in (such as electroplating) historically produce a larger quantity of HW, but may have only very few employees and limited financial resources. Whether these small companies, though generating > 1000 kgs/month, be allowed to store the same amount of HWs for the same duration as with SQGs is worth considering (especially when these small companies satisfy a higher level of regulatory requirements for the protection of human health and environment).

(3) MULTIPLE WASTE STREAMS (p. 10161)

A statement in the third column of p. 10161 states "...generators that have multiple waste streams which are managed at different facilities may actually be subject to different accumulation time limitations for the different waste streams." Such a situation would make an inspector's job more difficult to verify and enforce compliance. If complex regulations and even more complex exemptions make an inspector's job more difficult, then the vast universe of companies may be even more confused. The inspector would have to:

(1) determine the nature and quantity of waste (taking into account the numerous exclusions for the purpose of quantity determination as described on p. 10151-3),

(2) determine the accumulation practices and times of each stream,

(3) verify the designated facility of each stream,

(4) verify the designated facility type and its distance from the SQG facility (> or < 200 miles).

I believe that it is a nightmare to the Inspector and possibly to some facilities also.

(4) CONTINGENCY PLAN (p. 10164)

If a SQG is big enough to accumulate 6000 kgs of HWs, then it must be large enough to meet the full generator requirements including full CP. EPA states that the Agency "was careful to modify the standards

only where administrative requirements not essential to the substantive functioning of the standards were involved," and the EPA's final rules are "sufficient to protect human health and the environment." These rules seem to imply that a SQG accumulating 6000 kg does not pose a sufficient risk to require a full CP, but a generator accumulating a much lesser amount poses enough risk to require a full plan! It is like saying that 6000 kg HW is less dangerous than 1000 kg HW.

A full CP is more than just "administrative" in nature; it contains valuable information for use in an actual emergency. In other words, by not meeting all or nearly all of the substantive requirements of a full CP, than the "substantive functioning of the standards" will not be met. This part of the rules is an example where EPA has tried to balance the various pressures (Congress, Industry, etc.). However, I believe that EPA's logic in this instance seems inappropriate. One way to bring a measure of logic into the implementation and continued compliance under the new RCRA program may be to increase the generators' ability to store the same quantity of waste for the same period as with SQGs (or vice versa).

The present watered down CP required of SQGs may not be of much use in case of an actual emergency. It doesn't have even an evacuation plan! It is my experience that the vast majority of SQGs and even some CESQGs have voluntarily developed CPs, and submitted them for the department's review and comments. Developing a CP often seems more difficult than it really is. Even if difficult, it is basically a one-time effort and that it can help save lives in an emergency. My efforts have made the preparation of CP simpler by developing a concise, easy to follow guidance which the inspectors hand out routinely to facilities. Most facilities including many SQGs and CESQGs, were able to develop a good contingency plan for use by their employees.

(5) PERSONNEL TRAINING (p. 10164)

This rule merely states that the SQG "must ensure that all employees are thoroughly familiar with proper waste handling and emergency procedures." No other criteria or records as in § 265.16 are required. How will the inspector verify compliance of such a vague rule? How will SQGs demonstrate compliance without records? The personnel training requirements for SQGs need to be more specific and enforceable, at least to the same level required under the "Right-to-Know" rule.

(6) CONTAINERS (p. 10165)

EPA has exempted SQGs producing flammable wastes (F.P. $140^{o}F$) from the 50-foot buffer zone requirement, until EPA promulgates the final buffer zone rule. EPA provided this exemption because the rule "would put many small businesses in a situation in which it would be

impossible to comply." This is also sometimes true of generators (who may also be small companies but happen to generate 100 kg/month). If SQGs are to be exempt (even with 6000 kgs), then so should generators. But since EPA has not exempted generators, if an SQG had enough space to store 6000 kg with adequate aisle space, then the facility is probably large enough to meet the 50-foot rule. In addition, NFPA rules will require compliance, so the SQG will probably not avoid the 50-foot rule.

In the interim, I believe in having the 50 ft. rule that makes both engineering and regulatory sense, while also ensuring fairness to both SQGs and generators; and also for reducing the risk of fire and thereby help protect lives at and near facilities with SQG status who may store up to 6000 kgs with only a minimal contingency plan. A practical way to reconcile the interests and concerns of various segments of the society may be for EPA or the authorized state to have the option (on a case by case basis) of giving a variance from the 50 ft. rule based on (1) the recommendation of the State Fire Marshal, (2) consideration of improved design of HW storage area (such as erecting a fire wall), and/or (3) stipulating the method of storage (including maximum quantity stored) until the SQGs (and for that matter large quantity generators also) meet the minimum protective distance for storing flammable HWs.

There appears to be a belief that bigger the size of a company, the larger the quantity of HW generated and vice versa. The truth is that a giant corporation may produce very little of HWs while a small company may produce large quantities of HWs. The quantity of HW generated is basically a function of the nature of the business a particular company happens to be in, and of course, it also depends on the kind of industrial process employed. In the eagerness to provide regulatory relief to SQGs, it appears that protection of human health may have been compromised.

(7) CESQGs ($\leq$ 100 kg/month) [§ 261.5(g)(2)]

An inconsistency exists in this section. The CESQG will be subject to increased regulation, only if he accumulates $>$ 1000 kg. But, a SQG has to meet increased regulation generating and storing $>$ 100 kg. In other words, the SQG could have less waste on site, but be subject to more regulation. This would be analogous to not requiring SQGs under existing rules to meet generators rules for accumulating $>$ 1000 kg.

(8) EPISODIC GENERATORS [p. 10151, 10153-4]

In spite of the best efforts to help CESQGs and SQGs, all of the regulatory breaks disappear when they become "episodic generators" at any time (e.g., emptying a tank, clean up of HW spill) and they then must meet full generator standards as if they are large quantity generators. For instance, once a full contingency plan is developed,

it does not appear to matter whether the SQGs legally require a full CP later on.

I have also observed that there is a tendency for many SQGs not to disclose episodic generation, because the inspector is told that there was never any need to empty the tank (such as the rinse tank, wash tank, etc.) even though the same tank may have been in service for the past several years. When the SQG is permitted to store up to 30 drums on-site (with its numerous exclusions in counting HW quantity) for as long as 270 days with practically no record keeping, basically the inspector has to accept what the operator tells him.

(9) REGULATORY IMPACT (p. 10172)

EPA states that the cost of these new rules is not "major" (i.e. < $100 million per year). Since EPAs total cost estimate is only $58.9 million, per year average cost estimates per firm are low, and therefore annual recurring cost is very low. Hence, there is considerable leeway to fine tune or modify the current regulations with a view to eliminate some of the obvious inconsistencies existing on many CESQGs vs. SQGs vs. generators requirements, all without reaching the "major" category. Certain obvious paradoxes can be eliminated by taking an approach based on incremental, step-wise level of regulation with each change in the level of generator category, and that will make the inspector's job easier, and will also reduce confusion and thereby increase compliance in the regulated community.

(G) PESTICIDE SPILL

A pesticide drum accidentally spills in a golf course grounds. Since this pesticide is referenced in § 261.33, excavation had to be conducted till all of the spilled material was removed. The contaminated soil resulting from clean-up is a listed hazardous waste and therefore requires manifesting to a TSD facility. While the excavated material was waiting to be manifested, the same spilled material was being applied by a licensed pesticide applicator to the turf grass for the control of insects.

In the above scenario, I believe that it is sensible to have the excavated soil applied to the turf grass with the application rate adjusted to yield the proper pesticide dose rate per acre. However, whether such application constitutes disposal or beneficial use appears uncertain under the present regulations.

Also, in the case of a spill as above, the clean-up has to be such that none would be detected or be at the background level in the remaining soil after excavation. Any level of a listed commercial chemical in soil at the spill site will remain as a listed HW, and it can only be re-classified as non-hazardous through the delisting

procedure (260.22). However, if the residual soil after excavation shows a level at or below the drinking water standard (or other conservative standards such as GW standard, one in a million cancer risk, etc.), it may be unnecessary to excavate and manifest huge quantities of soil in order to remove the last ppb or go through the time consuming resource intensive delisting procedure.

(H) HAZARDOUS WASTE DISPOSAL IN GARBAGE DUMPSTERS BY CESQGs

Is it legal? Yes. Proper? No. The current HW regulations do not prohibit CESQGs from disposing their HWs in garbage dumpsters. In fact §261.5 allows disposal of CESQG wastes at facilities permitted by the state to accept municipal or industrial waste. Since permitted landfills are typically authorized to accept municipal and industrial wastes, a CESQG sending its hazardous waste to such a landfill is not in violation of § 261.5, even though such practices clearly pose great risk to both human life and environment. Therefore, rule making by EPA is needed to plug this regulatory loophole. Given below are three case histories to highlight my concerns:

(a) A testing laboratory has placed ignitable, toxic, and possibly reactive chemicals in a trash container (along with other regular trash such as waste paper) destined for disposal in a local landfill. Local fire department brought this improper (if not illegal) HW disposal practice to the attention of the State environmental officials. The laboratory analysis of a discarded foam material found in the trash container showed 13% (by weight) toluene. Also, the adjoining tenants in the industrial plaza complained about severe odor problem to local fire and county health departments. Fortunately the problem was amicably resolved. Had this practice continued, it is probably a matter of time before a fire or explosion occurs, and if that happens especially in a plaza, there could be significant loss of life and property.

(b) A major department store in a shopping center dumped significant amounts of discarded pool chemicals (hypochlorite and muriatic acid) into their dumpster. Fortunately a passerby soon retrieved most of these chemicals for use in his pool. In fact, the same person as a concerned citizen alerted the incident to regulatory agency personnel. if it were not for the quick retrieval of the chemicals, a fire may have resulted or toxic chlorine gas could have been generated if the hypochlorite and acid mixed. It also poses a health threat to garbage collectors and landfill operators. It also increases the potential for spontaneous fire to both garbage truck and the landfill.

(c) Recently, the Department staff responded to fire in a garbage truck carrying trash picked-up mostly from small industrial plazas with some residential garbage. When smoke profusely started coming out of the truck, the driver had the good sense to empty the truck right on the street, thereby avoiding a potentially dangerous explosion. The trash spontaneously ignited in the street with flames reaching about 100 ft. high. Fortunately, nobody was hurt (this time). There was a strong solvent odor area wide and many partially burned 5 gallon and 1 gallon solvent containers were retrieved. Analysis indicated a number of hazardous chemicals (mostly flammable solvents).

Despite the best efforts by the landfill operators to prevent HWs from reaching their landfills, the dumping of HWs by CESQGs still continues. Even where such practices pose a great risk to human health and environment (e.g., hazards in the landfill and prior to being delivered to landfill, potential damage to landfill liners that protect GW, etc.), the regulators cannot cite a violation under RCRA. Most CESQGs are short on floor space, generally located in populated areas, and operate on shoe-strings. Until HW collection centers are established within reasonable distances and where CESQGs (and even home owners) can take their hazardous wastes at an affordable rate, the cumulative effect of all these HWs ending up in landfills across the nation will be felt increasingly with time. We have the option to pay now or pay dearly later on for both the proper closure of landfills as well as for the clean up of groundwater.

(I) CONCLUSION

During the past five years, I have been directly involved in the field implementation of federal HW regulations at the state level in Southeast Florida involving compliance inspections, permitting, enforcement, emergency response operations as well as in RCRA and CERCLA clean-ups. I have come across many situations where a strict application of the HW regulations may not be appropriate. For example, if somebody spills a bucket of listed solvent in the Potomac River, will any of us dare to say that the Potomac River is all HW, even though technically that may be correct because of the mixture rule 261.3(b)(2), and furthermore, would anybody go to the extent of expecting a closure under 264 Subpart G. The moral of the story is that having a good dose of common sense, pragmatism, and even more important keeping in mind the intent of the law both by the regulators and the regulated will go a long way in making the new RCRA program a success, despite all the growing pains.

I could point out only a few problem areas within a short period of time. Part of the problem is that EPA was and still is under tight time constraints to meet the various deadlines of HSWA for producing regulations. Therefore, EPA has to rush through rule making process without the needed time to think through the problem and to broaden

the public's participation. I believe that the rule making process as well as the fine tuning of existing regulations could be improved by the following steps:

(a) Increased participation of field personnel (engineers, scientists, and technicians) from both private sector (including consultants) and regulatory agencies in the early stages of writing the regulation.

(b) Be prepared to modify regulations when its application in a particular field situation doesn't make sense or does not meet the intent of law.

(c) All regulations (or at least the significant and perceived controversial regulations) when introduced for the first time may be interim regulations. Use it for a period of time (say two or three years), and then in the light of that experience and comments received, incorporate any changes if required, and then adopt the interim as final regulations.

(d) An incremental, step-wise level of regulation is to be applied depending on the maximum amount of HW generated per month or the maximum quantity stored at the facility premises anytime. In other words, the regulatory requirements should increase (from CESQG to SQG to generator and TSDF) in proportion to the increase in potential risk.

(e) Regulations have to be written in plain English. For clarity of meaning, avoid very long sentences. Use of these simple concepts could reduce confusion at all levels and help increase regulatory compliance. It would also reduce the need for interpretative and guidance memos both from the federal and state environmental officials.

In the final analysis, the regulators, the private sector, and the public at large have to work together and certain compromises/trade-offs have to be accepted on the basis of risk-reward ratio. Until realistic options are provided and the public gets educated, regulations alone will not solve our HW problem. Ultimately everybody has to ask and answer this one important question. "What kind of quality of life do I want and at what price?"

ACKNOWLEDGMENTS

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REMEDIAL INVESTIGATIONS GUIDANCE STRATEGY

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ABSTRACT

As an alternative to the conventional approach of initiating a Remedial Investigation based on limited information gathered from a site investigation, the Division of Hazardous Site Mitigation has developed a Remedial Investigation Guidance Strategy (RIGS). The RIGS calls for a phased approach that will allow a progressive site assessment and selection of the best possible remediation scheme. Current RI's are often based on a limited number of samples collected during a site investigation. Instead of focusing on specific site conditions and contaminants these RI's are broad in scope. Samples collected often generate data of little real value in making decisions regarding remediation. One cause of this phenomena is that the environmental systems affected are not adequately defined. Also, conventional parameters (pp + 40, HSL) are included for analysis, though analysis for only site-specific, clean-up driving contaminants would be more valuable and more economical. A more focused, phased approach will allow for the generation of more meaningful, useful data as a means to the end of choosing a design for clean-up.

The Phased RI must be built around information collected during the Site Investigation and the Pre-RI activities. The Pre-RI, an essential preliminary study that will determine the future course of the remedial process, initiates the investigation by evaluating the potential for contaminant migration.

Phase I of the RI will be a systems defining phase. In order to assess and predict the behavior and movement of contaminants at a site it is critical to explore the particular environment setting of concern. Phase I includes: topographic, geotechnical, radiation and biological systems studies, and detailed studies of the site's physical features (i.e. air, surface water/sediment, subsurface elements including soil gas and groundwater). The emphasis will be on identifying site characteristics such as groundwater flow and geological features. By installing two inch PVC wells, investigating groundwater flow, performing gamma logging and analyzing samples for surrogate parameters such as TOX and TOC, a broad overview of the site can be achieved.

Phase II of the RI will be similar to the current approach but will have the advantage of information gathered in the Pre-RI and

Phase I. Stainless steel wells can be logically placed based on Phase I findings and their numbers and the expense limited. Similarly, the locations of the collection of other samples can be logically chosen. Analysis should be for extended parameters (pp + 40, HSL) to investigate the full extent of the problems on site. The purpose of measurements made during Phase II is to determine the variability, distribution and concentration range of contaminants.

Based on this information, monitoring will continue in Phase III. Additional wells, borings and samples will be placed as needed, but analysis will be limited to the parameters identified as contaminants in Phase II. These are the contaminants that will drive the clean-up, influence the decision for a remedial design, and determine the scope of future site activities.

INTRODUCTION

The Remedial Investigation/Feasibility Study (RI/FS) was established in 1980 as the means to achieving the end goal of choosing cost-effective, health protective, clean-up designs for CERCLA sites. In its infancy, it was thought that the Remedial Investigation (RI) would be of short duration, and relatively inexpensive. However, the data generated from RIs of this scope was inadequate to characterize the site. Consequently, RIs evolved into lengthy and costly studies in an effort to gain enough information about the site to promote a responsible and appropriate clean-up choice. Though additional time and resources have been allotted in attempts to assure complete assessment of the site, RIs still are often not implemented as efficiently as they could be.

The current RI/FS approach is initiated with limited background information. The New Jersey Department Of Environmental Protection (NJDEP) is recognizing that additional information gathered upfront could improve the efficiency of the RI/FS by reducing the associated costs and shortening the schedule. Often RIs are initiated based only on the data generated from the CERCLA funded Site Investigation (SI) and the Hazard Ranking System (HRS). In these CERCLA activities the focus is on source identification. The site's physical features and environmental setting are not adequately addressed at this stage. Additionally, the RIs are broad in scope rather than being focused on a particular contaminant, matrix or area of concern. Quite a bit of time and resources are being expended in the RI stage of the remedial project to make up for this deficiency in site specific information. Once obtained, this specific information may lead to changes in the RI scope in mid-course, since the scope was based on previously available limited or faulty information.

The guidance that is available on how to perform an RI/FS specifies what should be included in the investigation but does not detail the

RI process. Ideally, certain measurements should be performed first in the study to allow a characterization of the site's physical systems and migratory pathways. Then, with this information known, samples to define the problem can be collected in the appropriate areas. Recently some investigators have recognized the logic of the sequential gathering of data and organized their work plans so that they conform with this procedure. A comprehensive guidance strategy that defines a more systematic, phased RI/FS is needed.

The Remedial Investigation Guidance Strategy (RIGS) outlined here is intended as an alternative to the current, accepted RI/FS approach. RIGS promotes the generation of site specific information before the RI begins, then allows a focused, phased approach once the particular site's features and problems are identified. In this way, data gathered will prove more useful in narrowing down remedial alternatives and ultimately in making a final decision regarding a design for clean-up.

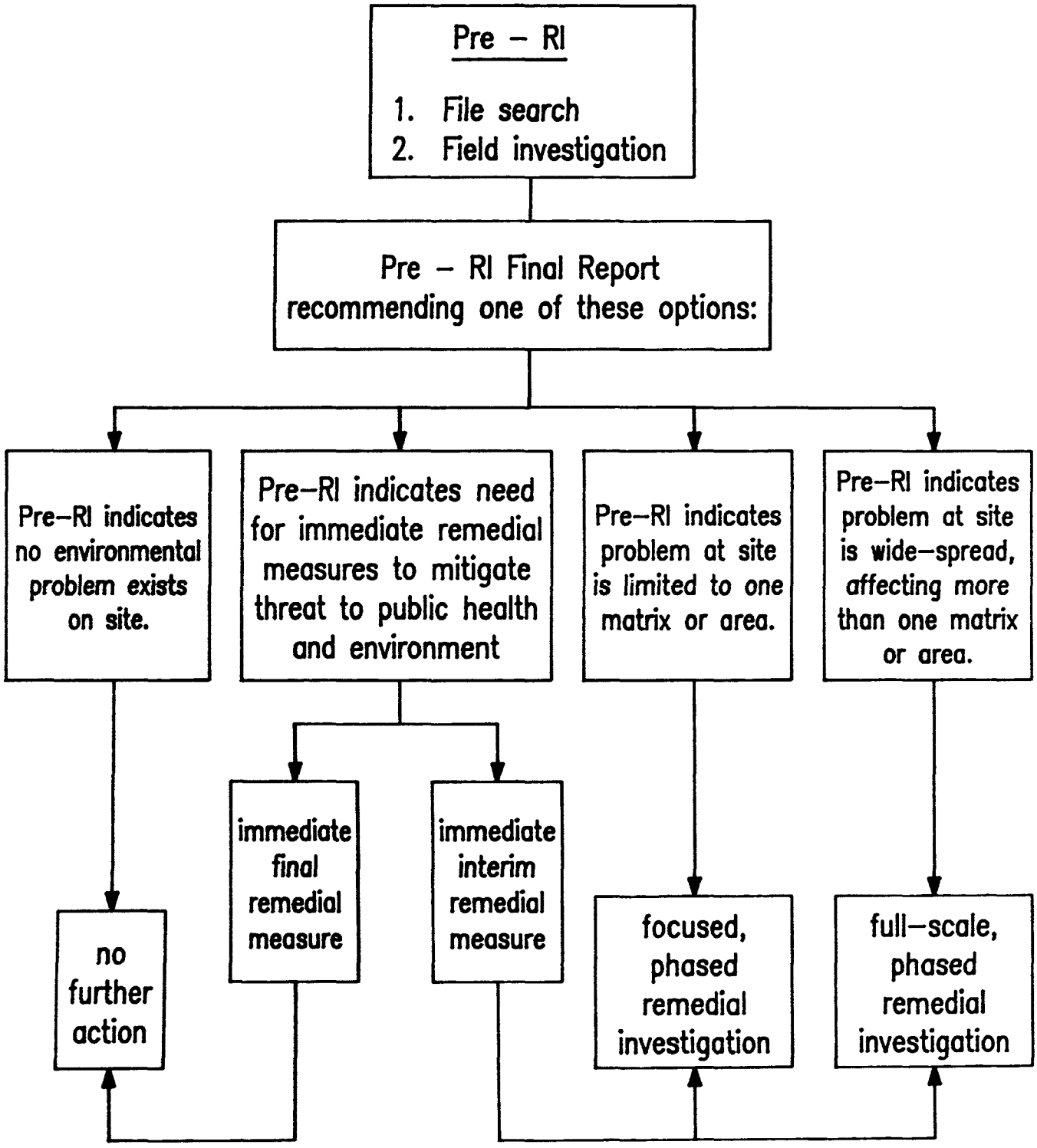
RIGS is applicable to all types of hazardous waste sites, whether privately or publicly funded. By detailing a focused mechanism of site study, RIGS allows a cost effective assessment of the site conditions. Of concern to government agencies, RIGS assures accountable spending of public money, reinforces decisions made in the public's best interest and, most importantly, builds in mechanisms for maximum protection of the public's health.

OVERVIEW OF RIGS

RIGS consists of three phases, each of which play a critical role in the overall strategy. During Phase I information about the site's physical systems is gathered. Measurements made in Phase II are intended to define the variability, distribution and concentration range of contaminants present. Phase III may be used to perform limited confirmatory sampling and treatability studies. However, before the RI can begin its scope must be identified through the use of a Pre-RI. The purpose of a Pre-RI is to gather site specific information that will dictate the site's fate in terms of what kind of remedial investigation will be performed, if any. Figure 1 shows how information gathered in the Pre-RI is used.

Sampling performed during the Pre-RI is intended to establish a baseline of data for future monitoring of the site's migratory pathways. Possible receptor populations and environments are considered. Through an indepth file search and on-site investigation, each potential hazard that the site poses is prioritized and samples are collected accordingly. An approximate time frame of six (6) months is anticipated for completion of the Pre-RI. All the data gathered during the Pre-RI is compiled and included in a Pre-RI Final Report. This Final Report will include a recommendation of one of the four options shown in Figure 1.

Figure 1 : PRE–RI and RIGS



If the Pre-RI reveals that no environmental problem exists on-site a recommendation of no-action is submitted. Any concern that caused the site to be considered in the first place must be addressed before a no-action alternative to a remedial investigation is accepted. The Pre-RI report must detail the specific results each step of the Pre-RI yielded.

Recommendations for remedial measures, including interim or final actions, will be made if an immediate action is necessary to mitigate a threat to public health or the environment. An immediate interim remedial measure, such as fence installation, lagoon stabilization or the removal of leaking drums, will help to secure and preserve site conditions until a remedial investigation can begin. By proceeding with an immediate final remedial measure, such as the removal of intact drums or waste piles and limited sampling of associated soil/water, the discrete hazards posed by the site are addressed without the need for an extensive site study.

In some instances, the site specific problem will be limited, by either matrix, area or some other factor. Here, a focused, phased remedial investigation will be recommended in the Pre-RI report. A focused RI may be recommended, for example, at a site where the contamination is limited to groundwater, or only in a part of the site where underground tanks are found.

Finally, the Pre-RI will allow successful identification of those sites that require the full-scale application of a phased RI, sties where environmental problems affect more than one matrix and/or are spread throughout the site.

In addition to determining the course of remediation the Pre-RI affords several advantages. The Pre-RI can preclude time delays. The document "Guidance on Remedial Investigations Under CERCLA" (EPA, 1985) points out that, under the current system, an RI does not have to proceed to completion but may terminate at any level provided that sufficient data has been obtained for selection of an alternative. This provision is an effort to preserve the necessity of timely action. However, through the use of a Pre-Ri, a site with limited problems may never even get to the full scale RI phase and thus will not be subject to the delays associated with project bidding and contractor mobilization.

Along with saving time, ultimately the Pre-RI can save money. By providing the necessary up front information the Pre-RI allows a scope of work to be formulated that is appropriate for the needs of the site. In doing so, changes in scope once the project is underway are less likely. So, costs associated with this re-grouping are minimized, as are the costs of filling data gaps. Finally, the Pre-RI study provides a baseline for consistency. Assessing all sites in the same manner assures that each will be

dealt with in the appropriate way. Each site will be investigated to the same degree before the RI is initiated to decide on the need for an RI and what the RI's scope should be.

Once it has been determined that a site requires a remedial investigation the phased approach can begin. (The scope of a full-scale, phased RI is detailed here. For a focused RI, the phased approach would be the same but the investigation is limited to the matrix or area of concern.)

PHASE I

The purpose of the measurements made during Phase I of the RI is to define, specifically, the site's physical characteristics and identify sensitive environments. It is necessary to explore the particular environmental setting of concern in order to assess and predict the behavior, movement and fate of contaminants. With this information, an evaluation can be performed of the system's potential to allow contaminant migration, its degree and direction. By defining the site's physical systems early in the investigation, more costly measurements (e.g., samples collected for Priority Pollutant + 40 analysis), taken later in the investigation, can be collected in the most logical locations.

Phase I includes various physical studies. A topographic study will be performed to provide a detailed map which will be used as a reference for all subsequent operations at the site. A grid will be established, if it is not still available from the Pre-RI field investigation, to facilitate field measurements. Along this grid a thorough radiation survey will be performed, if the need is indicated by Pre-RI results. Similarly, soil gas measurements will be taken on a grid to help establish the existence of a contaminant plume or surficial soil contamination.

Geophysical techniques will be utilized to locate buried objects, help define horizontal extent of plumes, and aid in determining geologic strategraphy. By installing two (2) inch PVC piezometers during Phase I more information about the site's geology can be determined through borehole gamma logging.

These piezometers can be used to determine groundwater level, flow and general quality. Analysis of samples collected from these piezometers will be for surrogate parameters (i.e., TOC, TOX, COD, TDS, specific conductance, pH, ...) to allow a general indication of water quality to be ascertained.

By looking at the biological systems within and adjacent to the site area during Phase I, identification of critical, sensitive environments can be achieved upfront and a determination of a need for immediate action can be made. Also, conclusions regarding the

extent of contamination can be drawn based on the patterns of disruption that may be present.

The studies just outlined represent examples of Phase I measurements that focus on defining the site's physical characteristics. To date a generic scope of work for Phase I has been prepared to offer guidance and define the specifications required to meet the objectives of each study. The information gathered in Phase I is compiled and a scope of work for Phase II is prepared based on Phase I and the Pre-RI. With this more complete picture of the site specific setting and contaminant problem the scope of Phase II can be focused and detailed.

PHASE II

The purpose of measurements made during Phase II is to determine the variability, distribution and concentration range of contaminants. Based on the findings of the Pre-RI, and utilizing data gathered during Phase I, the scope of work drawn up for Phase II will be very site specific. Stainless steel wells can be logically placed based on soil gas data, gamma logging data, geotechnical data, and ground water quality data from the piezometers. The number of wells needed, and the associated expense, can be limited by the benefit of more up-front information. Similarly, the locations of other sampling points can be more efficiently chosen.

In some ways Phase II of RIGS is similar to the current approach in remedial investigations. The goal of Phase II is waste type, source, and concentration range definition, and determination of the areal extent of contamination. The mechanism for acquiring such information is the collection of environmental and waste samples, and the analysis of those samples for an extended range of parameters (e.g. Priority Pollutants + 40, Target Compound List + 30). The quality of this data is critical and is assured through the requirement of EPA Contract Laboratory Program (CLP) laboratory deliverables. However, RIGS differs from the current approach in that the use of the data is not the same for both. Data collected in Phase II of RIGS will be subject to methods of data reduction. This factor must be considered during sampling plan development for Phase II of RIGS.

The Phase II investigation is intensive in nature to assure that any and all contaminants are identified, their concentration range and distribution known. Consequently, large amounts of data will be generated. This data must be reduced using a standardized, statistically - based method that takes into account the complexities inherent to environmental data. Through data manipulation, contaminant prioritization can be achieved, allowing the determination of limited parameters for the next phase of sampling and/or to facilitate cleanup design. One mechanism of data

reduction includes ranking the contaminants according to the number of times each is found. Each contaminant's contribution to the total problem is determined by calculating the percent occurrence of each. By cumulative addition of these percentages new values are given that represent the additive problem posed by the various contaminants. Once a remediation level has been determined (e.g. remediate to 90% clean), based on associated risks and costs, these percentages will be useful to show the means of achieving the set goal. Therefore, in preparing the Phase II sampling and analysis plan, familiarity with the data reduction mechanism is essential. A basic overview of the spatial relationship of non-parametric variables, as presented in the RIGS guidance document, will be helpful in planning Phase II activities. In addition to data reduction, cartographic representation should be achieved by use of computer mapping systems that employ mechanisms for accurate depiction of spatially correlated variables (e.g. kriging). Three-dimensional mapping can be used to give an overview of site trends, while contour mapping, with confidence limits defined, can be valuable in showing clean and dirty areas. Such mechanisms can be invaluable when utilized in making remedial decisions as they allow an objective assessment based in science. When the assessment is based on a decision making model the process ultimately makes the decision rather than individuals. Phase II will permit a determination of the contaminant(s) of concern and an accurate depiction of the areal extent of the problem, and allow recommendations to be made for the limited Phase III scope of work.

PHASE III

Activities to be performed in Phase III will be determined jointly by Phase II results and the needs of the ongoing feasibility study.

Phase II may dictate that additional sampling and analysis for extended parameters, with CLP reporting, is required to fill data gaps. In addition, sampling and analysis only for the contaminant(s) of concern, which will drive the cleanup, may be needed to delineate a clean/dirty line.

To supplement the ongoing Feasibility Study, more sampling may be required along with bench and pilot scale treatability studies. Sampling and analysis and treatability studies performed in Phase III are intended to fill data gaps, confirm conclusions regarding the contamination and supply information needed to select a design alternative. While Phase II of the Feasibility Study plays a major role in Phase III RI activities, the activities of the RI's first two phases play a major role in progression of the Feasibility Study. The interaction and concurrent progression of the Remedial Investigation and Feasibility Study is shown in Figure 2.

Phase I of the RI and FS progress concurrently. The Feasibility Study begins by identifying potential treatment technologies and applicable or relevant and appropriate requirements (ARAR), using the Pre-RI results along with Phase I results as they become available. For example, if Phase I identifies a radiation problem, suspected from the Pre-RI file search but not found during the Pre-RI field investigation, communication of this information to the parties performing the Feasibility Study is essential. The potential treatment technologies must be expanded to include radiologically contaminated material and ARARs that relate to such materials must be identified.

Phase II of the FS is directly dependent upon Phase II of the RI. In fact the data reduction and mapping which occur in the second phase of the RI may reduce the scope of the second phase of the FS. The nature of the information provided by Phase II of the RI may allow a realization that certain alternatives will be more viable than others and allow treatability needs to be more accurately identified. Once Phase III of the RI is complete Phase III of the FS can begin. At this point, all the data will be available that is required to confidently choose a protective, cost-effective cleanup design.

Each Phase of RIGS, in association with the Pre-RI, allows specific determinations to be made as part of a consistent, cost effective and technically sound overall approach. The Pre-RI defines the need for further action and scopes the initial Phase. Phase I provides information about the physical environment where the site is located and whether the contamination on-site is migrating, both of which are critical for future actions. During Phase II the contamination itself is characterized, allowing the remainder of the study to focus on the specific problem. Phase III provides the opportunity for confirmatory sampling, filling data gaps and treatability studies.

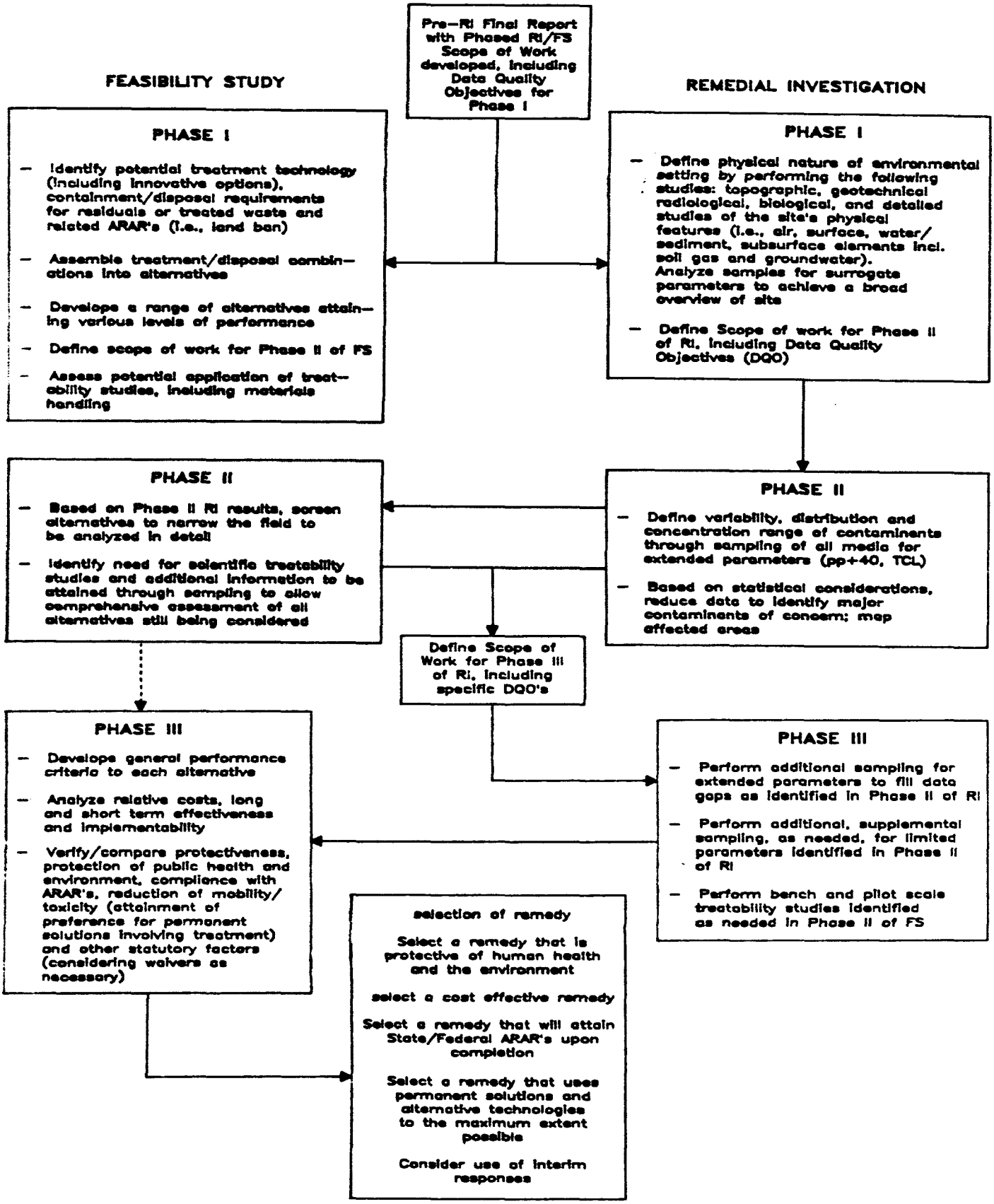
RIGS promotes the generation of critical data early in the investigation and the focusing of the study as more is learned. In this way, an applicable design alternative can be chosen in a timely, cost effective manner.

REFERENCE

EPA Guidance on Remedial Investigations Under CERCLA. EPA/540/6-85/002, June 1985.

Note: The authors of this paper are staff members of the New Jersey Department of Environmental Protection (NJDEP), Division of Hazardous Site Mitigation and Division of Hazardous Waste Management. The options and opinions expressed herein represent those of the authors and not of NJDEP.

Figure 2: RI/FS INTERACTION



* Adapted from an attachment to an EPA memorandum from J. Winston Porter re: Interim Guidance on Superfund Selection of Remedy.

DEVELOPING AN ENVIRONMENTAL LABORATORY ACCREDITATION SYSTEM

John W. Locke, Executive Director, American Association for Laboratory Accreditation

ABSTRACT

This paper describes the development of a laboratory accreditation program to recognize the competence of testing laboratories which test waste water, solid waste, hazardous waste, and drinking water. The need for a program which combines these testing skills is summarized and a description of how these skills have been combined is presented.

The approach used by the American Association for Laboratory Accreditation (AALA) is feasible, in spite of the complex nature of the testing which must be accomplished. A number of laboratories have already been assessed and there is great interest in continued development of the program.

International criteria for assessing the competence of testing laboratories developed by the International Organization for Standardization (ISO) and U.S. Environmental Protection Agency Quality Assurance (EPA QA) Project Plans are used as the basis for defining competence. Each laboratory is visited by an assessor and examined to see if it meets these criteria and to determine if it has the personnel, equipment, testing procedures and quality control/quality assurance programs necessary to perform the EPA tests competently. Any deficiencies are noted and the laboratory is required to attend to those deficiencies before accreditation is granted. Performance samples are required in certain testing areas, depending on the availability of programs.

This paper concludes with a discussion of problem areas being addressed by AALA and recommendations for the kind of technological support needed.

INTRODUCTION

Performing tests on samples of the environment is a growing business. Testing is the key to making decisions about drinking water -- ground water -- waste water -- solid waste -- toxic substances -- and pesticides in individual communities and industry facilities throughout the nation.

The Environmental Protection Agency (EPA) is developing new standards and test methods and defining new levels of performance which must be obtained in order to meet the requirements of our environmental laws. It is complicated work, made even more complicated because the standards and test methods are continuously

changing. On top of these ever changing test methods is the uncertain quality of the test data obtained by laboratories. Those who are responsible for environmental monitoring must select qualified laboratories to do the work, and the data generated by these laboratories must be accurate.

Citizens concerned about their environment continuously ask: Where can I find a competent laboratory? States responsible for environmental control are concerned: Are the data being generated good data?

EPA has provided some assistance and guidance for those primacy states who must develop their own lists of approved testing laboratories. For example, it has developed performance evaluation (PE) programs for water supply and water pollution studies in support of state (or regional) drinking water and wastewater programs. Participation is available every six months. Laboratories seeking approval by the states must register with a state or regional office responsible for preparing the list of "Approved Laboratories". In order to retain its approval, a laboratory must obtain test results within specified ranges on two sequential semiannual performance evaluation tests. Some states have developed their own performance evaluation programs in which their approved laboratories must participate.

This approval is called laboratory certification in some states; the international terminology used for this kind of recognition is called laboratory accreditation. EPA seems to be adopting the performance evaluation approach as the basis for all of its testing approval processes, but without trying to coordinate the requirements of the different environmental testing areas.

THE BASIS FOR AN ACCREDITATION SYSTEM

A fundamental question is: Does this EPA guidance provide a reasonable model for a national laboratory accreditation system? Two aspects come into question in particular. One relates to the efficiency of the system across environmental testing areas. The other relates to the adequacy of relying only on performance tests for judging the competence of laboratories. In practice, we are seeing EPA and various state environmental departments accredit laboratories for narrowly defined fields of testing and very narrow testing procedures. Accreditation is granted for drinking water -- and waste water -- and groundwater -- and solid waste -- and Superfund site testing. Often the same testing equipment and facilities are involved -- but each area is handled separately and there is little if any communication among approvers. A duplicative and confusing mixture of regulations, fees, and inspections has arisen and is growing. Some states are trying to put their own programs together. But approval by one state often does not mean acceptance in another state.

EPA management espouses the principle that the only proof of testing capability is a demonstration of a laboratory's ability to obtain accurate test results. But, it only has proficiency tests for about one-third of the parameters of interest. Where is the proof of capability for the other parameters?

Performance evaluations run every six months certainly do not provide sound statistical evidence that a laboratory can continually perform competently. The use of on-site assessment of laboratories wherein peers examine the laboratory operations and evaluate them against widely accepted criteria is frowned upon by some EPA managers as a paper exercise. Yet, can laboratories be required to participate in performance evaluation for each of the hundreds of parameters involved when we know that the limited frequency of performance evaluation does not statistically prove their accuracy in testing?

A combination of techniques must be employed to arrive at the most effective mechanism for approving laboratories. This combination will include on-site visits to laboratories to evaluate them against accreditation criteria, participation in performance testing, and establishment of sound quality control procedures -- including control charts -- in the laboratory.

THE AMERICAN ASSOCIATION FOR LABORATORY ACCREDITATION

AALA is a nonprofit, membership, professional society whose sole purpose is to recognize competent testing laboratories. Membership is available to all persons and particularly to those interested in developing a basis for eliminating or substantially reducing the increasing number of unrelated, narrowly based, substantially duplicative accreditation schemes that are developing.

The American Association for Laboratory Accreditation (AALA) has embarked on a program for accrediting environmental laboratories based on the combination of features described above. Internationally developed criteria for accrediting testing laboratories, International Standards Organization (ISO) Guide 25, have been adopted as the basis for accreditation. This guide sets requirement for laboratory organization, quality system, staff, testing and measuring equipment, calibration, items to be tested, records, and test reports.

ASSESSING THE LABORATORY

Table 1 presents a check list to guide the assessors in evaluating a laboratory's ability to meet the general criteria. Key to the evaluation is the laboratory's quality manual. This manual normally goes to the assessor before the visit to the laboratory so that the assessor can be familiar with what to expect during the visit to the

laboratory. The quality system in the laboratory is flexible as it must be in order to reflect the individual style of management of each organization. AALA does provide the laboratory with a guideline developed by the International Laboratory Accreditation Conference (ILAC) that identifies all items which should be addressed in the manual. The laboratory must be practicing quality control as described in its manual, otherwise the assessor will cite a deficiency.

The assessor's evaluation of the laboratory's actual testing operation is focussed on the particular testing equipment and process, rather than on particular areas of the environment because the measurement process is often comparable, whether a test is for drinking water, waste water, or solid waste. Care is taken to ensure that the laboratory procedure reflects the requirements for accuracy for each area of the environment (i.e. the accuracy demanded for drinking water testing for one parameter may be much greater than for the same parameter in solid waste testing). Performance testing (called proficiency testing) is required. The results of proficiency testing are reviewed by assessors for clues to determine deficiencies and unsatisfactory performance.

INTEGRATING TESTING REQUIREMENTS

EPA and many of the states are organized in response to specific legislation: drinking water; clean water, pesticides; and solid wastes. Laboratories are not typically organized along lines specified by EPA's enabling legislation. Rather they have biological sections and chemical sections, and in each of these sections they may have units which focus on testing technologies such as radio chemistry or spectroscopy. The laboratory accreditation system must be able to accredit laboratories as they are organized to provide the relevant data.

In order to do this, AALA has developed an assessor checklist for each testing technology, and has set requirements based on the most stringent requirements in EPA's regulations. Table 2 presents a description of how the checklist is broken down by testing technology. For each testing technology, the checklist is further broken into elements shown on the bottom of Table 2.

Each of the relevant EPA regulations has been consulted and the specific requirements reviewed. The references include the following EPA guidance:

Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures
Manual for Chemical Analysis of Water and Wastes
Contract Laboratory Program, Inorganic and Organic Analysis
Test Methods for Evaluating Solid Wastes (SW846)
Standard Methods for the Examination of Water and Wastewater (13th - 16th editions)

To be accredited for a given parameter, the laboratory must meet the most stringent requirement in these references. Table 3 presents an example in one testing area, Ion Chromatography.

DEFICIENCIES

At the conclusion of an assessment, the assessor prepares a report of findings, identifying deficiencies (i.e., deviations from the criteria and test method procedures for which accreditation is requested) which in the opinion of the assessor the laboratory must correct in order to be accredited. The assessor holds an exit briefing with top management of the laboratory, going over the findings and presenting the list of deficiencies (deficiency report). The authorized representative of the laboratory or his designee is asked to sign the deficiency report to attest that he has reviewed the deficiency report with the assessor. The laboratory is requested to respond within one month of the date of the exit briefing. It is entirely possible that the laboratory will disagree with the findings that one or more items are deficiencies. In that case, the laboratory is required to write to AALA Headquarters explaining why it disagrees with the assessor.

ACCREDITATION DECISIONS

Assessor reports, communications from the laboratory, and results of proficiency testing are submitted to the members of the AALA Accreditation Council for evaluation and vote on accreditation. Any negative votes are reviewed by AALA staff with the Council member and with the laboratory for resolution. If resolution is not possible, the laboratory is not accredited.

If accreditation is granted, the AALA staff prepares and forwards a certificate and scope of accreditation to the laboratory for each enrolled field of testing and special program. The laboratory should keep every scope of accreditation available to show clients or potential clients the testing technologies and test methods for which it is accredited. AALA staff also uses the scopes of accreditation to respond to inquiries and to prepare the AALA Directory of Accredited Laboratories.

APPEALS PROCEDURE

The AALA staff advises the laboratory of its right to appeal adverse accreditation decisions to the whole Accreditation Council. If not satisfied with the Council decision, the laboratory may make a further appeal to the Board of Directors. All decisions by the Board are final. Details of the appeals procedures and the laboratory's right to a hearing are contained in the AALA Bylaws.

UPDATING ACCREDITATION

Accreditation is granted for two years. However, before the second year of accreditation, each laboratory must pay interim fees and submit updated information on its organization, facilities, key personnel, and results from proficiency tests. Any changes in location, ownership, management and supervisory staff, authorized representative, or major facilities of the laboratory must be promptly reported to AALA headquarters.

Well in advance of the expiration date of its accreditation, each accredited laboratory is sent a renewal questionnaire. A successful on-site reassessment must be completed before accreditation is extended for another two years.

AALA conducts a full on-site reassessment of all accredited laboratories every two years. Reassessments are also conducted when evaluations and submissions from the laboratory or its clients indicate significant technical changes in the capability of the laboratory have occurred.

CONTINUING DEVELOPMENTS

AALA has formed an Environmental Advisory Committee to continue the development of this program. This committee will be responsible for:

- Recommending changes to the program, including changes in scopes of accreditation now offered to successful participants if deemed necessary;
- Reviewing current assessor checklists and recommending changes;
- Updating the list of test methods and parameters covered by the program;
- Identifying appropriate proficiency tests in which laboratories would be required to participate;
- Suggesting potential assessors and overseeing assessor training programs, recognizing that assessors are the fundamental link in the implementation of the program.

Additional areas of environmental concern may be considered for addition to the program. These could include air monitoring, indoor air quality, radon and other specific parameters of public interest.

The key to the successful implementation of the program is involvement -- involvement of all those who would be willing to work to see a national accreditation system capable of meeting their

specifications developed. You are invited to join the Advisory Committee and to join AALA. Our only purpose is to formally recognize competent testing facilities.

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Table 1

AALA ASSESSOR CHECKLIST: GENERAL CRITERIA

Each entry below represents a criterion statement from ISO/IEC Guide 25. Record comments for any entry on your own sheets. Any entry checked "no" (indicating a deficiency) must be explained.

Laboratory Name: _____

Address: _____

	Yes	No	N/A
3. Organization:			
Satisfactory organization structure	___	___	___
Can perform representative tests	___	___	___
No undue pressure observed	___	___	___
Staff responsibilities are clear	___	___	___
Identify technical manager: _____			
Adequate security for client data	___	___	___
4. Quality System:			
4.1 Laboratory operates internal quality system	___	___	___
Quality manual available for staff use	___	___	___
Quality manual maintained regularly	___	___	___
Identify quality manager: _____			
4.2 Quality manual contents:			
Organization charts	___	___	___
Staff duties pertaining to quality	___	___	___
General quality assurance procedures	___	___	___
Q/A procedures specific to each test	___	___	___
Proficiency/reference materials use	___	___	___
Feedback & corrective action program	___	___	___
Technical complaint handling procedure	___	___	___
4.3 Quality system periodic reviews recorded	___	___	___
5. Staff:			
5.1 Necessary educ., training, knowledge, & experience	___	___	___
5.2 Job descriptions for senior technical positions	___	___	___
5.3 Adequate supervision	___	___	___
5.4 Technical/quality staff backups/deputies	___	___	___
5.5 Qualifications/training/experience recorded	___	___	___
6. Testing and Measuring Equipment:			
6.1 Equipment available for scope of tests	___	___	___
6.2 Equipment maintained & instructions available	___	___	___
6.3 Overload & mishandling procedures available	___	___	___
6.4 Equipment records maintained:			
6.4.1 Name of equipment item	___	___	___
6.4.2 Manufacturers name/type/serial number	___	___	___
6.4.3 Dates received/placed in service	___	___	___
6.4.4 Current location (where appropriate)	___	___	___
6.4.5 Details of maintenance	___	___	___

	Yes	No	N/A
6.5 For measuring equipment:			
6.5.1 Date of last calibration & reports	___	___	___
6.5.2 Maximum time between calibrations	___	___	___
6.6 Calibration labels used	___	___	___
7. Calibration:			
7.1 Prog. for initial & periodic calib. established	___	___	___
7.2 Traceable measurements (where applicable)	___	___	___
7.3 Reference standards for calibration only	___	___	___
7.4 Reference standards calibrated appropriately	___	___	___
7.5 In-service test equipment checks (where relevant)	___	___	___
7.6 Reference materials traceability	___	___	___
8. Test Methods and Procedures (use field checklists as applicable):			
8.1 Equipment operating instructions up-to-date	___	___	___
8.2 Methods are as required by specification	___	___	___
8.3 Non-standard test methods fully documented	___	___	___
8.4 Calculations & data transfers checked	___	___	___
8.5 Data processing accuracy checks	___	___	___
9. Environment:			
9.1 Equipment protected & environment monitored	___	___	___
9.2 Access to test areas controlled (as needed)	___	___	___
9.3 Adequate housekeeping	___	___	___
10. Handling of Items to be Tested:			
10.1 Sample identification procedures adequate	___	___	___
10.2 Bonded storage available (if needed)	___	___	___
10.3 Sample protection procedures adequate	___	___	___
10.4 Rules for receipt, retention, disposal	___	___	___
11. Records:			
11.1 Records adequate to permit repeat of test	___	___	___
11.2 Records & reports secure	___	___	___
12. Test Reports:			
12.1 Work in laboratory covered by test reports	___	___	___
12.2 Each test report contains:			
Name & address of laboratory	___	___	___
Unique identification (including pages)	___	___	___
Name & address of client	___	___	___
Test item identification & description	___	___	___
Date of receipt of test item & test	___	___	___
Test results relate to tested item	___	___	___
Identity of test method used	___	___	___
Description of sampling procedure	___	___	___
Any deviations, additions, etc. to test	___	___	___
Identity of any non-standard test used	___	___	___
Results and any failures identified	___	___	___
Measurement uncertainty (if relevant)	___	___	___
Signature and date	___	___	___
Statement regarding reproduction of report	___	___	___
12.3 Report format OK?	___	___	___
12.4 Supplemental procedures	___	___	___

Table 2

ENVIRONMENTAL ASSESSOR CHECKLISTS

Specific Criteria by Testing Technology:

Microbiology
Radiochemistry
    Gross Alpha, Gross Beta, Liquid Scintillation, Proportional Counters
Atomic Absorption/Inductively Coupled Plasma Spectrophotometry
Visible Spectrophotometry
Automated Spectrophotometry
Gas Chromatography (Drinking water)
Gas Chromatography
Gas Chromatography/Mass Spectrometry
Ion Chromatography
High Performance Liquid Chromatography
Titrimetry
Gravimetry
Miscellaneous, Electronic Probes (pH, Fluoride Specific Ion, Dissolved Oxygen)
Thin Layer Chromatography
Turbidity
Chemical Oxygen Demand
Biochemical Oxygen Demand
Carbonaceous Biochemical Oxygen Demand
TOC
TOX
MBAS
RCRA Tests (Flammability & Corrosivity only)
Cyanides

For each of these we have broken down the requirements into the following elements:

1.0 Organization and Personnel Requirements
2.0 General Facilities
3.0 Instrumentation
4.0 Documentation
5.0 Analytical Methodology
6.0 Quality Assurance

Table 3
Specific Criteria & Assessor's checklist
ION CHROMATOGRAPHY

1.0 Organization and Personnel

1.1 Is use of the method (300.0) restricted to use of personnel experienced in IC?
1.2 Are users experienced in interpretation of ion chromatograms?
1.3 Before using this method, does each user demonstrate the ability to generate acceptable accuracy and precision using a laboratory control standard?
1.4 Is 1.3 documented for each user?

2.0 General Facilities

3.0 Equipment

3.1 Ion Chromatograph
3.1.1 Anion guard column
3.1.2 Anion separator column
3.1.3 Anion suppressor column
3.1.4 Detector - Conductivity cell
3.1.5 Strip chart recorder
3.2 Are interferences solved by sample dilution or spiking?
3.3 Is suction taken to eliminate the water dip?
3.4 Is the action documented?
3.5 Are samples and solutions containing particles over 0.20 microns filtered?

4.0 Documentation

5.0 Analytical Methodology

5.1 Is reagent water free of anions of interest in use?
5.1.1 Is the reagent water quality documented?
5.2 What is the element solution?
5.3 What is the regeneration solution?
5.4 Are diluted working standards prepared weekly except nitrite and phosphate?
5.5 Are nitrite and phosphate standards prepared fresh daily?
5.6 Is sample holding time determined by the anion that requires the most preservation time and shortest holding time?
5.7 Are holding times documented?
5.8 Is system calibration checked daily?
5.9 Is same size loop used for standards and samples?
5.10 Is spiking done to produce adequate resolution?

6.0 Quality Assurance

6.1 Are Calibration curves for each analyte prepared with a minimum of three concentration levels and a blank?

6.2 Is one of the points of the calibration curve near the method detection limits?
6.3 Are retention times recorded and documented during calibration?
6.4 Is the working curve verified daily?
6.5 If more than 20 samples are run, is the working curve verified?
6.6 If results vary by more than ± 10 %, is the test repeated using fresh calibration standards?
6.7 Does the laboratory maintain performance records to define the quality of data?
6.8 If method modifications are made, does the user repeat 1.3?
6.9 Are a minimum of 10% of all samples spiked to monitor performance?
6.10 I sample operator precision determined?
6.11 Is method performance calculated?
6.12 Does the laboratory maintain separate accuracy statements of performance for water and wastewater?
6.13 Does the laboratory demonstrate by analysis of reagent water that all glassware and reagent interferences are under control?
6.14 Does the laboratory analyze field duplicates?
6.15 Does the laboratory perform quality control check sample analyses?

A PRE-REMEDIAL INVESTIGATION STUDY AS AN ALTERNATIVE APPROACH IN THE SITE REMEDIATION PROCESS*

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ABSTRACT

In and of itself, a Site Investigation (SI) as currently applied under the RCRA 3012 & CERCLA 104 programs does not provide sufficient information to structure subsequent remedial activities at hazardous waste sites. Site Investigations, by virtue of their limited scope and purpose, provide limited information about the extent of hazards posed by specific site conditions. The result of employing data generated from current SI practices could lead to unnecessary time delays, cost overruns, confirmatory resampling, additional sampling, and in the worst case reimplementation of the RI.

As an alternative to proceeding from an SI to a full scale RI/FS, the Division of Hazardous Site Mitigation has developed a Remedial Investigation Guidance Strategy (RIGS) that utilizes a Pre-RI Study that will determine the course a Remedial Process will follow. A pre-RI study must be performed before any remedial activities can occur.

Sampling during the pre-RI is intended to better define site conditions as well as define migratory pathways that exist on-site. These pathways include air, surface water and sediment, and groundwater. The possible receptors in all cases are the human population. In assessing the air route, both on and off-site locations will be considered. Contamination may also be present in the surface water and sediment on-site. Other influences may cause contamination to move to off-site surface water bodies. This portion of the pre-RI investigation will further investigate the nearest streams, rivers, marshes, lakes and bogs. A limited number of surface water and sediment samples may be collected for analysis. Another major migratory pathway to be investigated is groundwater. As groundwater is utilized by most municipalities to supply the demand for potable water, it must clearly be addressed. Consideration will be given to the saturated as well as unsaturated zones.

Mechanisms and locations for sample collection and measurement are dependent on site specific conditions and parameters selected for site characterization. For example, a series of biased samples reflecting natural and man-made influences will be collected and analyzed for selected parameters. Air, surface water and sediment, and groundwater systems will be surveyed. In addition, anthropogenic routes of

*The options and opinions expressed in this paper represent those of the authors and not of the N.J. Department of Environmental Protection.

contaminant transport will also be investigated. This includes vehicular transportation, as well as collection systems (i.e. stormwater, wastewater).

Also to be addressed during the pre-RI are areas of highest probable contamination; these areas will be assessed but not necessarily evaluated through field samples. Included in this survey are (1) areas of known disposal; (2) waste and waste treatment systems; (3) storage facilities; (4) on-site laboratory facilities; (5) production facilities; and (6) miscellaneous items such as transformers and/or asbestos. Based on site specific characteristics, the need for sampling during this phase will be determined.

A time frame of approximately three to four months is projected for completion of the pre-RI. Utilizing the results of this preliminary sampling, an interim report will be generated. This report will recommend one of the following: (1) no action; (2) final or interim remedial measures; (3) initiation of a focused RI; or (4)initiation of a full scale RI/FS. The information obtained during the pre-RI will be instrumental in planning further remedial activities.

INTRODUCTION

In and of itself, a Site Investigation (SI), as currently applied under the RCRA 3012 and CERCLA 104 programs does not provide sufficient information to structure subsequent remedial activities at hazardous waste sites. Site Investigations, by virtue of their limited scope and purpose, provide limited information about the extent of hazards posed by the site. Current Remedial Investigations proceed directly from an SI to a full-scale RI/FS. Activities for the RI are based on the limited data obtained during the SI. The time lag which exists between obtaining SI data and initiating the RI may be considerable. In an attempt to provide sufficient information to make subsequent decisions about remedial activities at a site, NJDEP, Division of Hazardous Site Mitigation (DHSM) has developed a pre-RI study. The pre-RI will attempt to fill the data gaps which exist and time delays which arise when proceeding from SI to the RI. The results of employing data generated from current SI practices could possibly lead to unnecessary time delays, cost overruns, additional sampling, confirmatory resampling, and in the worst case, reimplementation of the Remedial Investigation (RI) study.

The pre-RI study will determine the potential for off-site migration of contaminants. It will expand the information known about the site which was provided by the SI. The pre-RI study is intended to be a mechanism for determining the need for implementing a full scale RI/FS at a hazardous waste site. The data generated, and information obtained during the pre-RI, in conjunction with SI data, will indicate whether there is a need to assess only one migratory pathway and focus the remedial investigation or whether there is need to implement a full-scale RI to address a number of possible contaminant systems. The pre-RI will be used to develop the Scope of Work (SOW) for the next phase of remedial activities as well as prioritize the actions which will be conducted at the site. In addition, the pre-RI

investigation will assess any immediate threat the site poses to the general public and the environment. This will be done by thoroughly addressing the potential for off-site contamination; migratory pathways will be reviewed and evaluated. The protection of the public health and the environment is of the utmost importance. If there is an impending risk posed by existing site conditions, immediate actions will be taken to stabilize and/or remediate the situation. Any actions conducted at the site will be consistent with recommendations made for further remedial activities. And lastly, the pre-RI will provide a broad data base from which future actions may be decided. A large number of field measurements and limited analytical data, used in conjunction with past data and file information, will be used to formulate an accurate picture of existing site conditions. From this information, a well defined Scope of Work for subsequent remedial activities may be developed. NJDEP-DHSM has projected a time frame of six (6) months and $50,000 to complete the pre-RI utilizing in-house personnel. While NJDEP-DHSM is proposing to use in-house personnel to conduct the pre-RI, contractors may also be engaged to perform the study. However, the uncertainties associated with engaging a contractor may increase the overall cost and increase the time frame proposed to complete a pre-RI study. Hence, the pre-RI study should be used as a foundation for any future remedial activities at the site. When used to its fullest potential, the pre-Ri will prove an invaluable asset to the existing Remedial Investigation process and as such should be utilized to refine the Remedial Investigation strategy.

Regardless of the funding source (Superfund, Spillfund, Private party), a pre-RI should be performed to guide future RI activities at the site. Performing a pre-RI has numerous advantages. First, there will be standardization of procedures and practices which will be carried out at all sites. The same criteria will be used to evaluate all sites; the results will direct future work. Second, significant cost savings may be realized if the pre-RI results indicate that the site requires a focused RI/FS that is not warranted. The individuals performing the study will be evaluating the data and developing the Scope of Work for the next phase of the RI. This progression insures consistency which is a critical factor in the environmental evaluation area.

The pre-RI study, which precedes RIGS, is intended to fill the data gaps which are not answered by the SI. The SI provides primarily source data, while the pre-RI will provide data indicating the potential for off-site migration of contaminants. The pre-RI will be conducted between these two activities and will provide valuable information on impending threats which have arisen at the site since the initial SI. Information gathered during this study will be used as the basis for planning future remediation activities. The purpose of this paper is to briefly describe and outline the strategy of the pre-RI and activities to be considered in the study.

The overall strategy of the pre-RI may be summarized as follows. Sampling performed during the pre-RI is intended to better define site conditions as well as define migratory pathways that exist on the site. These pathways include air, surface water and sediment, and

GENERIC SCHEDULE OF WORK FOR PRE - RI

PRE-RI ACTIVITIES	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20	Week 21	Week 22	Week 23	Week 24	Week 25	Week 26	Week 27
Referral receipt	X																										
File review *	X	X	X	X																							
File sources checklist		X	X																								
File summary		X	X	X																							
File hazard ranking chart			X	X																							
Procure funding **	X	X	X	X	X	X	X	X	X	X	X																
Obtain enforcement clearance **	X	X	X	X	X	X																					
Conduct initial site visit	X																										
Interim site visit			X	X																							
Site visit prior to sampling										X	X																
Site hazard ranking chart			X	X																							
Preliminary site map	X	X																									
Final site map															X												
EMS briefing				X																							
Prepare Interim Pre-RI Report & Work Plan					X	X	X	X			X																
Review interim report **								X	X	X	X																
Engage contractors **												X	X	X													
Laboratory procurement												X															
Field sampling preparation												X															
Initiate field activities												X	X	X	X	X	X										
Analysis ***																	X	X	X	X	X	X	X				
Data Validation																							X	X	X		
Final Pre-RI Report & Recommendations																									X	X	X

* On-going throughout the project.

** May be deleted if not required and will significantly reduce the timeframe.

*** Priority turn-around time will reduce the time frame but will increase overall cost.

Figure 1

groundwater. Mechanisms and locations for sample collection and measurements are dependent on site specific conditions and parameters selected for site characterization. A series of biased samples, reflecting natural and man-made influences, will be collected and analyzed for specific parameters. The contaminant transport systems mentioned above, as well as anthropogenic routes of transport will be investigated. Based on file searches and site investigations, areas of the site will be prioritized based on environmental risk. Also to be addressed during the pre-RI are areas of highest probable contamination; these areas will be evaluated although not necessarily evaluated through field samples. Included in this survey are (1) areas of known disposal; (2) waste and waste treatment systems; (3) storage facilities; (4) on-site laboratory facilities; (5) production facilities; and (6) miscellaneous items such as transformers and/or asbestos.

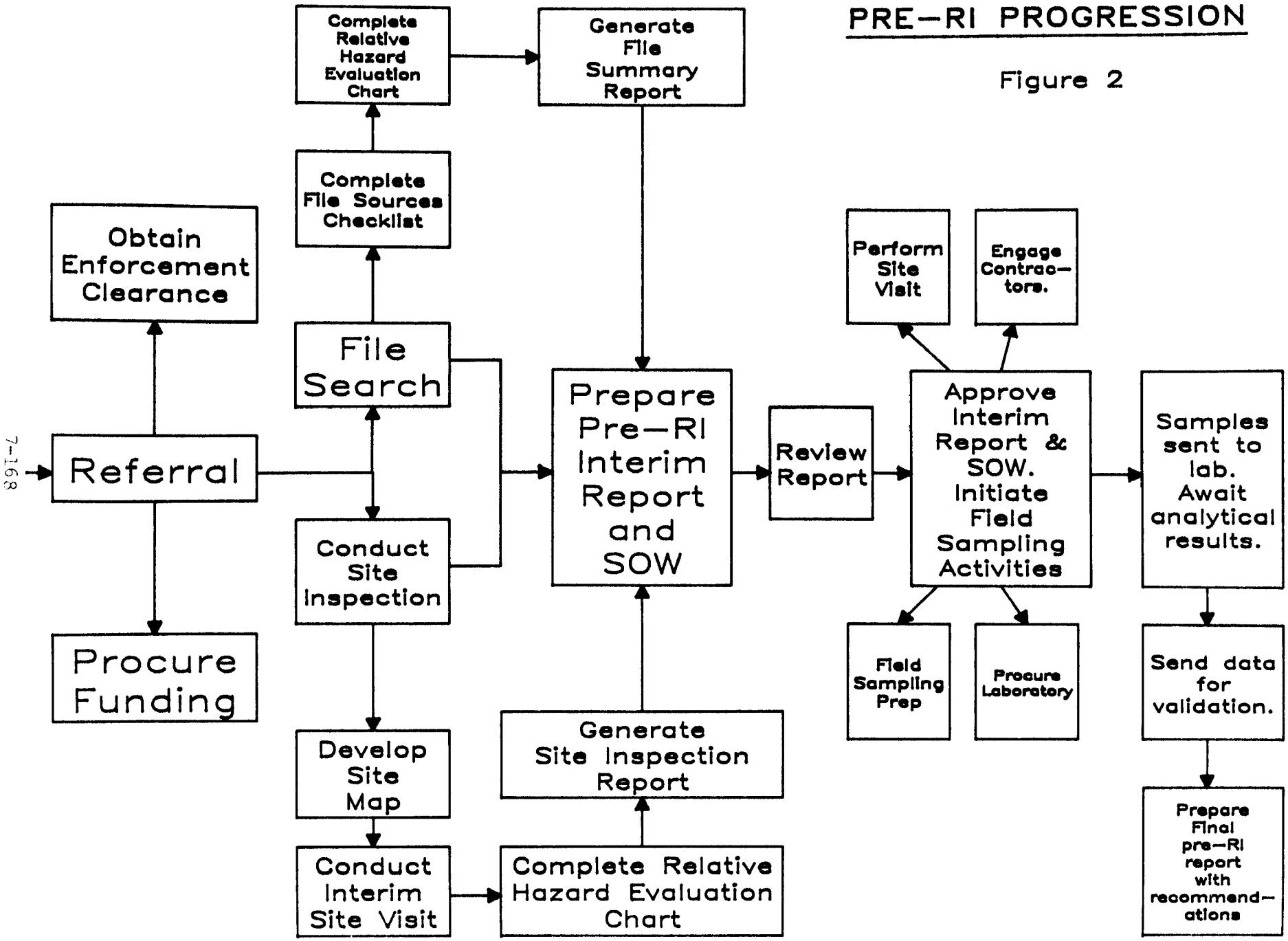
The pre-RI can be subdivided into a number of activities which correspond to a projected time frame. Figure 1 outlines these activities and indicates the overall time table for completion of a pre-RI study. A time frame of six months has been projected for completion of activities and preparation of the final pre-RI report. Figure 2 details the pre-RI progression during the course of the study. As evident in both figures, a number of items may be performed concurrently. When a pre-RI is conducted at a site, a file investigation and site visit should occur within the first week. Depending on past activities at the site, the files may provide valuable information which will be useful in guiding sampling activities. In addition, a site visit should always be conducted early in the project. Any voids or questions which arise during the intial file search may be readily answered by a site visit. Where files are sparse and/or conflicting reports exist, a site visit may clarify these items. A preliminary site map should be developed and used as a base map to indicate all pertinent structures, waste areas and past and future sampling locations. The site map should be drawn to an appropriate scale. An additional site inspection should be conducted prior to writing the interim report to insure an accurate and detailed account of existing site conditions.

The interim pre-RI report will summarize the existing file information about the site. It will include site history, background, previous analytical data, enforcement actions, previous remedial activities and all other pertinent information which will help to determine future activities. In addition, the interim report will include a summary of the site inspections highlighting the areas of concern. A preliminary site map will also be included. Based on the files and site inspections a Scope of Work (SOW) will be developed for the remaining field activities at the site. The site specific SOW will be used as the basis for developing the Field Sampling Plan (FSP).

One final site visit should be conducted just prior to initiation of field activities to prepare for actual field sampling. While the file search and site visit are being conducted, attempts should be made to procure funding and obtain the appropriate enforcement clearance. These activities should be initiated as soon as possible due to the

PRE–RI PROGRESSION

Figure 2



additional time which may be incurred for completion of these activities.

Based on the file search and site investigation, completion of two checklists are required. While the file seach is on-going throughout the project, the initial thrust of activities is during the first few weeks of preliminary activities, prior to actual field work. A File Sources Checklist was established and must be completed indicating those sources which have been utilized. This is to include interviews, enforcement actions, newspaper articles and any other information which should be considered in the interim report package.

In addition, a Relative Hazard Evaluation Chart must be completed. There are two categories: one based on files and one based on the site inspection. A numerical system has been utilized to help prioritize different areas of the site. A low priority rates a one, a medium priority rates a three and a high priority rates a seven. Field ratings are selected based on the following criteria:

Low (1) - Lack of reference; documented release which has been remediated.

Medium (3) - Consistent enforcement actions; citizens complaints; water quality monitoring data; underground utilities as conduits.

High (7) - Documented release which has not been remediated; documented release which has been stablized but not remediated; impending structural failure of container or vessel; documented fish kills or other biota adversely impacted; potential for subsurface gas production; documented reports of discolored soils/stressed vegetation; sampling data indicating contamination.

Site investigation ratings are selected based on the following criteria:

Low (1) - No visual evidence of a problem. No reading on field instrumentation.

Medium (3) - Sporadic readings on field instrumentation; permitted discharge pipes; runoff pathways; seepage along a bank; underground utilities as conduits; stressed vegetation; odors; unusual physical characteristics (oil slicks/foam).

High (7) - Obvious signs of release (documented/ undocumented); potential release probable; areas suspected of undocumented release(s); sustained instrument readings above background; uncontrolled releases; non-point source discharges; evidence of subsurface gas production; aquatic stress; discolored soils.

The two ratings are added together in an attempt to indicate the areas

of greatest concern. An additional column is provided to indicate the route which will be affected. An overall score of seven (7) or better indicates an area of high priority. The overall priority rating should be considered when making Scope of Work recommendations in the Interim Report.

Upon completion of the aforementioned tasks, a pre-RI interim report must be generated. This report is a written summary of the field inspection and file investigation. It will include the File Sources Checklist and Site Prioritization Chart which have been completed for the particular site. The report will prioritize the potential routes of exposure (air, surface water and sediment, soil, groundwater) based on site conditions and file data. Lastly, the report will provide recommendations and the Scope of Work (SOW) for the pre-RI field investigation. Included will be a site specific sampling plan detailing the field activities to be performed in the next segment of the pre-RI. Upon completion of the Interim Report a review period may be required. During this time, any necessary modification may be incorporated.

The study will include investigating the release potential to all environmental media at the site. Objectives of the air study include (1) assessing radiological conditions; (2) characterization of off-site migration of air-borne contaminants; and (3) continuous determination of ambient air conditions on-site. A series of stationary monitoring units will be located upwind, downwind and on-site in an attempt to characterize air-borne contamination that are migrating off-site. In addition, a radiation survey will be conducted on-site. Based on information known about the site, grids will be set up ranging form 25' x 25' to 200' x 200'. A survey will be conducted along the horizontal and vertical transverses. And lastly, ambient air monitoring will be conducted at the site during all site activities. Instrumentation will include on OVA, PID, explosimeter and other applicable monitoring equipment. The surface water and sediment study will (1) attempt to determine whether on-site contaminants are migrating off-site and concentrating in sediments; and (2) assess direct discharges from the site which are entering adjacent water bodies. Surface water samples will be collected only when there is direct evidence of a current discharge from the site. This may include a running leachate seep, a discharge pipe coming from the site, runoff or similar. Sediment samples will be collected upstream, adjacent to and downstream from the site. If there are no surface water bodies, sediment samples are not required. Field measurements such as DO, pH, conductivity, temperature and flow rate will be determined. The objective of the soil/groundwater study is to determine whether the unsaturated zone is the medium for contamination to enter the groundwater. If monitoring wells exist on site, samples will be collected. Depending on site conditions, production wells and/or potable wells may be sampled. Gamma logging will be performed if continuous boring log information is not available for the current wells/piezometers. In addition, a soil gas survey of the site will be performed. Using 100' x 100' grids, eight (8) data points per acre will be sampled. The grid size may be modified based on site conditions. Surface soil samples for chemical analysis will be

collected if site conditions warrant. This may be required if stressed vegetation or leaking tanks or drums are present. On a site where none of the conditions mentioned above exist, test pits, soil borings and piezometer installation may be required. Careful consideration should be given to selection of these alternatives as they will significantly increase cost and may not provide sufficient information from which to make subsequent decisions. And lastly, consideration will be given to the Universal Soil Loss Equation to determine the gross amount of soil loss migrating off-site which may potentially carry contaminants.

Samples collected for chemical analysis (Target Compound List + 30 or Priority Pollutant List + 40) will be limited; selection will be based on requirements established for each area. Field measurements with portable instruments will dominate the pre-RI study. A soil gas and radiation survey will be conducted on site. Dissolved oxygen, pH, conductivity and temperature measurements will be collected where applicable. All measurements will be performed in the field by trained DHSM individuals. Field collection of data will significantly limit analytical costs while maximizing data generated.

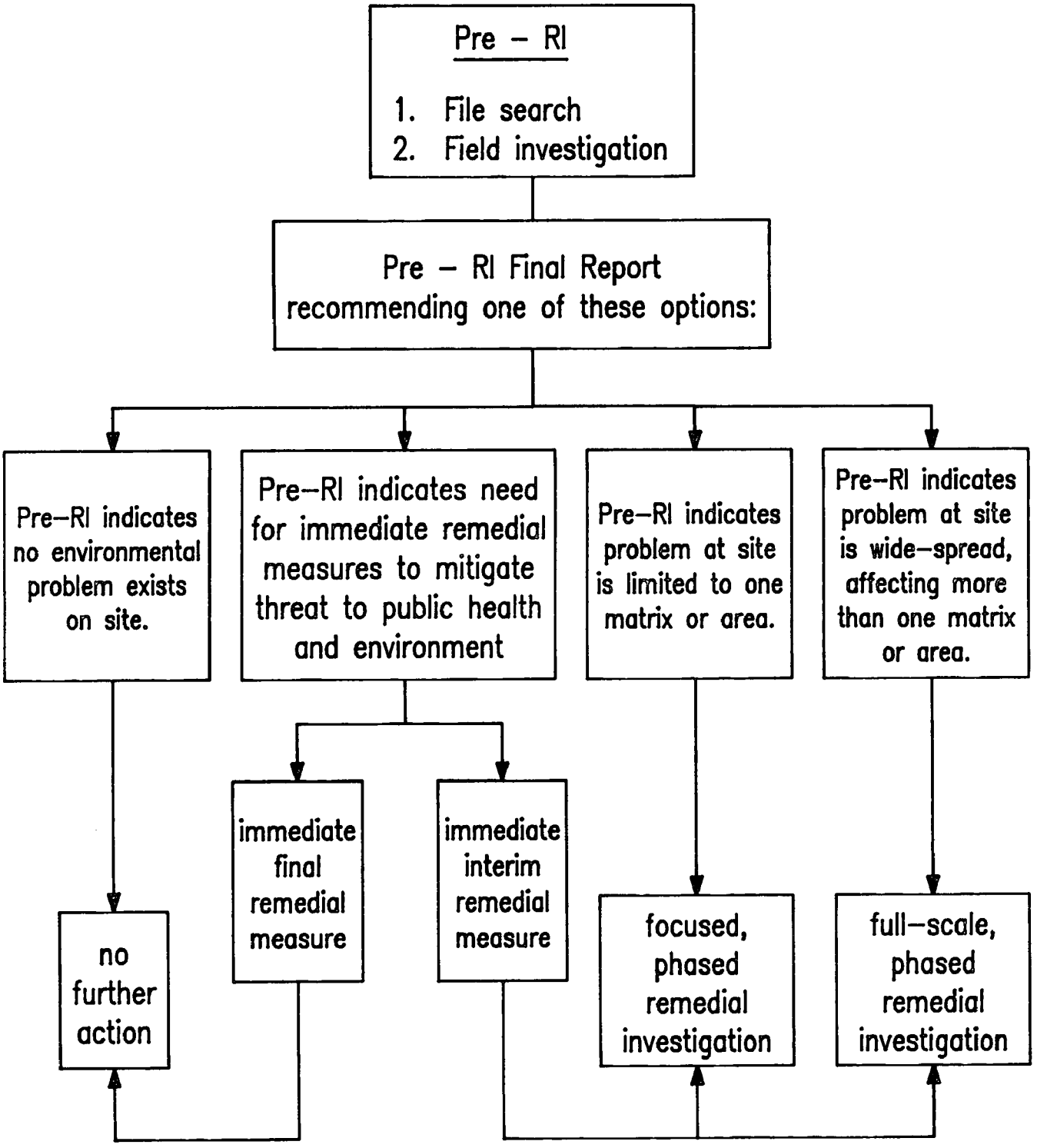
Once the interim report is accepted, field sampling activities may be initiated. The laboratory and any necessary contractors should be engaged and field sampling preparation commence. Actual field activities may take from one to six weeks depending on the Scope of Work and personnel allotted for field activities. Barring prolonged periods of bad weather, field activities should not delay the project.

Once field activities are complete, analytical results may take up to eight weeks. This time frame has been built into the generic schedule but may be reduced significantly if priority turn-around is requested. This will however significantly increase the overall project cost. Best judgment and the critical nature of a project must be taken into account when making this decision.

Upon receipt of analytical results, data will be validated by the Quality Assurance Section of DHSM.

Based on the analytical results, field measurements, field searches and site inspections, EMS will generate a final pre-RI report. This report will make recommendations for the next action to be undertaken; it will provide the Scope of Work for phase I of the proposed three-phase RI. Figure 3 shows how the information gathered during the pre-RI will be used. The no action alternative will be recommended when all information indicates that there is no significant environmental problem which warrants additional action. Immediate final remedial measures will be recommended if the site poses an impending threat to the population or environment surrounding the site. This action might be recommended if intact drums are present. Immediate interim remedial measures may be recommended if there is a lagoon on site which requires stabilization until further remedial alternatives can be determined. The interim remedial measure alternative will more likely be followed up by a focused RI or full-scale RI depending upon overall site conditions. The immediate

Figure 3 : PRE–RI and RIGS



final alternative may require limited sampling during remedial activities and no further action. The pre-RI measurements/analysis will provide sufficient information to determine whether a focused RI (only a groundwater study) or full scale RI is warranted at the site.

Depending upon the scope of the problem, immediate remediation may occur under the supervision of the NJDEP or USEPA. However, if the scope of work identified in the final report is beyond the capabilities of the DHSM staff, a full-scale or focused RI will be initiated.

In summary, the pre-RI strategy was developed to fill the gap that exists between the current SI process and initiation of the RI/FS. The information obtained during the study will provide a broad data base from which future remedial decisions will be based. Regardless of the funding source, a pre-RI investigation should be conducted on all sites where a full-scale Remedial Investigation is being considered. The results of the pre-RI may indicate conclusively that a full-scale RI/FS is not warranted. Rather, a focused RI/FS may be more appropriate. Thus, a significant cost savings may be incurred. In addition, the pre-RI is intended to be conducted by in-house personnel in an attempt to maintain consistency from site to site. The underlying thrust of any pre-RI study is to obtain enough data and information about the site to develop the Scope of Work for the next phase of remedial activities. This will insure that the next action taken will protect the public and the environment from any existing hazard. Use of the pre-RI strategy will assure accountable spending of public money, reinforce decisions made, insure maximum protection of public health, and most importantly, maximize the efficiency of ensuing remedial activities.

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SAMPLING AND FIELD METHODS

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USING BARCODES AND PORTABLE COMPUTERS FOR SAMPLE TRACKING

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ABSTRACT

Midwest Research Institute is currently doing work in support of EPA's hazardous waste "Listing" and "Relisting" programs. Because of the demanding QA requirements in maintaining the integrity of samples and legal defensability of the data, new tracking procedures have been developed to meet these objectives in an efficient manner.

A chain-of-custody/sample tracking system was developed to improve quality assurance and management of project resources. The objectives of this system were to identify incoming samples received at MRI, expedite sample transfers under traceability and chain-of-custody criteria, and to monitor work-in-progress. Ideally, it was the intent that this system reduce the time required for effective documentation and remain flexible to meet changing quality assurance and project requirements. By incorporating barcodes for sample labeling and data-entry, and using "lap-top" computers programmed to read barcoded information, we were able to achieve a versatile and portable sample tracking systems.

Barcoding, a technology that has been time-tested for about 20 years, provides an accurate and fast way to record information. Preprinted barcoded (and human-readable) labels are used to encode samples and make them traceable to the source and history of each sample. Exact replicas of these labels are affixed to corresponding forms, lab glassware, data charts, in other words, anywhere where sample identification is needed. Encoding samples this way also allows confidential business information to be more easily protected in the performance of day-to-day activites. Laboratory worksheets that contain lists of barcodes and task descriptions are used to enter routine information such as sample status and type of analysis. Code 3 of 9 barcode format allows alphanumeric encoding so that analysts, equipment, etc., can be easily identified.

Portable lap-top computers offer a flexible and completely portable means of recording sample analysis information and a convenient way for reporting that information. These computers can record information by scanning barcodes with an attached light pen, directly connecting to other instruments (such as a balance) through RS-232 ports, and manual entries typed on the key board. Customized software allows you to "prompt" for the required information and automatically document exact dates and times tasks are performed. The information that is collected can be printed, then signed by the analyst to validate its accuracy; or the information can be sent to a host computer using the computer's built-in modem via standard telephone lines.

Finally, by using the electronic files received by the host computer to

automatically update the sample database, many different types of reports can be generated to monitor sample holding times, document sample traceability, and better manage project resources.

INTRODUCTION

Midwest Research Institute is a research and development organization located in Kansas City, Missouri. One major area of effort is the investigation of environmental problems associated with hazardous waste, including sampling and analysis tasks involving identification, characterization, and incineration of hazardous waste.

Sample tracking has become very important to these types of research because of the need to produce and document data that is both legally defensible and of known quality. Today's research requires proof that samples were uniquely identified, that chain-of-custody handling procedures were followed, and that critical tasks were performed within specified holding-times. In addition to these concerns, as an organization there is always a need to efficiently manage resources and control the documentation process.

SYSTEM REQUIREMENTS

The technologies needed to set up computerized sample tracking were found to be both available and inexpensive.

The system that evolved was comprised of two basic elements: the use of barcoded information for fast, accurate data entries, and the use of "lap-top" computers for portability and flexibility.

Preprinted barcode labels are commercially available in just about any size, material, or format imaginable. High-quality labels provide very accurate scanning and direct computer entry of information (estimated to be 20 times faster and more reliable than recording information manually). For our application, six-replicate labels in sequentially numbered series are used to identify samples. These labels are also used to reference containers, forms, data charts, and laboratory notebooks relevant to that sample. This number serves as a reference point that uniquely identifies a sample from the time of collection through data reduction and reporting.

The Radio Shack Model 100 portable computer was chosen for the sample tracking system because it is completely portable and programmable. It becomes an "electronic notebook" for recording and transferring data without manual entries. Information is captured by simply scanning a barcode with a wand. Data are printed in real-time or saved into a file. Time and date of critical tasks are automatically recorded using the computer's built-in clock/calendar. This computer can also be used to print customized barcodes for routine data entries, creating a "bar-code" worksheet.

Code 3-of-9 format is used to code both alpha and numeric characters, giving the system the flexibility to use descriptive identifiers.

A microcomputer with a modem is used to receive and store the data files that are imported from the satellite "lap-top" computers.

The microcomputer is used to effectively manage the system by maintaining inventories, providing current status information, monitoring holding time performance, and generating reports for project management.

Multiple software programs are used to make the sample tracking system actually run. Among these are commercial programs available to read and write barcoded information, communication programs for transferring data files electronically, word processing software for review and verification of data files, and data base management software for the import and management of data.

Simple programs were written in BASIC to provide flexibility for the system, not unlike using a typed form for manually recording data. These programs allow for "prompting," time/date labeling, multiple choice selection, and rejection of inappropriate information.

EXAMPLES:

This system was used to document chain-of-custody transfers by using the following procedure:

Samples are labeled with a unique bar-coded identification number. Lab worksheets were prepared for the analyst with barcodes describing each sample split and analysis step for the particular phases of the sample analysis.

Cards were issued to each analyst with their name and (barcoded) initials to use as an "electronic signature" in documenting sample transfers.

The chain-of-custody transfer is initiated by scanning the split code and analysis code from the lab worksheet, then scanning the "electronic signature" cards of the persons relinquishing and receiving the sample.

By scanning the barcode of each sample transferred, the identification, time, and date of the transfer is printed immediately by the computer in a chain-of-custody report. The analysts review the computer report and verify its accuracy by both signing and dating the document. This becomes the official chain-of-custody document that is archived for the project records.

An identical data file is stored in the computer for exporting to a microcomputer's data base, where the status of the samples can be reviewed, holding times can be monitored, and complete sample histories may be listed.

Another example of how this system can be incorporated into other laboratory situations is the interfacing of the "lap-top" computer with electronic balances for automatic weight recordings. This extension of the computer system reinforces the idea of an "electronic notebook"

that changes the ways and speed in which data are recorded.

Robotics also incorporates barcode technology as a means by which computers can read and verify sample identification and allows for orderly processing of sample analyses.

SUMMARY

The benefits of computerized sample tracking are improved accuracy, efficiency, and flexibility.

Barcodes offer error-checks on reading, are simple to use, and reduce the likelihood of transcription errors. Computerization reduces written forms, standardizes and speeds data entry, and provides a tool for resource management and real-time documentation. Flexibility is achieved by using a low cost and expandable system, a system that can be customized to specific project needs and changing quality assurance requirements.

EVALUATION OF A PROTOTYPE FIELD-PORTABLE X-RAY FLUORESCENCE SYSTEM FOR HAZARDOUS WASTE SCREENING*

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ABSTRACT

A prototype field-portable X-ray fluorescence system developed by EPA and NASA was evaluated at a site contaminated with Pb, Zn, and Cu. The objective of the field test was to evaluate the effectiveness of the instrument as a field analytical tool for locating hot spots and as a preliminary screening device where immediate data feedback aids in decision-making in the field.

By making use of an analytical method designed specifically for the XRF system, all routine field measurements for Cu, Zn, and Pb were made on site by placing the probe on the surface of the ground ("in situ" measurements). Subsequently, confirmatory samples were collected and analyzed in the laboratory with an Inductively Coupled Plasma spectrometer (ICP) while adhering to EPA Contract Laboratory Program (CLP) protocols.

The quality assurance consisted of measuring NBS standard reference materials to verify the data measured in the field and in the laboratory in addition to duplicates, blanks, and replicate sample analysis.

The analytical results were plotted in the sampling grid. One can immediately locate the hotspots for Cu, Zn, and Pb on site. The instrument detection limits for Cu, Zn, and Pb are 250, 200, and 70 ppm, respectively. Comparison of the XRF results with the ICP results showed an overall mean percent error (MPE, which means lack of precision and bias incorporated into one term) from NBS concentrations of only a few percent for Cu, Zn, and Pb. Precision and accuracy of the in situ measurements were within plus or minus 10 percent of the true value when compared to the samples analyzed in the laboratory.

This document is a preliminary draft. It has not been formally released by the U.S. Environmental Protection Agency and should not at this stage be construed as present Agency policy. It is being circulated for comments on its technical merit and policy implications.

INTRODUCTION

The Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas asked Lockheed Engineering and Management Services Company, Inc. (LEMSCo) to field test and evaluate the performance of a field-portable X-ray fluorescence system for making in situ measurements. In situ measurements are those measurements made by the XRF probe while in direct contact to the ground surface. These measurements are conducted without any sampling and sample preparation other than clearing the ground surface to expose the soil. An in situ XRF measurement represents the data obtained from only the exposed ground surface and does not reflect any of the subsurface. The contaminants in a hot spot would not register a response to the X-rays if the hotspots were covered with as little as 1 cm of uncontaminated soil. Therefore, caution must be exercised in the use of data obtained from in situ measurements. The use of in situ measurements with the XRF system would allow technicians to immediately locate surface hotspots of lead, copper and zinc on the national priority list (NPL) sites and other sites. The objective of this report is to describe the steps necessary to complete the field test, review the analytical work, and assess the instrumental performance. These steps are as follows:

- design a sound in situ analytical method for a field-portable X-ray fluorescence system prior to the field test
- analyze each of the 40 samples in situ with the field-portable XRF system at 40 locations on a 60 foot by 150 foot grid with sample intervals at every 15 feet.
- subsequently collect confirmatory surface soil samples from the same locations.
- analyze the samples in the laboratory following the ICP CLP protocol (an in situ measurement by a field-portable XRF system has no homogenization technique as a part of sample preparation. The only preparation necessary for an XRF in situ analysis is to clear a flat surface on the soil. Therefore, the sample area of the in situ measurement cannot be considered homogeneous. Acceptance of an in situ XRF measurement dictates the acceptance of a certain amount of error in measurement's accuracy. To validate the in situ XRF measurement, the sample area of the in situ analysis represents one sample and the volume of sample collected represents another. The values of these two samples will closely approximate one another but are technically not the same. However, the difference in two values should fall within the acceptance range for the overall inaccuracy of the XRF in situ measurements. For the intents and purposes of this report we will assume the in situ sample area and the

collected sample containing the same area to be one and the same sample.)

- o compare the XRF results with those obtained from the ICP.

The EPA has recently expressed more interest in XRF systems than in previous years because the use of microprocessors and state-of-the-art technology have made the equipment smaller and thus portable. Such field-portable XRF systems have been used to delineate hazardous waste site hotspots for priority metals in the field (Chappell et al., 1986; Mernitz and Olsen, 1985; Furst et al., 1985; and Kendal et al., 1984). With immediate data feedback from the field-portable XRF system, all samples can be collected with the knowledge of their approximate concentration. This leads to a decrease in the number of unnecessary samples which would be analyzed normally. The XRF field data allows an analyst in the laboratory to calibrate his laboratory instrument to the proper concentration the first try; thus decreasing the number of attempts at bracketing the correct one. Another use is as a laboratory analytical instrument to screen samples of unknown concentrations quickly providing the analyst with an approximate concentration. All of these applications of the XRF systems net an overall decrease in time and in money spent.

Furst et al., 1985 described three levels of analytical requirements for establishing the extent of environmental contamination. The first or highest level of analysis is used to develop data for litigation and regulatory enforcement (see Figure 1). This level demands the most rigor in sample preparation and instrument time as well as the highest degree of precision and accuracy. The second level of analysis is used to evaluate and assess average contaminant exposures to people and animals. The data from the third level of analysis is used for screening in order to obtain a preliminary profile of sites. This data can be used for decision making while in the field. Third level data may be used also to select which samples should be sent to the laboratory for first level analysis following the Contract Laboratory Program (CLP) analytical protocols. This report discusses the results obtained by using a portable XRF system under the third level of analytical requirements.

The area that the EPA selected for the field test was the Smuggler Mountain NPL site in Aspen, Colorado, northeast of the Aspen city limits. The site was listed on the NPL June 10, 1986. The Smuggler Mountain mine produced lead, silver, and zinc ores. The site is located on one of the slopes of Smuggler Mountain; some of the mining, milling, and smelting was located here. These slopes are a mixture of native soils, mine tailings, and other mine wastes. Much of the surface has been subjected to reworking by prior and recent construction projects. Several such projects used mine tailings as fill.

Three Levels of Analytical Requirements for Metals

	Degree of Analytical Requirement			Purpose
	(Precision)	(Accuracy)	(IDL)	
LEVEL I :	Very High			Litigation and Regulatory Enforcement
	(±5%)	(±10%)	(ppb)	
LEVEL II :	Moderately High			Evaluate and Assess Average Pollutant Exposure to Humans and Animals
	(±10%)	(±15%)	(ppm)	
LEVEL III:	Moderate to Low			Screening, Preliminary Evaluation, and On-Site Decision Making
	(±10%)	(±50%)	(≤ ppm x 1000)	

Figure 1. Three levels of analytical requirements for metals.

Martin Marietta Aerospace people brought a prototype XRF system to field test at the Smuggler Mountain site. The first prototype system had evolved from technology used in the Martian Viking lander. This system had to be redesigned to measure metals in contaminated soils because of the changes in its intended usage. Prior to the field test, the software was not programmed for efficient evaluation of soil samples and field application. Reprogramming the software took place subsequent to the field test.

The Martin Marietta field-portable XRF system consists of three units (see Figure 2): (1) the sensor head (when filled with liquid N_2, weighs 32 pounds), (2) the Canberra main unit analyzer (16 pounds), and (3) a Gridcase 2 portable computer (12 pounds). The filtration unit shown in Figure 2 was designed for laboratory use only to preconcentrate metals in water samples. The cooled semiconductor detector has excellent energy resolution and is capable of simultaneous detection of a wide range of X-ray energies. The cooled semiconductor detector decreases the dead time response to the X-rays it senses, thus decreasing the length of time needed for analysis. A typical analysis with the system lasts between 120 and 300 seconds. The X-ray tube uses a molybdenum target operating at 30,000 volts to produce a wide enough spectrum to fluoresce the priority elements. The detector is a semiconductor made of lithium drifted silicon. The detector must be cryogenically cooled and must have a continuous supply of liquid nitrogen.

CONCLUSIONS

- The XRF system produced data of known quality from 229 *in situ* measurements (defined as measurements made by placing the probe on the ground surface and by analyzing the same surface without moving the probe). The XRF field results on the NBS standards compared relatively well with the certified NBS values of the same standards.

- Field personnel can greatly decrease the time spent on site by making *in situ* measurements. If necessary, the technician can collect a confirmatory sample after each XRF analysis.

- The detection limits are low enough for obtaining data when third level requirements are necessary for analytical work on hazardous waste site investigations.

- The NBS standards were adequate for quality control and quality assurance. These standards were SRM 1633a, coal fly ash; SRM 1645, river sediment; and SRM 1648, urban particulate.

- The instrument uses cryogenics to cool the silicon-lithium detector which requires a Dewar container filled with liquid

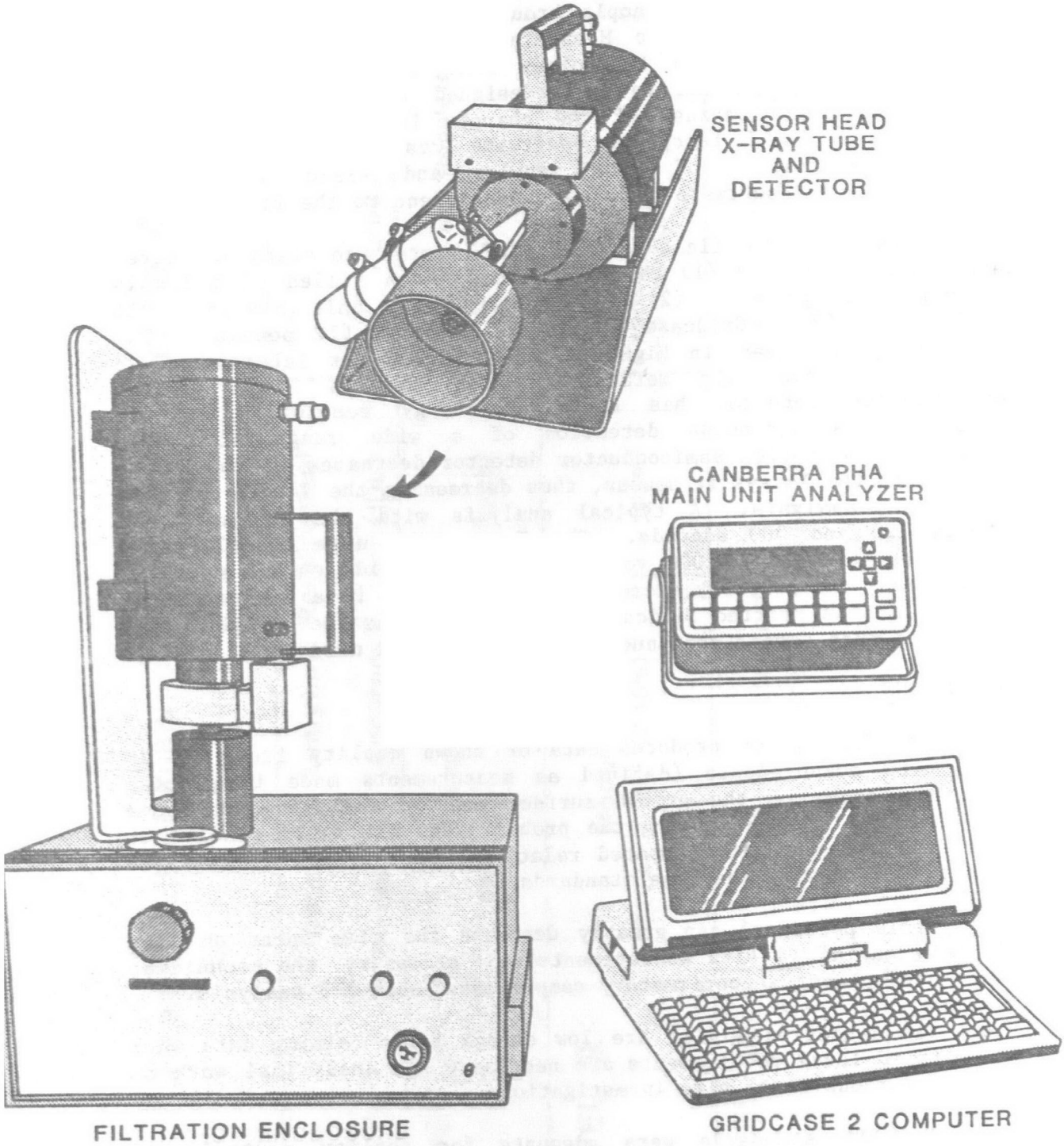

Figure 2. X-ray fluorescence subsystem identification.

nitrogen. Even though the Dewar container will last 8 hours before a refill is necessary, maintaining a continuous supply of liquid nitrogen in the field can be difficult in some locations.

- The overall advantages of all X-ray fluorescent systems include: minimal sample preparation time, rapid turnaround time for analyses, multi-element analytical capability, nondestructive analyses, and sample size required for analysis is small or possibility of surface analysis without the need for sampling at all. These advantages make the XRF system very cost effective.

RECOMMENDATIONS

- A field methods manual should be written for field XRF measurements and should incorporate field sampling, sample preparation techniques, and analysis.

- Characterized spike soils should be prepared for the XRF systems as reference standards. These would be spiked at concentrations ranging from 5 to 10 times the IDL, to the highest likely to be encountered; or at levels considered to be a public health hazard.

- A procedure for primary calibration, field update of calibration and of QA/QC checks of the instrument accuracy and precision should be worked out.

- The investigation of a sample preparation method for non in situ measurements should be tested. This should include examination of both the pelletizing and fusing techniques, and the use of loose soil. Indications are that one would obtain different levels of precision.

- The Martin Marietta XRF system should be compared with other commercially available field XRF systems. The detection limits, precision, and accuracy of each instrument could be determined side by side in the laboratory with the ICP or AAS by using rigorous QA/QC protocols, characterized samples, and certified spiked standards.

- Once the instrument detection limits are established for XRF field-portable systems, the initial steps may be implemented in developing these instruments for characterization of uncontrolled hazardous waste sites with respect to specific toxic metals.

FIELD TEST

Personnel from EPA, Martin Marietta, NASA, LEMSCo, and Camp Dresser and McKee, Inc. were present during the field test at the Smuggler Mountain NPL site (Figures 3 and 4). The objective of the field test was to assess the performance of the Martin Marietta field-portable XRF system on an NPL site with regard to effectively identifying hotspots of lead, copper, and zinc. This was accomplished by analyzing *in situ* and by subsequently collecting surface soil samples (see Section 5, Procedures for exact method) on site at 40 locations on a 60 feet by 150 feet grid with sample intervals at every 15 feet (Figure 5). Technicians analyzed each of the 40 samples *in situ* for total Pb, Cu, Zn, and Fe with the field-portable XRF system and processed the data for on site decision making.

NBS standard reference materials (SRM) were used as quality assurance/quality control standards. The NBS standards were incorporated to give us reference data of known quality. Those used were SRM 1633a, coal fly ash, SRM 1645, river sediment, and SRM 1648, urban air particulate. The NBS standards were analyzed in the field with the XRF system. These values were compared against the SRM-certified values.

A field method was designed specifically for the use of a field-portable XRF system for this field test. This field method is described later under "Analytical Procedures and Sampling Protocol for the Field-Portable XRF System and the ICP." The same samples[1] were then collected for later confirmatory analysis in the laboratory. To further corroborate the XRF field data, we used the known and accepted CLP methods of preparation and analysis. Because the CLP method of sample preparation uses a relatively weak extraction, we also used a Parr bomb method to provide a stronger extraction method that was likely to more closely approach the NBS certified values. The Parr bomb method was performed on 13 selected samples but under CLP instrumental requirements for the ICP.

The quality assurance (QA) procedures developed for the XRF field analysis allowed for the proper verification of the data. The verification establishes the quality of the data. To evaluate the reproducibility of measurements (i.e. QA procedures) and to minimize statistical error, the blank, the instrument calibration standard, and the same aliquot from each of the three NBS standards were analyzed seven times each without disturbing the sample.

The results showing high concentrations of Cu, Zn, and Pb on the sampling grids (Figures 6, 7 and 8) can be processed immediately on a computer from this data produced by the XRF system. The capability of immediate analytical results offers many advantages. The data from the initial screening allows field crews to:

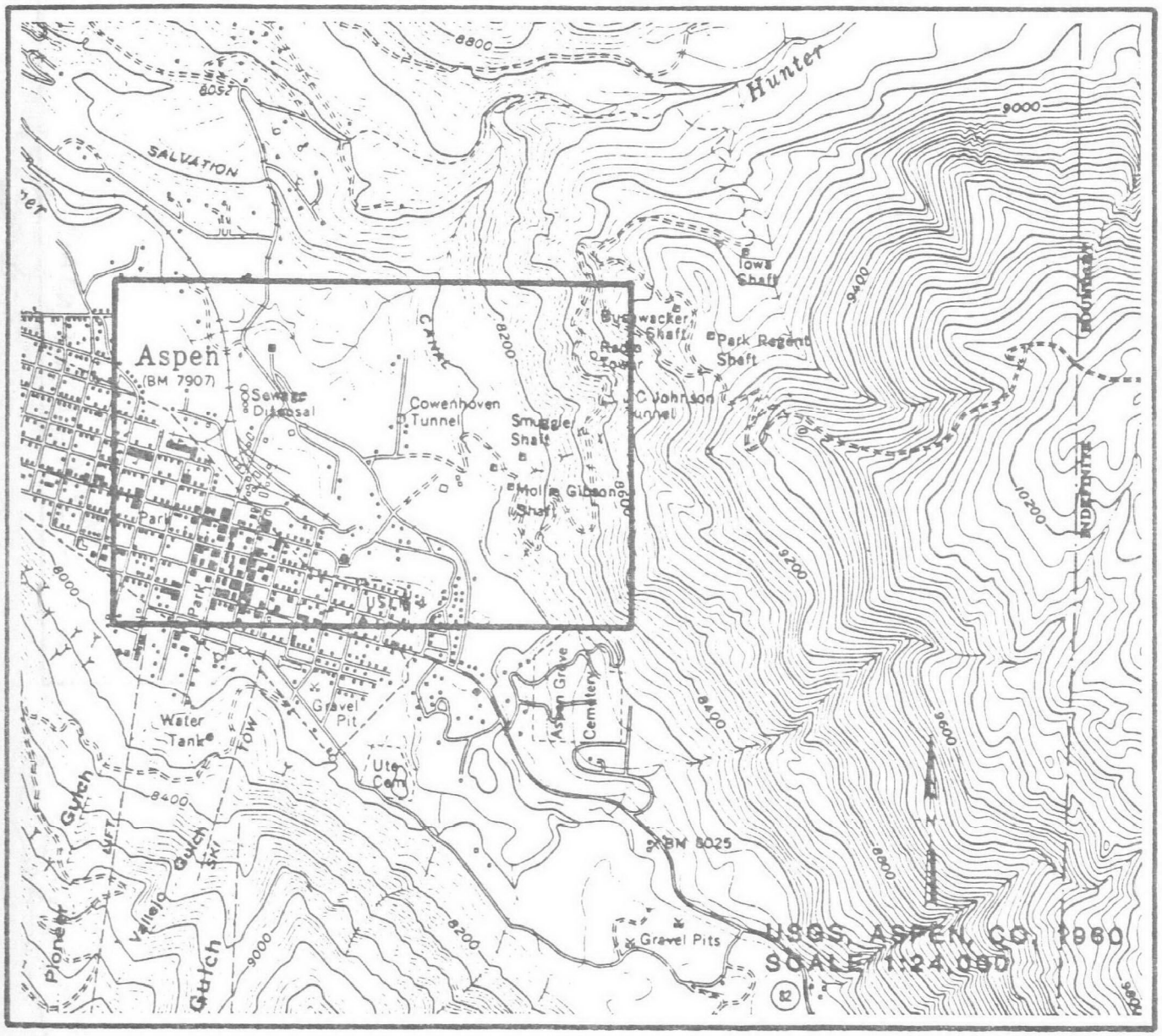

Figure 3. Contour map of Aspen, Colorado.

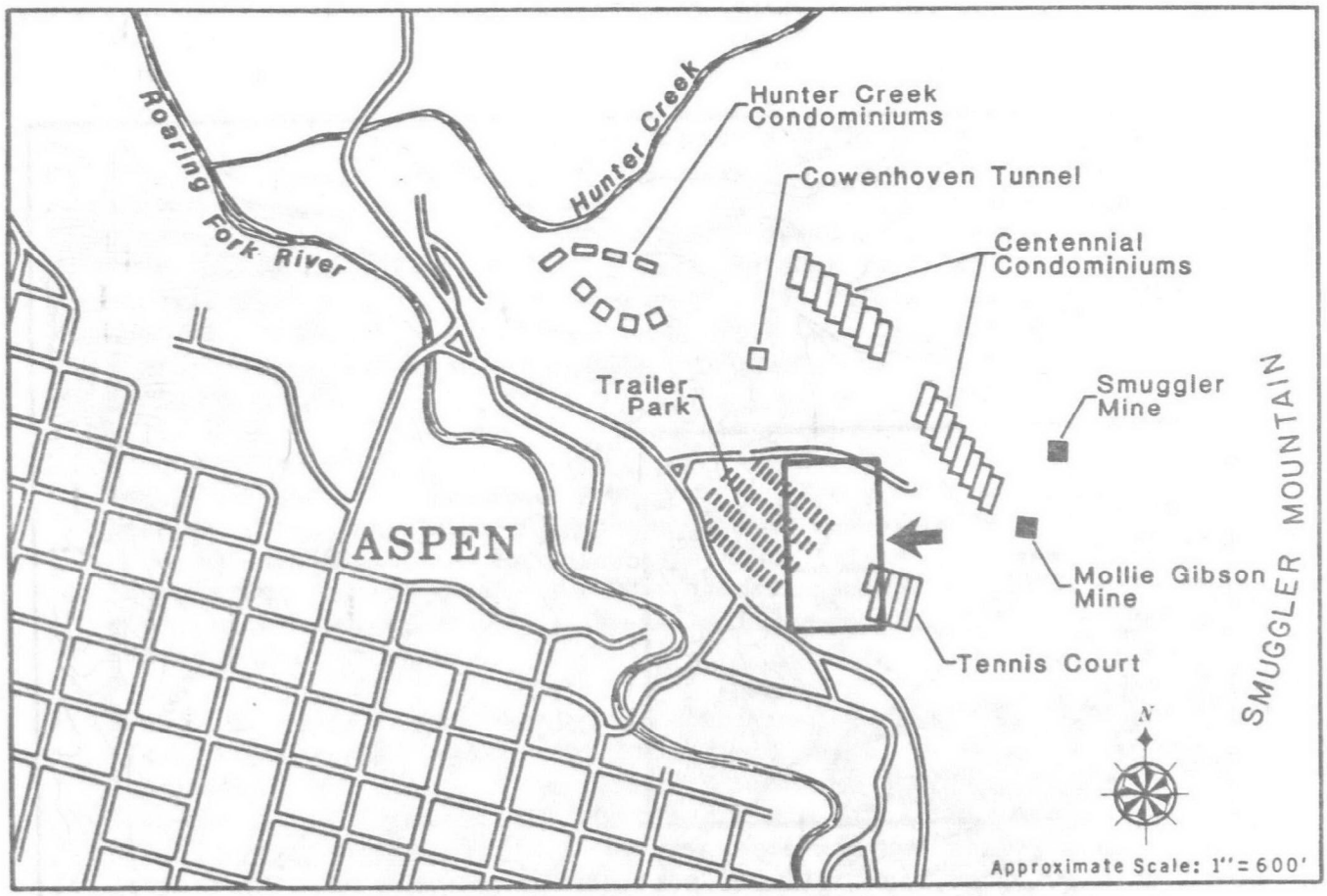

Figure 4. Closer view of site location. Sampling grid is found within the square located by arrow.

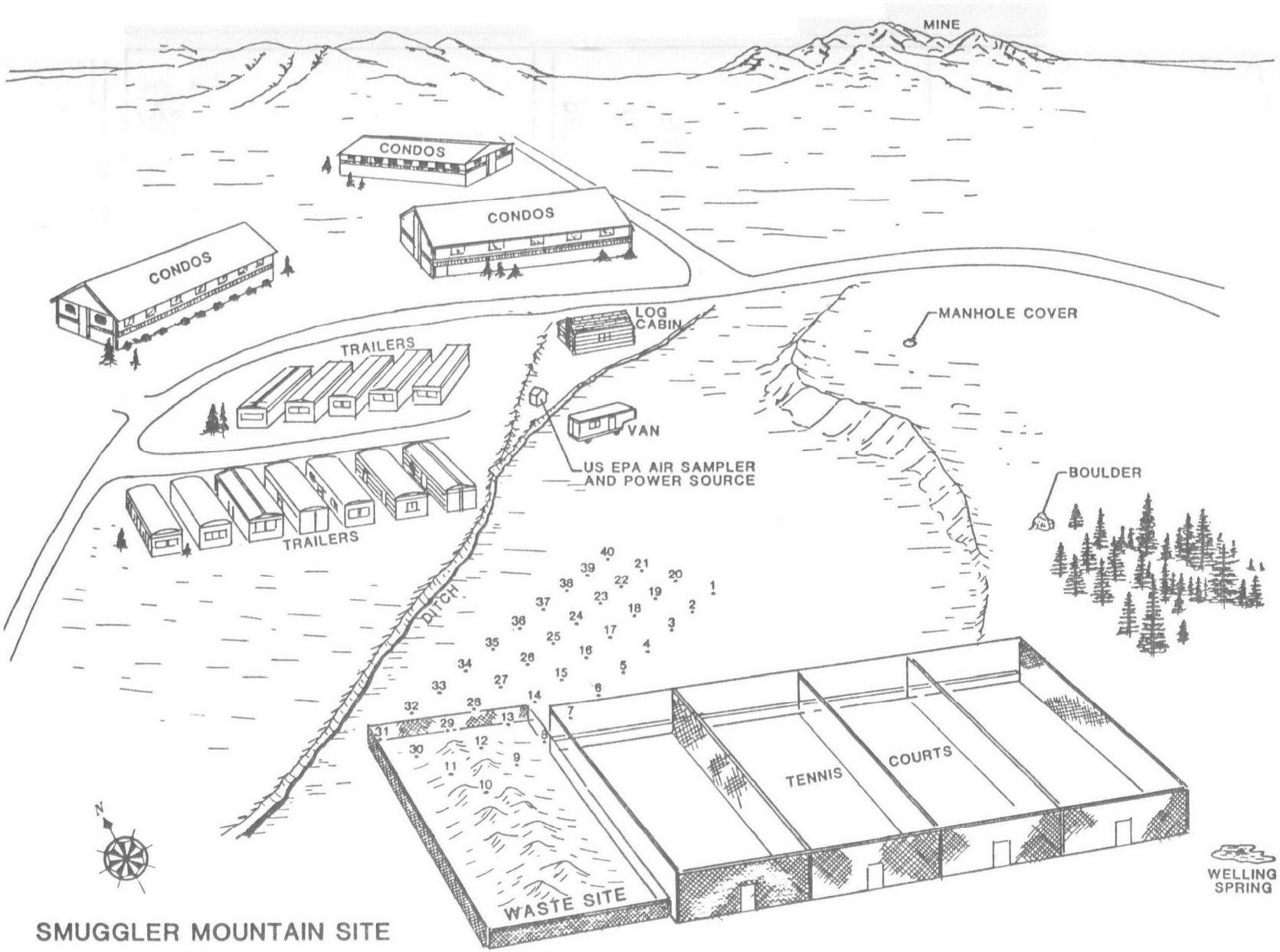

Figure 5. Sampling grid on NPL site.

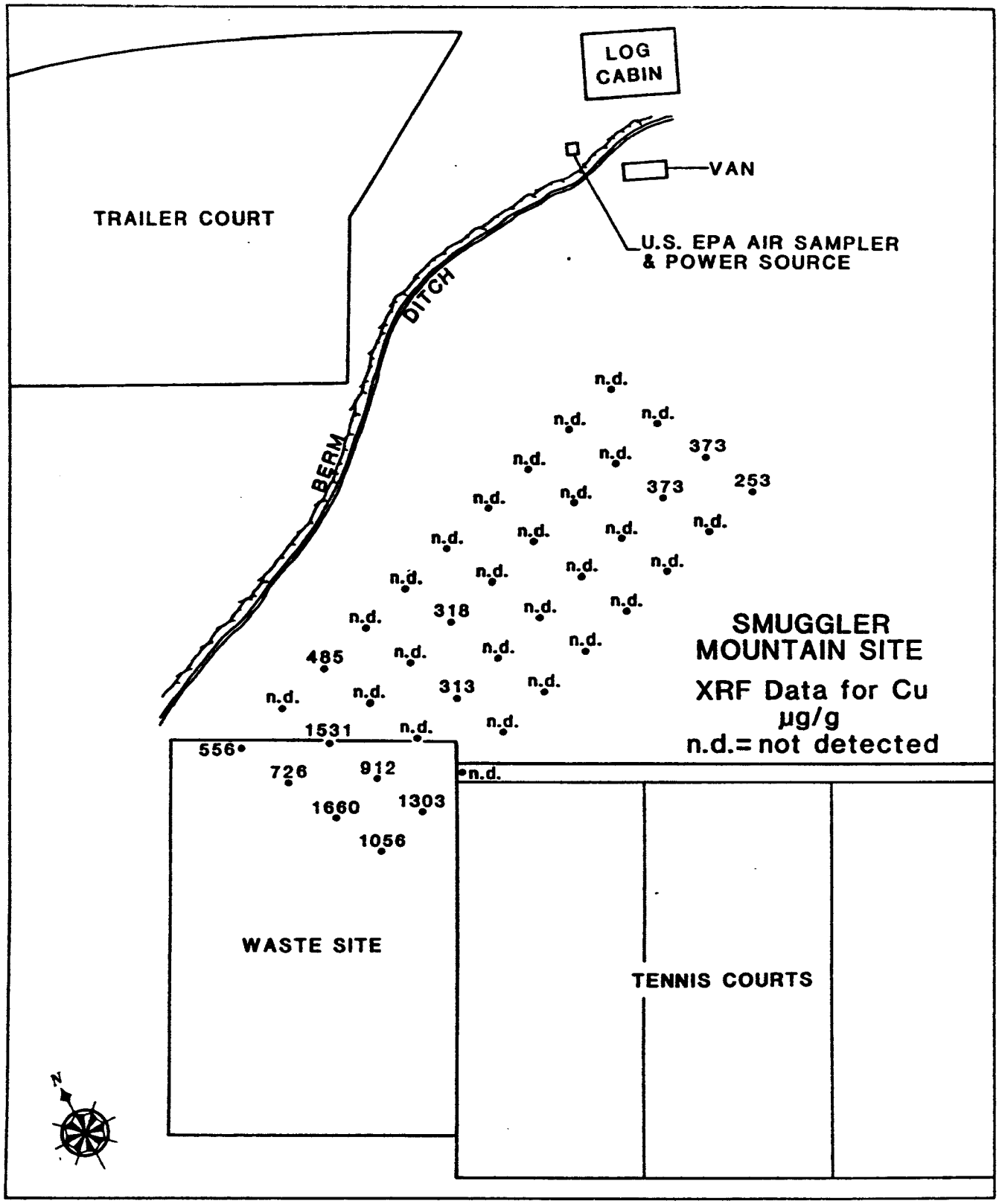

Figure 6. XRF values for Cu plotted on sampling grid.

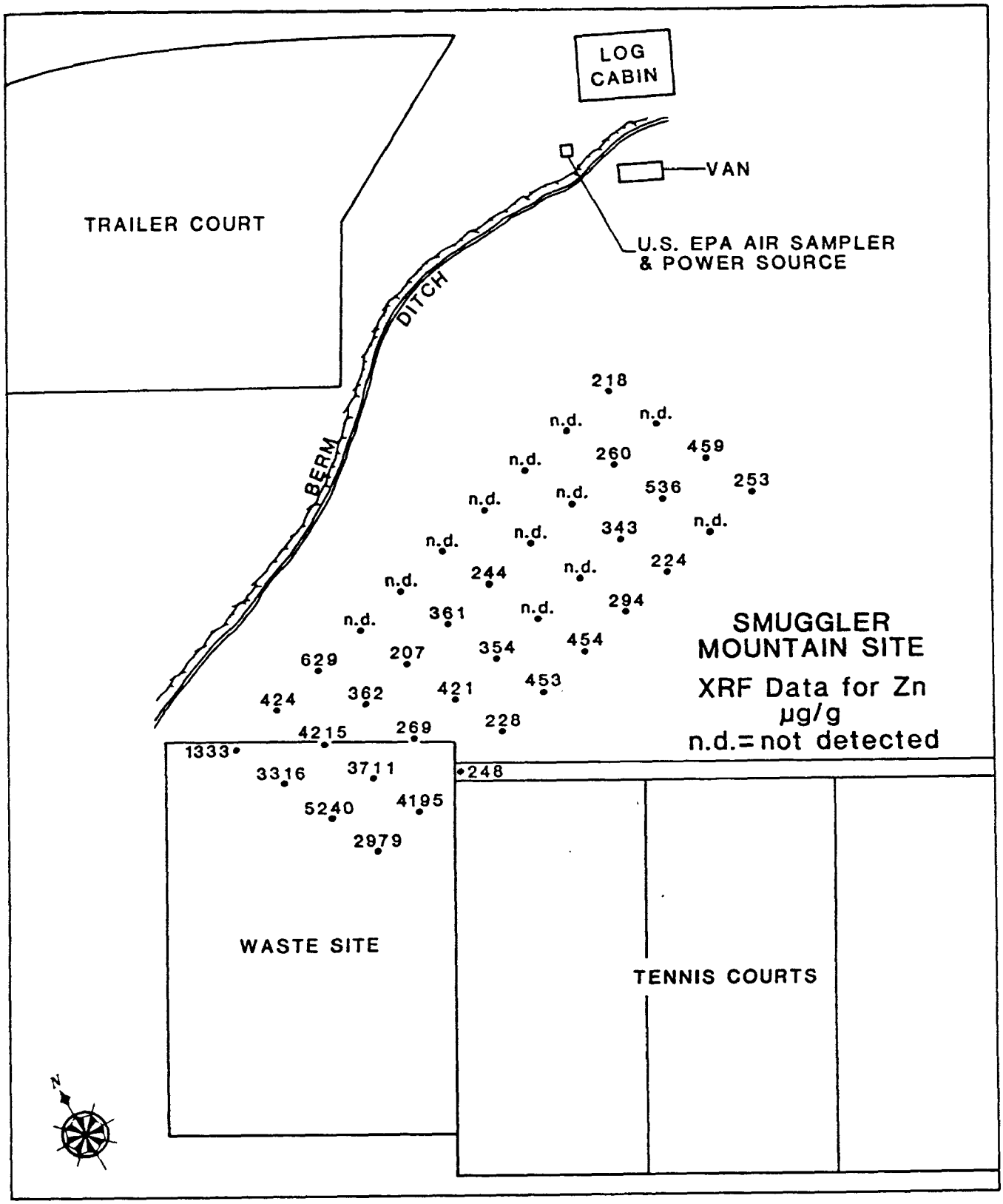

Figure 7. XRF values for Zn plotted on sampling grid.

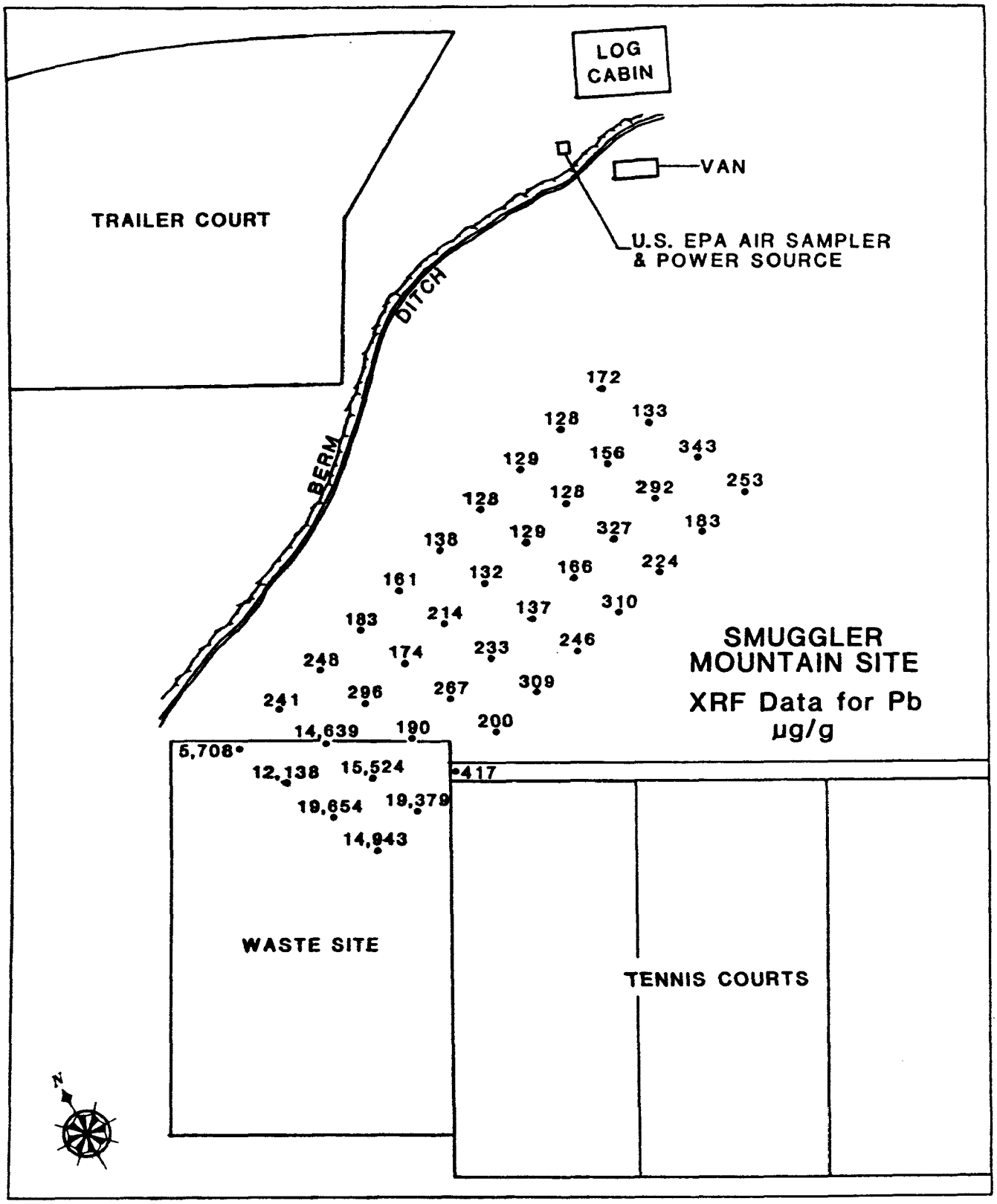

Figure 8. XRF values for Pb plotted on sampling grid.

(1) identify the hotspots,

(2) restrict the investigation to the contaminated area,

(3) either go to the next level of investigation or stop at the screening level, and

(4) make decisions based on the data base which is generated from the analyses.

The next level of investigation above screening requires confirmatory samples be taken and analyzed. These can be analyzed in the field. If this were in an area being investigated for the first time, the hotspot would be identified and the locations registering as "background" (non-contaminated) by in situ XRF analysis need not be sampled for confirmation. In our case, the intensified effort would be restricted to the area marked "waste site" in figures 6, 7, and 8. This would decrease the number of samples, which might otherwise be analyzed, and thereby reduce overall analytical costs.

As more samples are analyzed, the data base for the area grows. The initial screening provides the foundation from which the investigation proceeds. The subsequent measurements then provide data of higher quality from which plots can be generated. Field crews can make decisions based on these plots and this data base.

It should be noted that the Martin Marietta XRF field-portable system was required to perform in adverse weather conditions. It began snowing during the field test and the XRF system did not malfunction. The authors feel that the system performed well under these conditions.

PROCEDURES

X-RAY FLUORESCENCE PRINCIPLES

The X-ray fluorescence (XRF) system used in this study is energy dispersive by design. All XRF depends on either an electron or X-ray beam bombarding the sample. The X-rays produced by an X-ray tube impinge on the electron clouds or orbitals in the atoms within the sample. When the X-ray displaces an electron from an inner orbital of an atom, such as the k-shell, a vacancy is created. This causes an instability below the electrons in outer shells. As the outer electrons seek stability by filling the inner shell vacancies, a cascade of electrons spontaneously follows. Energy is released or emitted for each shell vacancy that is filled. This emitted energy is characteristic of the atom from which it was produced. This emission is call fluorescence. All elements excited by the X-rays fluoresce simultaneously to produce a spectrum of characteristic and

backscattered radiation. It is this spectrum that the detector senses and counts. The whole spectrum data is transferred to the analyzer where the software deconvolutes the peaks for the desired elements.

THE PROBLEM OF RESOLUTION WITH VARYING PARTICLE SIZE

The bulk density of the sample and the particle size distribution affect the characteristic X-ray intensity. When dealing with varied distribution of particle sizes, an accurate analysis of these particles is difficult if there is no attempt to make all the particles the same size, either by segregation or reduction.

The varied particle sizes have an effect on X-ray absorption and enhancement especially during *in situ* emission analysis. Collecting and grinding the sample to 0.075-mm (200 M) will generally solve the problem, but this is not always a practical solution in the field. It also defeats the purpose of using the field-portable XRF system with an *in situ* technique, i.e., a fast turn-around time. We can address this problem in a sample preparation step by using a mortar and pestel to break up the soil samples and by grinding the sample to approximately sand size assuming the sample is dry. Even though this approach does not entirely solve the problem, it does reduce the effect to an acceptable constant error while keeping sample preparation time to a minimum.

ANALYTICAL PROCEDURES AND SAMPLING PROTOCOL FOR THE FIELD-PORTABLE XRF SYSTEM AND THE ICP

Field personnel analyzed and collected 40 soil samples according to the following method:

XRF ANALYSIS:

a. The analyst will make seven replicate measurements, rotate the sample 90°, stir each standard, and make seven more replicate measurements on the following:

   - o a blank sample made of silica sand,
   - o the instrument calibration standard,
   - o the three NBS standards.

b. Clear the area for analysis by removing rocks and debris from the surface, mark the area, place the instrument on the designated area, and activate the X-rays.

c. The analyst will make single measurements on the following:

   - o the soil sample,
   - o standard with concentrations closest to the soil values,
   - o the instrument calibration standard.

d. The analyst will make a duplicate analysis on every tenth soil sample without moving the probe.

e. Record all data pertinent to the sample, its location in a logbook, and store the analytical data obtained from the instrument on a diskette.

f. After the analyst finishes measuring the soil sample in situ, collect the sample for later corroborative analysis.

g. Collect the sample using the following steps:

   - o Use a clean trowel to take a 200 cc sample. Penetrate a 2" x 2" area on the surface to no more than 2 inches deep. Be sure to include the area which has been analyzed in situ.
   - o Empty the sample into an acid-washed 150 mm x 25 mm plastic petri dish, being sure to fill the petri dish to aproximately two-thirds full, seal the petri dish inside a plastic zip-lock bag, and seal the bag with tape.
   - o Clean the trowel by wiping the blade with a paper towel and then rinsing with distilled water.

h. Take samples with contamination levels ranging from approximately five times the IDL for Cu, Zn, and Pb up to the maximum values found on site.

i. Use NBS standards for the reference calibration.

j. Use silica sand for the blank sample. The grains of silica sand will closely approximate the grain geometry of the soils.

The sample preparation for the ICP analyses was done by both the standard CLP method and the Parr bomb method which is described below. The CLP method and QA/QC protocol for analysis may be found in Exhibit D of the Invitation for Bid for the Contract Laboratory Program (U. S. EPA, 1984).

ICP ANALYSIS

Digestion of soil by a generic Parr bomb method (adapted from Bernas, 1968, Buckley and Cranston, 1971; and Dolezal et al., 1969):

a. Dry at 60°C and homogenize the sample.

b. Weigh 0.5 g of soil and place it in the Parr bomb.

c. Add 5 mL of concentrated nitric acid (HNO_3) and 2 mL of concentrated hydrochloric acid (HCl).

NOTE:
- o Do not add more than the 2 mL HCl prescribed. Too much can generate enough chlorine gas to cause the Parr bomb to explode.
- o Do not add any soil with carbonates; the evolution of CO_2 could cause the Parr bomb to explode.
- o Do not add the filter paper if it is a cellulose base. This could cause the formation of nitrocellulose which is explosive.

d. Seal the Parr bomb and place it an oven at 120°C for 2 hours.

e. Remove the bomb from the oven and allow it to cool to room temperature.

f. Open and rinse the contents into a filter funnel feeding into a 100-mL volumetric flask. Bring the flask up to volume with DI water. The digest is ready for analysis.

RESULTS AND DISCUSSION

DISCUSSION OF SOFTWARE

The application of the XRF system changed throughout its development, and the programming of the software did not keep pace. The software was not modified for field use or for soils analysis prior to the first field test. For the field test at Smuggler Mountain, the XRF system was calibrated in the laboratory with spiked soils for the metals of interest and was checked against certified NBS standards, but the software was set up for metal alloys. The data and the samples were collected in the field. Then the data was taken back to the Martin Marietta where the software was reprogrammed to process the data for field use and soils analysis.

The software program for peak deconvolution caused many of the non-priority metals to drop out. While beyond the scope of this study, the authors feel that the software should be investigated to optimize the deconvolution of the peaks.

COMPARISON OF XRF RESULTS VERSUS ICP (PARR BOMB AND CLP) RESULTS

To evaluate the performance of the field-portable XRF system, technicians analyzed the NBS standards and 40 soil samples from Smuggler Mountain on a Perkin Elmer ICP II by using two sample preparation methods. The first preparation method is an extraction procedure (Parr bomb described previously) and the second preparation method is the standard CLP instrument extraction procedure. Technicians analyzed the Parr bomb digest also according to CLP instrument requirements. We did not use a total dissolution procedure because most such procedures use hydrofluoric acid (HF). It is necessary to neutralize the HF with large quantities of boric acid. The high amount of dissolved solids tends to clog the nebulizer, thus affecting precision by causing drift.

The analytical results of the NBS standard reference materials (SRM) for four metals by XRF and ICP (both methods) are listed in Table 1. EPA requested that Pb, Cu, and Zn be examined. We added Fe to show how the XRF unit responded to a constant high value while analyzing the other metals in varying amounts.

When we compare the values overall, the XRF analyses tend to be higher then the ICP analyses. The analysis of the urban particulate, SRM 1648, showed the best results. The XRF results are between 95 percent and 105 percent of what the NBS has certified as present in the SRM 1648 with the exception of Zn. Since Martin Marietta designed the XRF system as a semi-quantitative instrument for the field, these analyses are excellent within the limitations of the standards. When the individual Pb values for the different standards from Table 1 are plotted, the XRF results of the NBS standards show excellent concurrence with the ICP, especially for Pb (Figure 9).

The detection limits for the XRF system were determined by Martin Marietta. Three 300-second spectra were collected for each element, and the ratios of the net K and the L peaks to net backscatter calculated. The instrumental detection limit was calculated from the formula:

$$IDL = \sqrt{3S \quad C_b/C_s}$$

where S is the quantity (in micrograms) of metal present in the sample, C_b is the background counts under the peak, and C_s the net sample counts. The peak background is calculated, and the net sample counts are calculated by subtracting the background level

TABLE 1. COMPARISON OF XRF AND ICP RESULTS FROM NBS STANDARDS

	Analysis Number	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
		Coal Fly Ash			
SRM 1633a	1	94,000	118	220	72.4
	2	91,555	178	261	152.4
	3	38,780	75.6	103	34.4
	4	17,944	54.0	84	n.a.
		River Sediment			
SRM 1645	1	113,000	109	1720	714
	2	313,686	183	1551	735
	3	84,410	109	1632	688
	4	n.a.	n.a.	n.a.	n.a.
		Urban Particulate			
SRM 1648	1	39,100	609	4760	6550
	2	41,252	584	2212	6247
	3	21,746	550	4486	5986
	4	20,857	432	3443	4192

No. 1 Certified by National Bureau of Standards.
No. 2 Martin-Marietta XRF unit. The Martin Marietta values for the SRM 1633a and 1648 are the averages of 7 replicates; for the SRM 1645, the values are the averages of 14 replicates.
No. 3 Perkin Elmer ICP II, Parr Bomb Method. The values are the averages of 3 replicates.
No. 4 Perkin Elmer ICP II, CLP Methods. The values are the averages of 3 replicates.
n.d. = not detected.
n.a. = not analyzed.

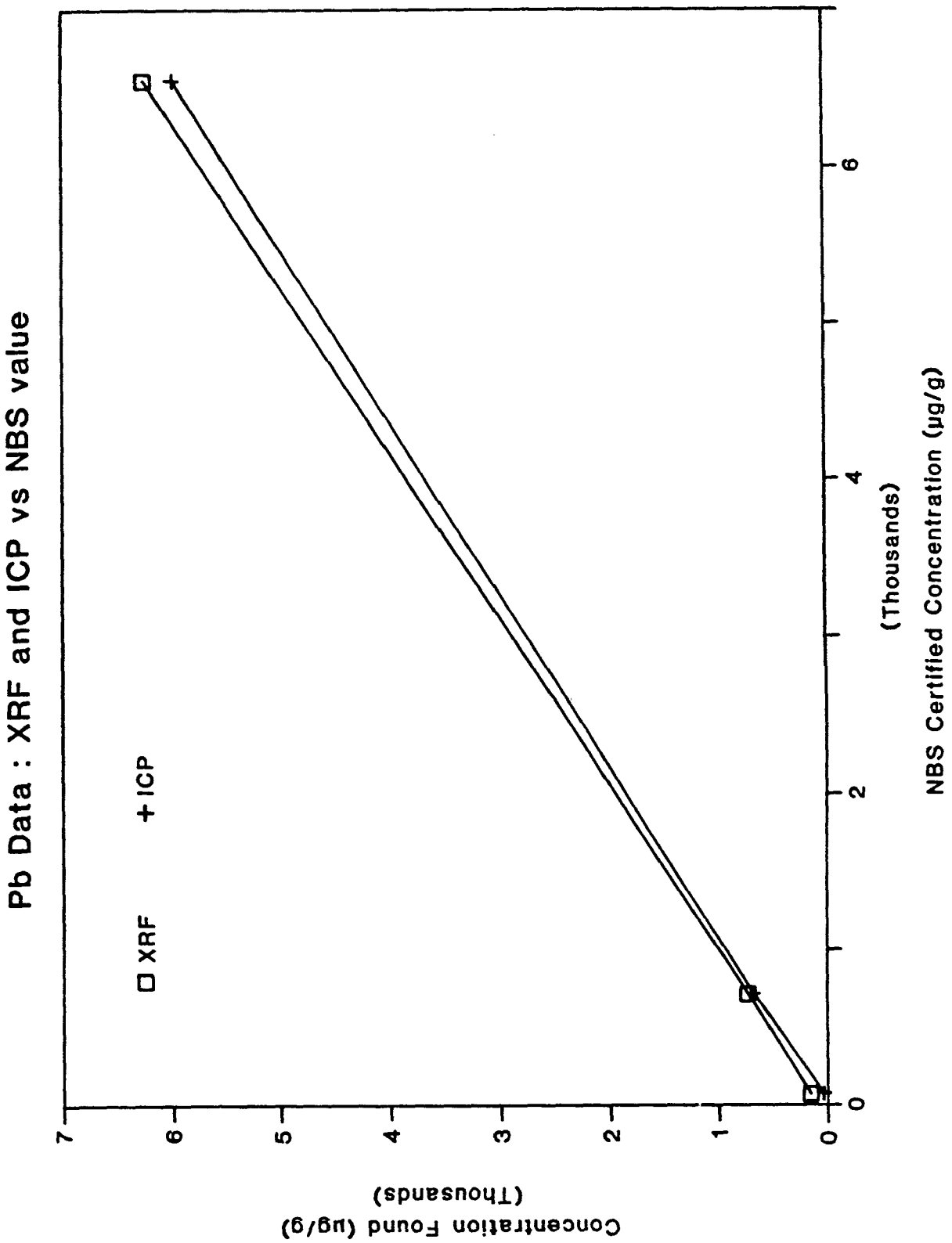

Figure 9. XRF and CLP results versus NBS certified concentrations.

from the total number of counts in the peak. The detection limits for the XRF (the IDL for iron was not included) and ICP instrumental detection limit (IDL's) are listed in Table 2 and are compared in the CLP contract required detection limits (CRDL). The CRDL's represent a level one requirement regime for analytical work. The XRF IDL's might represent a proposed level three requirement regime for hazardous waste site investigations with field-portable XRF systems.

In comparison of the IDL's for Cu, Zn, and Pb against the values for the soil samples in Table 3, what immediately becomes apparent is that 29 of the values for Cu measured by the Martin Marietta XRF system are less than or equal to the instrumental detection limit. Any values below five times the IDL should not be used. The variation of precision in this range is, as a rule of thumb, plus or minus the IDL. Between 5 and 10 times the IDL, the variation in precision ranges from 10 percent to 20 percent of the amount present. Above 10 times the IDL, the variation in precision is less than 10 percent of the amount present.

When a sample is wet, the bulk density changes, greater absorption of X-rays takes place, and the XRF values are lower. Compounding the absorption effect are the grain geometry and particle size distribution which also affect the absorption of X-rays (Rhodes and Hunter, 1972). These uncontrolled parameters account for some of the XRF results which are lower than the CLP results throughout Table 3.

Some 13 samples were selected to be analyzed by the Parr bomb method. Although the Parr bomb method is a strong extraction procedure, the nitric and hydrochloric acid extract did not dissolve all the metals because the silicates are not soluble in these acids. The silicates often entrap some of the metals within them. The CLP method is simply an HNO_3 extraction procedure, and thus, we expect the recoveries to be lower than a total dissolution or XRF analysis. The XRF analysis is comparable to a total dissolution in that the measured response of the fluorescence accounts for all elements with an atomic number greater than Z = 9 up to Z = 92. This range covers most elements occurring in a natural soil even with contaminants.

A problem developed with use of the Parr bomb while analyzing SRM 1633a and 1645. The addition of 2 mL of HCl caused the generation of too much Cl_2 gas. The Parr bomb was not sealed tightly enough and allowed the pressure to vent. This leakage strongly affected some of the Parr bomb results and accounts for the Parr bomb values for routine samples being less than the CLP values in Table 3, especially with reference to the iron results. The iron combines with the chlorine to form iron chloride which is volatile at 120°C and leaked out with the Cl_2 gas. The standards SRM 1633a and 1645

TABLE 2. COMPARISON OF THE MARTIN MARIETTA XRF SYSTEM AND THE ICP INSTRUMENT DETECTION LIMITS AGAINST CLP CONTRACT REQUIRED DETECTION LIMITS (CRDL)

Element	Martin Marietta XRF System[1] (ppm)	Perkin Elmer ICP[2] (ppb)	ICP CRDL (ppb)
Cu	250	8	25
Pb	70	35	(5)*
Zn	200	17	20
Cr	1000	5	10
Ni	300	30	40
As	150	80	(10)*
Se	140	170	(5)*
Ag	>1000	5	10
Cd	ND	4.8	5
Sb	ND	50	60
Ba	>1000	20	200
Hg	80	50	(0.2)*
Tl	75	160	(10)*

1 Data provided by Martin Marietta.
2 IDL's qualified for CLP.
* These metals are not required for analysis on the ICP under CLP protocols. The values in the parentheses are the measured IDL's for the atomic absorption spectrometer to show its capability.
ND = not detected.

TABLE 3. COMPARISON OF XRF AND ICP RESULTS FROM SOIL SAMPLES

Sample No.	Analysis No.	Elements			
		Fe	Cu	Zn	Pb
		(all units are in mug/g)			
G-1	1	25,511	253	323	253
	2	n.a.	n.a.	n.a.	n.a.
	3	13,461	17.1	364.9	315.1
G-2	1	23,396	b.d.l.	232	183
	2	n.a.	n.a.	n.a.	n.a.
	3	15,669	27.5	374.3	282.2
G-3	1	24,114	b.d.l.	257	224
	2	n.a.	n.a.	n.a.	n.a.
	3	19,016	20.6	434.3	416.3
G-4	1	33,460	n.d.	294	310
	2	n.a.	n.a.	n.a.	n.a.
	3	17,331	18.7	410.6	356.4
G-5	1	32,159	b.d.l.	454	246
	2	n.a.	n.a.	n.a.	n.a.
	3	14,460	15.7	323.6	342.3
G-6	1	43,749	b.d.l.	453	309
	2	n.a.	n.a.	n.a.	n.a.
	3	15.596	18.6	369.0	301.1
G-7	1	22,317	b.d.l.	228	200
	2	n.a.	n.a.	n.a.	n.a.
	3	16,872	17.7	442.7	503.5
G-8	1	21,237	n.d.	248	417
	2	19,410	59.8	1,617.3	3334.0
	3	13,359	22.9	676.1	1234.5
G-9	1	70.532	1,303	4,195	19,379
	2	23,758	55.3	4,517.6	11,492
	3	27,119	67.8	6,042.5	11,791
G-10	1	57,729	1,056	2,978	14,943
	dup	52,947	919.1	3,022.2	14,840
	2	32,620	100.0	6,544.6	18,539
	3	27,259	73.4	6,134.8	12,875

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-11	1	82,978	1,660	5,240	19,654
	2	23,422	42.4	5,265.9	11,615
	3	36,969	80.7	9,383.5	15,294
G-12	1	52,830	912	3,711	15,524
	2	27,606	77.8	6648.4	11,619
	3	26,673	102.7	6347.0	4,135.1
G-13	1	30,009	174	269	190
	2	11,405	13.0	241.9	165.1
	3	12,413	14.2	263.5	176.1
G-14	1	39,972	313	421	267
	2	n.a.	n.a.	n.a.	n.a.
	3	15,099	17.1	344.1	226.8
G-15	1	38,180	208	354	233
	2	n.a.	n.a.	n.a.	n.a.
	3	14,157	15.9	293.6	176.9
G-16	1	35,277	163	168	137
	2	n.a.	n.a.	n.a.	n.a.
	3	21,159.3	23.2	102.7	19.1
G-17	1	35,331	151	153	166
	2	n.a.	n.a.	n.a.	n.a.
	3	25,141	27.2	243.6	137.6
G-18	1	31,529	158	343	327
	2	n.a.	n.a.	n.a.	n.a.
	3	17,234	22.3	422.5	327.6
G-19	1	39,512	373	536	292
	2	n.a.	n.a.	n.a.	n.a.
	3	15,069	21.8	451.3	812.7
G-20	1	38,321	373	449	343
	dup	33,990	304.3	417.0	281.9
	2	n.a.	n.a.	n.a.	n.a.
	3	14,003	21.4	459.3	396.2

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-21	1	45,242	b.d.l.	b.d.l.	133
	2	n.a.	n.a.	n.a.	n.a.
	3	22,018	23.6	102.0	15.4
G-22	1	36,814	b.d.l.	260	156
	2	n.a.	n.a.	n.a.	n.a.
	3	14,868	18.9	329.2	436.6
G-23	1	36,202	n.d.	165	121
	2	n.a.	n.a.	n.a.	n.a.
	3	20,862	22.9	124.5	32.9
G-24	1	38,416	n.d.	b.d.l.	129
	2	n.a.	n.a.	n.a.	n.a.
	J	21,580	24.4	165.3	61.5
G-25	1	33,462	n.d.	244	132
	2	n.a.	n.a.	n.a.	n.a.
	3	20,231	22.5	111.7	17.3
G-26	1	28,503	318	361	214
	2	n.a.	n.a.	n.a.	n.a.
	3	14,765	20.1	390.2	281.3
G-27	1	31,856	b.d.l.	207	174
	2	n.a.	n.a.	n.a.	n.a.
	3	13,543	18.9	388.5	212.5
G-28	1	37,600	b.d.l.	362	296
	2	12,813	15.0	275.8	194.2
	3	14,903	20.5	375.7	314.6
G-29	1	56,334	1,531	4,215	14,639
	2	22,712	68.8	4,315.7	6,833
	3	26,774	90.9	8,467.3	8,924
G-30	1	57,050	726	3,316	12,138
	dup	58,350	742.9	3,489.6	11,927
	2	25,613	73.8	4,497.4	8,031
	3	20,075	81.4	4,780.1	7,235

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-31	1	47,989	556	1,332.5	5,707.9
	2	25,092	68.0	5,347.1	7,090.8
	3	27,010	79.9	6,164.1	1,016.3
G-32	1	34,662	b.d.l.	424	241
	2	9,521	11.4	234.5	240.6
	3	9,897	11.2	253.4	269.4
G-33	1	29,650	485	629	248
	2	7,902	8.4	175.3	159.6
	3	12,007	13.9	282.6	255.4
G-34	1	20,454	b.d.l.	b.d.l.	183
	2	46,904	41.3	209.8	178.5
	3	9,916	11.2	244.2	164.3
G-35	1	21,212	n.d.	b.d.l.	161
	2	n.a.	n.a.	n.a.	n.a.
	3	14,970	17.2	366.1	286.4
G-36	1	37,457	n.d.	b.d.l.	138
	2	n.a.	n.a.	n.a.	n.a.
	3	25,310	37.5	143.5	47.8
G-37	1	40,321	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	20,846	19.4	119.0	43.9
G-38	1	35,042	n.d.	b.d.l.	129
	2	n.a.	n.a.	n.a.	n.a.
	3	21,7α0	20.8	180.2	100.2
G-39	1	36,218	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	24,390	21.5	108.5	28.7
G-40	1	27,283	b.d.l.	218	172
	dup	30,954	n.d.	94.9	151.7
	2	n.a.	n.a.	n.a.	n.a.
	3	15,246	16.5	324.0	456.3

No. 1 Martin-Marietta XRF system.
No. 2 Perkin Elmer P-2 ICP, Parr bomb method.
No. 3 Perkin Elmer P-2 ICP, CLP methods.
dup = duplicate analysis of No. 1.
n.d. = not detected.
n.a. = not analyzed.
b.d.l. = below detection limit.

were reanalyzed, and the following changes were made: the sample amount was changed to 0.25 g, the amount of HNO_3 was changed to 3 mL, and HCl was changed to 0.5mL; and special attention was given to the sealing of the Parr bomb itself. The results show that the reanalysis of SRM 1645 recovered concentrations very close to the NBS certified concentrations. Recoveries for SRM 1633a, the coal fly ash, show low concentrations but they are still closer to the NBS certified concentrations than the CLP recovered concentrations.

COMPARISON OF TWO FIELD-PORTABLE XRF SYSTEMS

We sent 13 soil samples to the Kevex Corporation for analysis with their field-portable XRF system, X-site 9900 and Analyst 6700. Kevex agreed to analyze the samples at no cost. Because Kevex analyzed these samples without contractual requirements the analyses were not verifiable. Therefore, the data must be accepted only as approximate values. In spite of this deficiency, we gain enough insight from the data to warrant its inclusion here (Table 4). The samples were shipped as loose soils sealed in petri dishes. Kevex analyzed the samples by placing the probe of their x-site 9900 onto the samples in the petri dishes. No sample homogenization or preparation took place. Overall the Fe values of the two instruments are close enough for semi-quantitative work, but the values for the priority metals Cu, Zn, and Pb are diverse for the two instruments and need further investigation. The authors suggest that further comparative work in the laboratory with rigorous QA/QC would determine which XRF system is better suited for field work.

STATISTICS

The replicate precision on the standards of the Martin Marietta XRF system ranged from 1.2 percent RSD for Zn to a maximum of 34.4 percent for Pb on the NBS SRM 1648 (Table 5). The second column for each element represents the 90° rotation in the same horizontal plane after the seven-replicate analysis. The difference in the two sets of analyses could reflect the effect due to surface morphology from different areas within a sample which can affect the X-rays the detector senses.

The duplicate precision on routine samples of the Martin Marietta XRF system ranged from 0.88 percent RSD to a maximum of 10.19 percent RSD on the three samples run (Table 6). The relatively high percent RSD's which appear with sample G-20 could occur due to the counting statistics and being close to the instrument's detection limit. The more controlled studies need to be done in this area.

In Figure 10, the bar graph is a plot of the percent relative root mean square deviation verses the elements Fe, Cu, Zn, and Pb for each method. The data from Table 1 was used to calculate the mean percent error (MPE) using the formula:

TABLE 4. COMPARISON OF TWO FIELD PORTABLE XRF SYSTEMS

Sample No.	Analysis No.	Elements			
		Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-1	1	25,511	253	323	253
	2	25,052	111	n.d.	220
G-3	1	24,114	b.d.l.	257	224
	2	29,473	n.d.	64	268
G-7	1	22,317	b.d.l.	228	200
	2	24,326	45	n.d.	536
G-14	1	39,972	313	421	267
	2	28,127	n.d.	175	340
G-16	1	35,277	b.d.l.	b.d.l.	137
	2	22,019	n.d.	n.d.	n.d.
G-19	1	39,512	373	536	292
	2	33,488	n.d.	670	453
G-22	1	36,814	105	260	156
	2	30,882	n.d.	n.d.	621
G-25	1	33,462	n.d.	244	132
	2	36,179	n.d.	n.d.	268
G-27	1	31,856	b.d.l.	207	174
	2	32,121	171	n.d.	302
G-31	1	47,989	556	1,333	5,708
	2	30,904	n.d.	4,873	6,028
G-34	1	20,454	174	198	183
	2	22,339	52	422	275
G-37	1	40,321	39	103	128
	2	39,575	230	8,704	11,427

No. 1 Martin-Marietta XRF.
No. 2 Kevex Corporation XRF.
n.d. = not detected.
b.d.l. = below detection limit.

TABLE 5. REPLICATE ANALYSES OF THE NBS SRM 1648
(Data supplied by Martin Marietta)

Flux Factors	Gross backscatter (counts per second) Fe X100	Fe X100	Zn X1000	Zn X10	Pb X1000	Pb X10
A-1	3.464	6.150	2.818	1.853	5.795	1.563
A-2	3.289	5.999	2.203	1.854	2.870	1.629
A-3	3.225	5.909	2.820	1.873	4.857	1.541
A-4	3.401	5.818	2.951	1.871	2.333	1.640
A-5	3.206	6.429	3.909	1.830	3.469	1.642
A-6	3.316	6.371	2.591	1.813	3.810	1.596
A-7	3.684	5.887	3.523	1.843	2.578	1.564
mean	3.369	6.080	2.974	1.848	3.673	1.596
s.dev.	0.166	0.243	0.572	0.022	1.265	0.041
%RSD	4.927	3.997	19.23	1.167	34.44	2.569

TABLE 6. COMPARISON OF PERCENT RSD OF DUPLICATE ANALYSES BY XRF

Elements	IDL	Samples G-10	G-20	G-30
Fe	---	57,729	38,321	57,050
		52,947	33,990	58,350
%RSD		4.32	5.99	1.13
Cu	250	1,056	373	726
		919	304	743
%RSD		6.95	10.19	1.15
Zn	200	2,979	449	3,316
		3,022	417	3,490
%RSD		0.73	3.70	2.55
Pb	70	14,943	343	12,138
		14,840	282	11,927
%RSD		0.35	9.76	0.88

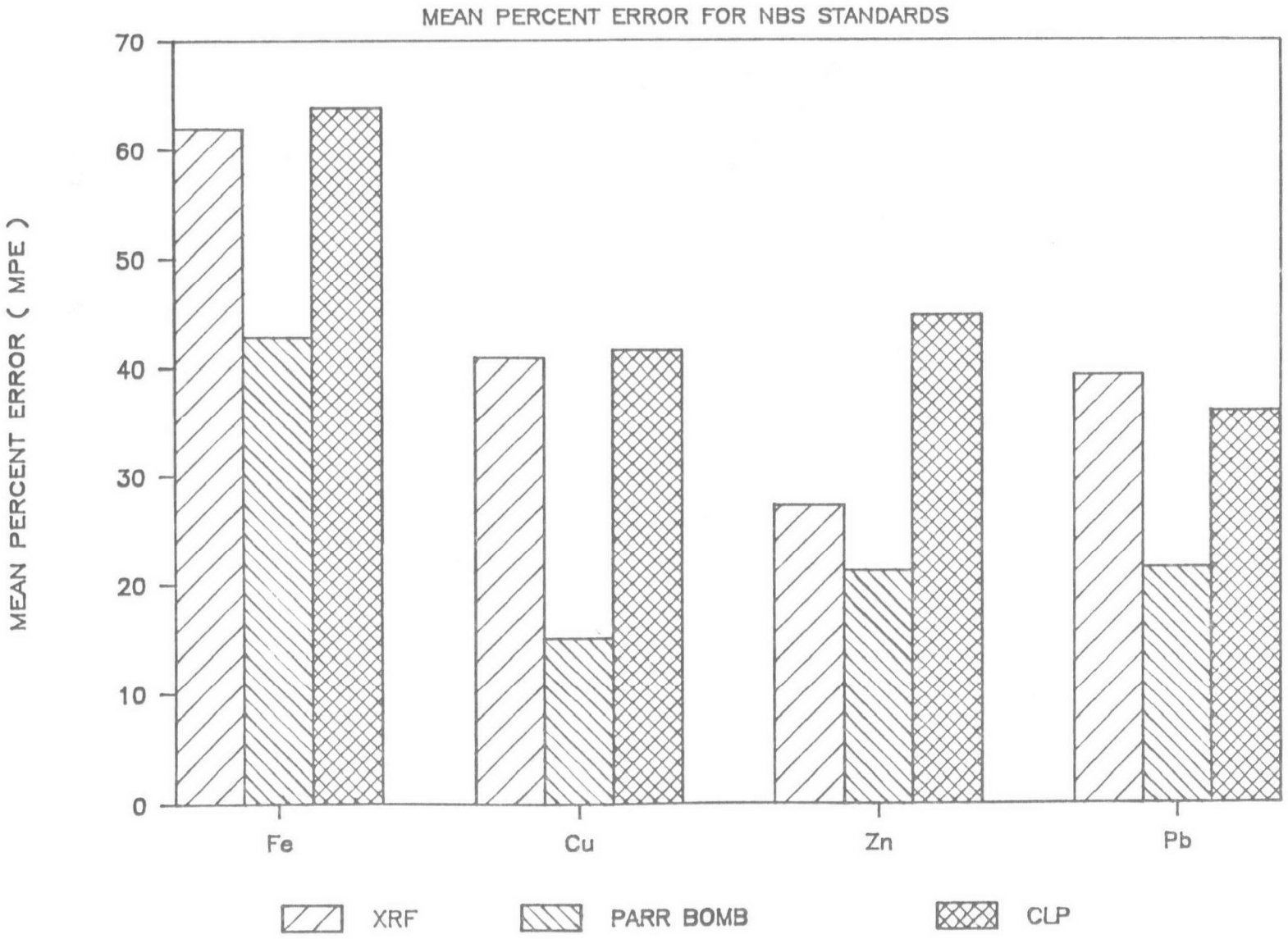

Figure 10. Bar graph of the mean percent error from NBS concntrations.

$$MPE = \sum_{i=1}^{3} \frac{|X_i - T_i|}{3T_i} \times 100$$

where:

X_i = recovered concentration for a method
T_i = NBS certified concentration

The NBS certified value is assumed to be the "true" concentration. Each method of analysis recovered concentrations equal to or less than the true concentration for each element. The deviation from the true concentration of each element represents the effect of both bias and lack of precision or MPE for each method. What is interesting to note is that while the Parr bomb method shows the lowest MPE of the three methods, the XRF is within a few MPE of the CLP for Fe, Cu, and Pb. The Zn values for XRF exhibited a lower observed MPE than the CLP values. The overall precision and bias of the results from the CLP and XRF methods are within acceptable scientific limits (±10%).

ABBREVIATIONS

AAS	atomic absorption spectrometry
CLP	Contract Laboratory Program
CRDL	contract required detection limits
DI water	deionized water
HF	hydrofluoric acid
HCl	hydrochloric acid
HNO_3	nitric acid
ICP	inductively coupled argon plasma spectrometry
IDL	instrumental detection limit
MPE	mean percent error
NBS	National Priority List
NPL	National Bureau of Standards
ppb	parts per billion
ppm	parts per million
QA/QC	quality assurance/quality control
RSD	relative standard deviation (sample standard deviation divided by the mean times 100)
SRM	standard reference material
XRF	X-ray fluorescence

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FOOTNOTES

An in situ measurement by a field-portable XRF system has no homogenization technique as a part of sample preparation. The only preparation necessary for an XRF in situ analysis is to clear a flat surface on the soil. Therefore, the sample area of the in situ XRF measurement cannot be considered homogeneous. Acceptance of an in situ XRF measurement dictates the acceptance of a certain amount of error in measurement's accuracy. To validate the in situ XRF measurement, the sample area of the in situ measurement is collected in a volume of sample. The area of the in situ analysis represents one sample and the volume of sample collected represents another. The values of these two samples will closely approximate one another but are technically not the same. However, the difference in the two values should fall within the acceptance range of the overall inaccuracy of the XRF in situ measurements. For the intents and purposes of this report we will assume the in situ sample area and the collected sample containing the same area to be one and the same sample.

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CANISTER-BASED SAMPLERS FOR VOLATILE ORGANICS

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ABSTRACT

Canister-based samplers for volatile organics are a viable alternative to samplers based on solid sorbent collection. Simple, low-cost units are available that operate for sampling periods of from one minute to several hours without the need for electricity. If electronic flow controllers are used, constant sampling rates can be maintained over 24 hours. Sample integrity of compounds passing through the samplers, and storage stability have been tested. Problems with sample integrity due to contamination in sampler elements upstream of the canisters are common, but have been prevented by proper cleaning procedures. Storage stability over seven days at the 1.0 ppbv concentration level has been established. Reactions among co-collected compounds needs further study. The weatherized versions of these units are suitable for monitoring near hazardous waste landfills.

INTRODUCTION

Canister-based sampling for volatile organics has recently experienced a revival in interest due to two main factors: (1) the characterization of Tenax® solid sorbent with respect to its use by EPA[1,2]; and (2) the demonstration that canisters can be used for controlled sampling and long term (days) storage of volatile organics of special concern.[3,4,5] In particular, the use of distributed air volume (DAV) sets for Tenax® sampling, which allows the screening of sample analyses to identify questionable results, shows that only about 50% of the data from DAV sets are acceptable based on the screening criteria.[6] This relatively low return in defensible data is perceived as unacceptable as long as reasonable alternatives are in prospect.

Canisters have been used for a number of years by scientists involved in the study of the role of hydrocarbons in atmospheric chemistry, and of concentration trends in organic trace gases.[7] However, a systematic evaluation of canisters for the storage and retrieval of "toxic" organics, mainly chlorinated and aromatic hydrocarbons has only recently been provided.[3,4] Based on this information, the canisters have been used to sample for toxic organics at locations remote from the analysis system and then shipped back through the mail system for analysis. Commercial suppliers exist for the canisters, for mailing cartons for the canisters and for the canister-based samplers. The samplers are available in configurations suitable for either indoor or outdoor sampling.

This discussion will touch on several issues that relate to the status of canister-based sampling and the tradeoffs vis-a-vis solid sorbent sampling. The reader should be aware that characterization of

canister-based sampling is not complete and that continued field use will provide the real test of the technique's viability.

PREPARATION FOR SAMPLING AND CERTIFICATION

Canisters are prepared by welding hemispheres or other shapes of stainless steel together and attaching a suitable valve to the shell. The interior surface is electro-polished. Procedures and recipes for accomplishing canister preparation vary, although SUMMA® electro-polishing is widely used. Cleanup of the canisters by the user both initially and after each use consists of heating, evacuation and repeated flushing with a "zero" gas. The sampler can takes any number of forms, several of which are shown in recent publications.[5,8] A generic design for the sampler is shown in Figure 1. The main options are with or without a pump, and with or without weatherized housing, including the temperature control elements shown in the figure.

The canister is the last element in the sampling train. As such, it is subject to contamination from all upstream elements. Hence, the one over-riding consideration, regardless of sampler design, is that these elements be clean. Furthermore, the compounds of interest must not be lost or significantly delayed in transit to the canister. A number of the early systems showed contamination.[8] However, by selection of sampler components and proper cleaning[8], a number of systems with minor or unobservable target compound contamination have been demonstrated. Certain compounds, such as Freon 113 and tetrachloroethene,[8] appear to be common contaminants in the so-called "K" type samplers,[8] although samplers made by one experienced operator do not appear to have contamination at ambient levels (the "R"-type sampler).

Based on our experience, we have proposed a one-step certification procedure that would identify any significant contamination in candidate samplers. The system for generating samples for certification sampling runs is shown in Figure 2. Concentrations of target gases in the manifold system are generated by controlled dilution of a reference concentration with humidified zero air. This humidified standard gas is then introduced into a distribution manifold and thus made available to the sampler inlet and for real time analysis. The sampler's manifold pump is capped to reduced the amount of dilution air needed for the certification. A series of analytical runs are then performed by sampling directly from the gas manifold and used as controls for a simultaneous, simulated sampling run. The comparison agreement should be $\pm$ 0.2 ppbv up to concentrations of 4 ppbv and no greater than $\pm$ 5% for concentrations greater than 4 ppbv. In our laboratory, reference standards containing 40 volatile organics are analyzed in this manner. Prior to, and during certification, the sampler is run at somewhat elevated temperatures by disconnecting the fan that is used for internal circulation of ambient air through the sampler box. This accentuates any outgassing so as to facilitate identification of contamination and also helps clean up a contaminated system. Generally, samplers that are initially free of contamination remain so. This statement is

supported by a year's worth of data from analysis of duplicate samplers located in Houston, TX at an EPA Toxic Air Monitoring System (TAMS) site. These samplers tracked each other very consistently for most compounds. Some example data is given in Figure 3 for 4-ethyltoluene and o-xylene.

SAMPLING

Referring to Figure 1, when sampling without a pump and using an electronic compensating flow controller, a constant flow rate can be maintained from a canister vacuum up to a pressure of approximately 0.8 atmospheric. To extend the sampling duration to 24 hours using a 6-liter canister the flow rate must be regulated at about 3.5 cc/min. With a pump a maximum canister pressure in the range of 20-40 psig can be attained, the exact value depending on type and condition of the pump. When using a pump, provision should be made to flush the sampling lines before diverting flow into the canister to minimize contamination that could accumulate between runs. A similar procedure can be implemented in the nonpumped system by adding a three-way valve and a secondary air pump between the flow controller and canister.

The automated sampling systems can be started and stopped with an electronic or mechanical timer. Before detaching the canister the operator can check the canister pressure to insure that the correct pressure valve has been reached. Such a check can also be made just prior to the sampling run to assure that an evacuated canister has been attached. In a pumped system the value of the canister pressure relative to the expected value can indicate that there has been a problem and help diagnose the location of a leak in the system. After sampling, the canisters are shipped to the analysis system through the mail (provided canister pressure does not exceed 40 psig).

ANALYSIS

Most current mass spectrometric systems for analysis of air samples for trace level volatile organic compounds (VOCs) are configured for thermal desorption of solid sorbent cartridge samples through which 5-80 liters of air have been drawn. After transfer of the concentrated sample to a reduced temperature trap, the scanning (SCAN) mode of operation is used to generate mass spectra which are then systematically compared to a mass spectral library to identify unknown compounds. To use a similar approach for canister samples, VOCs must first be concentrated before analysis. Because of the time required for this concentration step and the limited air volume available, this approach has not proven to be practical. Instead, we have used the selected ion monitoring (SIM) mode of our mass spectrometer. In this mode the list of target compounds is defined and no spectral library searches are attempted. Identification is made by the dominant ion fragment found in the source using retention time and two minor ion fragments as qualifiers. There is an enhanced detection sensitivity in the SIM mode compared to the SCAN mode, although unknown compounds are not identified. This tradeoff has so far been acceptable, since the list of VOCs of current interest is still in double digits. In the SIM mode, detection sensitivity is approximately equal to that of

a flame ionization detector or, in our case, ± 0.2 ppb for preconcentration of a 250 cc sample.

Our current analytical procedure includes a preliminary analysis by GC-FID/ECD to establish the level of concentrations and to provide information on polar and non-targeted compounds. Reduced temperature preconcentration of VOCs directly from the canister is followed by separation of VOCs on a megabore capillary column. Based on this initial run, the remaining sample volume is diluted, if necessary, to fall within the calibration range of our GC/mass selective detector (MSD). Provided unknowns are sufficiently high in concentration, a SCAN run on the GC/MSD may be considered. A subsequent SIM run requires sample conditioning through a dryer[9] to prevent column blockage by ice formation in the small bore capillary columns used on the MSD system. Upon elution, water vapor also causes a problem in the MSD's EI source by increasing pressure in the high vacuum region.

Sample introduction is accomplished using a positive pressure canister, typically above ~ 8 psig. Because some canisters arrive at the laboratory at lower pressures, pressurization with zero grade air can be required. The dilution ratio is noted and applied to subsequent analytical results. For analysis, a mass flow controller is attached to the canister and set for approximately twice the flow required by the analytical system. This flow is then vented past the system inlet.

APPLICATIONS

The canister-based samplers have been deployed by EMSL, EPA in four ambient air studies and two indoor air studies, and are being implemented in EPA's Toxic Air Monitoring System (TAMS) at 10 locations in four cities. Applications near hazardous waste landfills and waste water treatment facilities are planned for the fall of 1987.

DISCLAIMER

The research described in this article does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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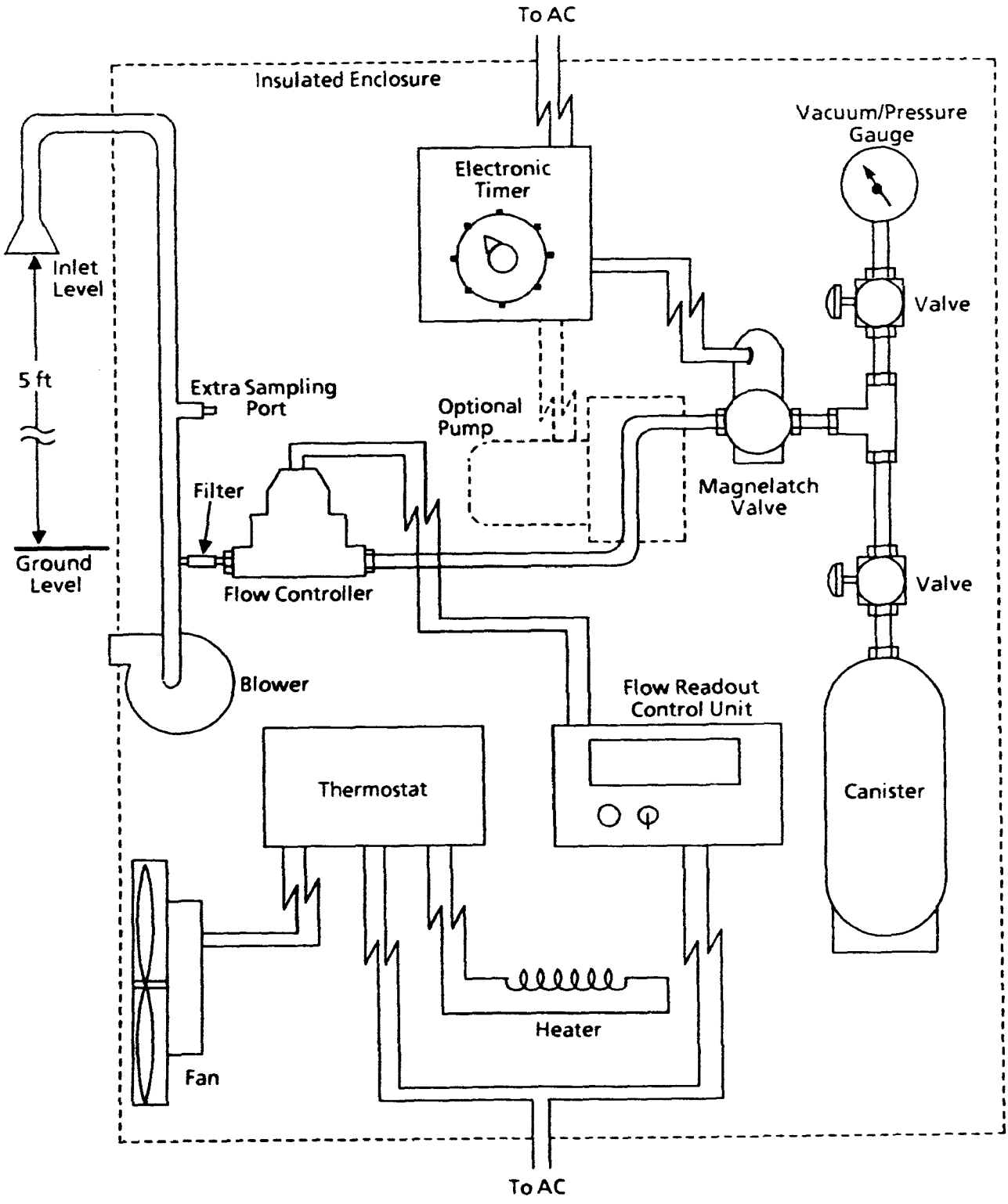


Figure 1. Updated sampler configuration.

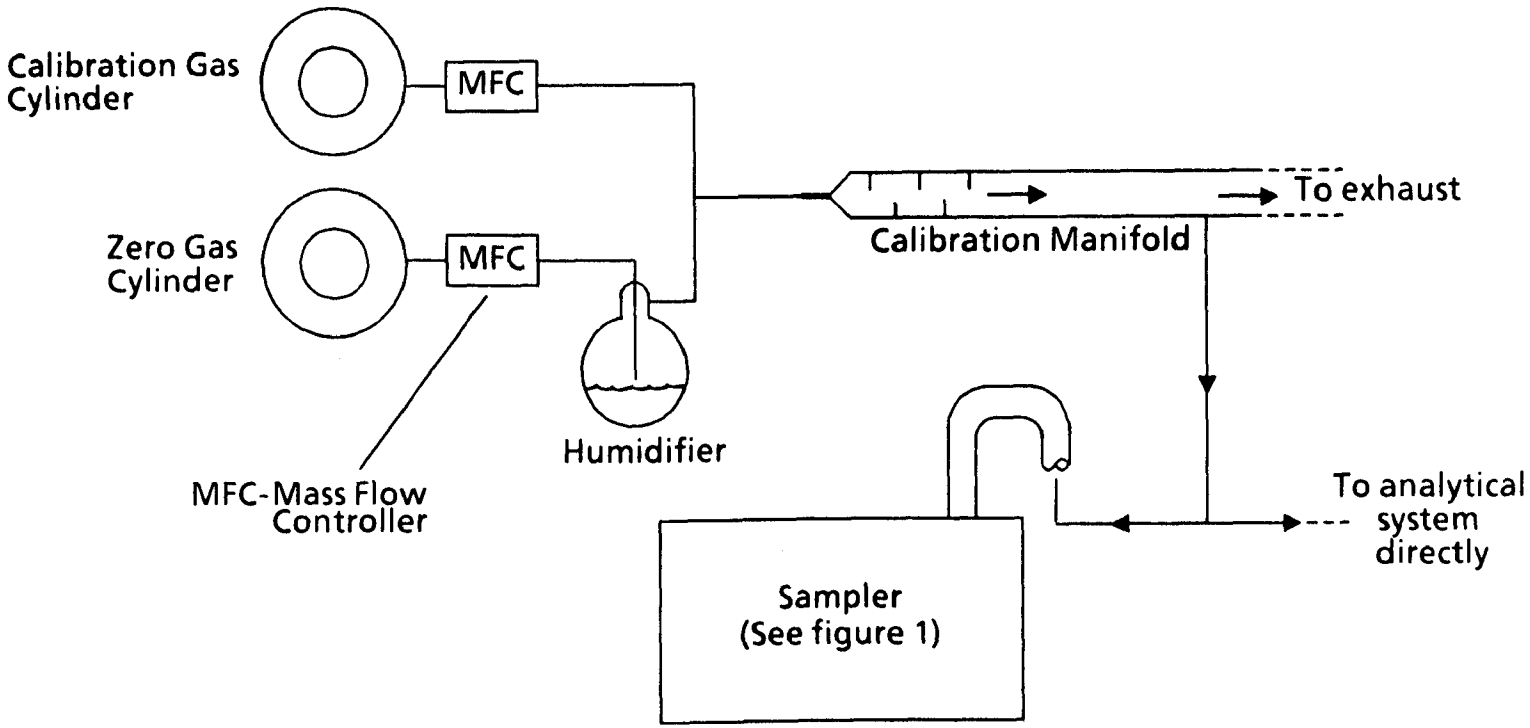
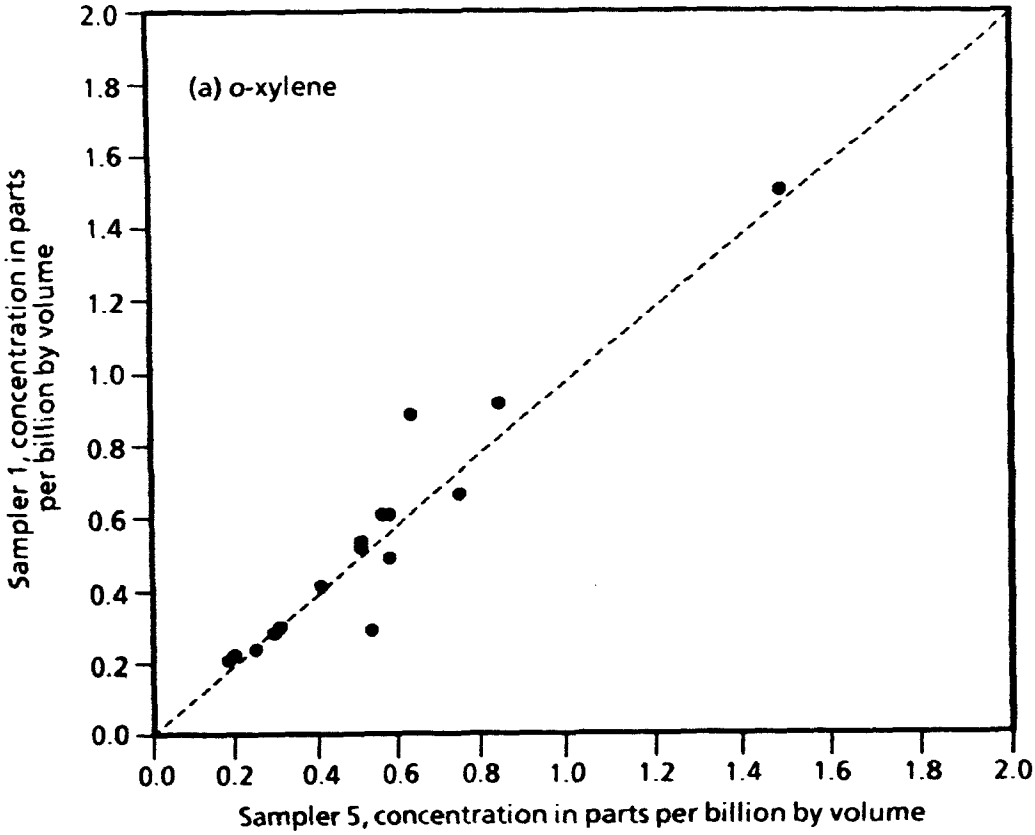


Figure 2. Apparatus used in canister certification.



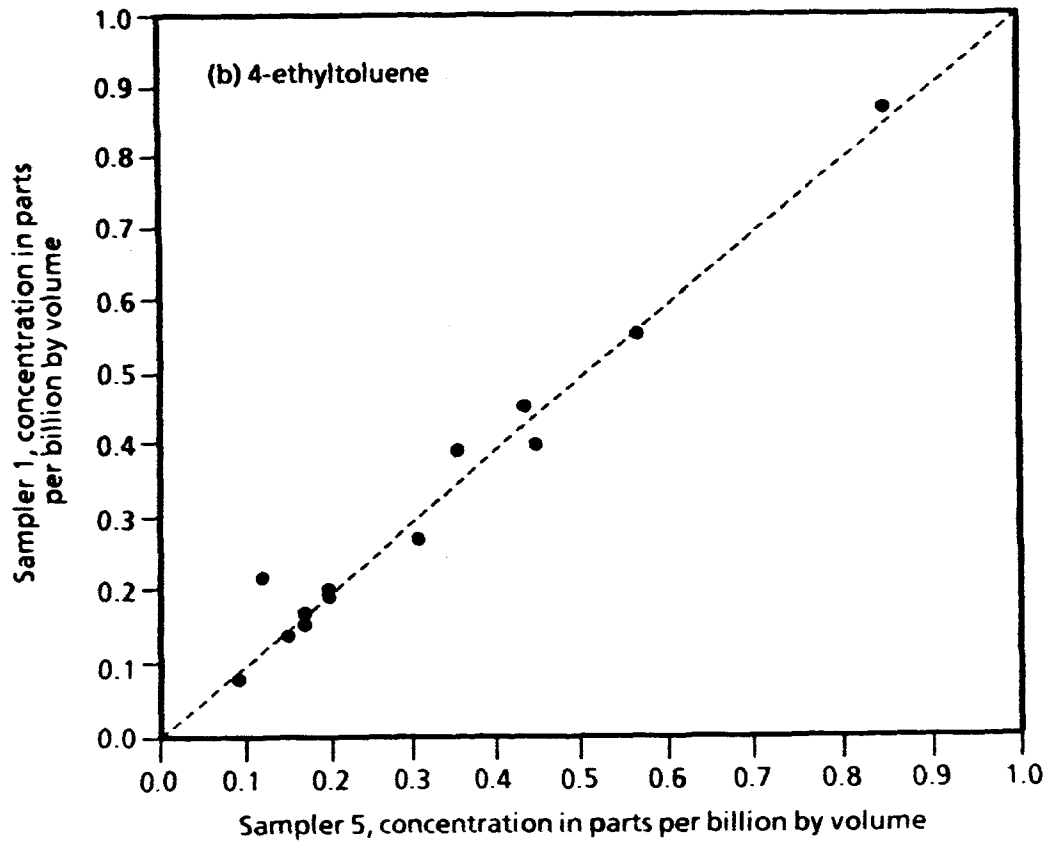


Figure 3. Comparison of (a) *o*-xylene and (b) 4-ethyltoluene data from two co-located samplers in an EPA field study. The dashed 45° line indicates theoretically "perfect" agreement.

CATALOG OF FIELD SCREENING METHODS

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ABSTRACT

The national Superfund program is decentralized in its conduct and management. For this reason, knowledge and skills gained in one Region or state, or even at one site, are not necessarily transferred to others. To facilitate transfers of information about methods for measuring and screening chemicals in the field and for quick-turnaround analyses, the U.S. Environmental Protection Agency (EPA) is developing a Catalog of Field Screening Methods. The Catalog will be provided to users as both a pocket guide and on disk in a dBase III system. The Catalog is provisional and will be revised and updated as new information becomes available. This paper describes the Catalog project initiation, sources of information about the methods, and the development and contents of the Catalog. The current status and plans for completion of the Catalog and data base are detailed. Finally, the paper indicates both how to obtain copies of the Catalog and data base and how to provide information to update the Catalog.

INTRODUCTION

Chemical constituents must be measured in various environmental media during the course of many Superfund site investigations. For example, measurements in surface and ground water, soil, sludge, air, and containers (e.g., drums or tanks) may be needed at a given site. Various types of monitoring and screening techniques are used to characterize "hot spots," define general site conditions, assist in well placement and screen setting, compare off- and on-site conditions, estimate potential population exposures, determine removal efficiencies, and establish long-term monitoring.

The appropriate type of monitoring or screening at a given site largely depends on the intended end use of the data and associated data quality requirements. Specific criteria that should be considered during selection of field methods include detection limits of equipment versus expected concentrations of contaminants, performance capabilities (accuracy and precision, for example), and time and cost constraints. The ultimate goal of any data

collection effort is to provide data of known quality to be used in subsequent decisionmaking. Therefore, one or several laboratory or field methods may be appropriate for any given data collection and analysis activity.

Options for sample analysis include the Contract Laboratory Program, other EPA, state, and private laboratories, mobile on-site laboratories, and field screening techniques. Some differences among these include:

- The Contract Laboratory Program (CLP) includes Routine Analytical Services (RAS) and Special Analytical Services (SAS) and provides a rigorous QA/QC and evidentiary documentation program, resulting in data of known quality. Cost is about $1000 per organic sample, and results are provided to data reviewers in about 30 days.

- Other laboratories (EPA, state, or private) may follow analytical methods that are similar to the CLP, but do not necessarily provide the same degree of QA/QC and evidentiary documentation. In some cases, costs may be lower and turnaround time shorter. All these factors must be weighed against data quality needs.

- Mobile laboratories and field analytical techniques often operate under less well controlled conditions. However, they can provide immediate results, which may be crucial, for example, to determining further sampling on a given site. Costs may be lower than CLP, but quantitative results may not always be possible.

Experience gained in the first five years of the Superfund program has shown that field analytical methods are suitable for use in many applications. Quick turnaround of samples, gross characterization of contaminants, and selection of sampling locations for more rigorous analysis (for example, by the CLP) are some of the possible applications. It also has become clear that methods are being developed and used to meet these needs. Discussions among EPA and contractor staff, occasional papers in scientific literature and at conferences are beginning to bring these methods wider attention. The primary factor that has limited the coordination and evaluation by EPA of these developmental efforts is the decentralized structure of the Superfund program. A mechanism to make field screening methods available to all program participants is needed. To fill this need, the Analytical Operations Branch (AOB) of EPA's Office of Emergency and Remedial Response (OERR) initiated a project in FY 87 to increase coordination and facilitate distribution of this information. This project has three objectives:

- To produce a Catalog of field analytical methods, which details demonstrated field screening and analytical techniques and focuses on methods used in the 10 EPA Regional Offices and the Office of Research and Development (ORD) laboratories.

- To demonstrate and evaluate up to three methods in conjunction with EPA Regions; and

- To create momentum in EPA and the private sector for development, demonstration, and appropriate use of field screening methods.

This paper describes the approach, progress to date, and future direction of the Catalog development portion of the initiative.

APPROACH

The U.S. EPA Hazardous Site Evaluation Division began this project in the Fall of 1986. As a first step, EPA contacted the 10 Regional Offices and interviewed staff who understood the Regions' overall use of field analytical techniques. Based on information obtained during these interviews, EPA determined that contractor assistance would be beneficial in the compilation and development of the Field Screening Methods Catalog. Through the REM II program, EPA contracted with CDM Federal Programs Corporation and Roy F. Weston, Inc., to develop the Catalog and data base.

Information collection methods included additional telephone and on-site interviews by contractor personnel to follow up on data collected by EPA and review of EPA reports and papers published in journals or presented at conferences. Contacts included the Analytical Services Advisory Committee, the Regional Environmental Services Divisions, Regional laboratory staff, EPA ORD laboratory staff, and various contractors. Methods for further assessment were selected from those identified by the various contacts. Selection was based on their availability for use in field situations and their ability to provide at least some quantitative data.

To date, approximately 30 methods that have been successfully used in the field have been identified and are included in this Catalog. The Catalog includes only those methods that were identified by EPA's initial interviews and for which sufficient data were available based on contractor followup work. The methods presented in this Catalog include analyses for metals, volatile and semi-volatile organics, phenols, pesticides, PCBs, and polycyclic aromatic hydrocarbons. Several soil gas sampling techniques have been included because of the expanding use of such techniques in assessing contamination.

Additional methods may exist within EPA, other governmental agencies, and private industry. Future updates of the Catalog will include these methods as appropriate.

After reviewing available documentation of each method, project staff relied on individuals who had worked with each method to provide additional details about their experiences using the method. This information was used to fill gaps in information and ensure accuracy. These and other field and laboratory personnel are involved in the Catalog review process, which includes commenting on drafts of the method descriptions and the data base.

The project provides both a pocket guide of the methods and a computer data base, which are designed to serve the needs of field staff and managers. For ease of use, a standard set of "fields" has been developed to organize the information about each method. In addition, the content of each field is standardized. The types of information provided for each method include:

- Method name and number (number is specific to this Catalog);
- Summary and method description;
- Application, limitations, and instrumentation used;
- Performance specifications, including detection limit, selectivity, accuracy, and precision/repeatability;
- Use of the method, including location, CERCLIS site number, and matrix;
- Preparation, maintenance, and cleanup;
- Calibration;
- Analysis time;
- Capital costs; and
- Source of technical information.

In addition, the description of each method includes two "comment" fields. At least one bibliographic reference is provided for each method.

The pocket guide provides a concise description of each method, which allows field staff to consider the range of analytical methods that might be appropriate for the site while in the field. It

provides only a brief overview of the method and refers to a source of detailed instructions for use. The data base would be used in the office for planning of field investigation and response activities. It provides search capabilities based on four main categories (chemical name, chemical class, CAS number, and method type) and two subcategories (matrix and detection limit). For example, the user might request information on analytical techniques for PCBs. To limit the number of PC3 techniques displayed, the computer system will ask which media are wanted (air, soil, water) and whether the user wants to set detection limits (e.g., only show the method if it detects less than 100 ug/kg). Similarly, the user could ask for methods for volatile organics (chemical class) or for all GC methods (method type). CAS number can be chosen to ensure that the correct chemical is selected if confusion among chemicals with similar names is possible.

The data base was developed using dBase III to run on IBM-compatible microcomputers. It is available on two floppy disks in a compiled version, and is menu-driven for ease of use. The system is designed to prevent tampering or accidental changes or erasures. The data base includes several options for printing requested information, ranging from method titles only to the full method description.

STATUS AND PLANS FOR COMPLETION

To date, about 30 field sampling or screening methods have been included in the Catalog. The methods in the Catalog include several gas chromatography methods, two x-ray fluorescence methods, ultraviolet fluorescence, fiber optic sensors, immunoassay, mass spectroscopy, and atomic absorption. The soil gas sampling methods all utilize GC equipment for analysis. The Catalog also includes variations of several analytical techniques based on sampling media, such as bonded sorbents, or extraction chemicals (e.g., hexane versus methanol). Figure 1 presents the titles currently included in the Catalog.

The Catalog is under review by EPA Headquarters and Regional personnel who are familiar with the development and use of the methods. Based on this review, the descriptions may be revised. The data base will also be reviewed. Both will be in final form, ready for distribution, by early Fall of 1987. The review and revision process will continue, however, with new methods being added and current methods being revised as new data become available. Several studies that are currently underway should contribute significant information in the coming year.

CONCLUSION

The limited amount of data available about precision and accuracy of these methods in the field caused problems in completing the Catalog entries. Field personnel using a method usually tested it to demonstrate the method's applicability to a particular site, but often did not perform extensive testing or provide QA/QC documentation. Several methods have been used at only a few sites. While limited performance criteria or field experience caused some problems in completing the Catalog entries, enough information is available for preliminary evaluation of a method's ability to meet specific data requirements. It remains important in every case, no matter how complete the Catalog entry or method protocol, for the scientist performing the analysis to develop clear specifications and operating procedures and to demonstrate acceptable performance of the method in his or her hands for the site. It is necessary to define data use and match the analytical method to this end use. Often, the results of field screening methods should be verified by CLP or another analytical procedure.

The Field Screening Methods Catalog, which contains approximately 30 sampling and analytical methods, will be available through EPA's Analytical Operations Branch. Call Carla Dempsey at (202) 382-7906 for information. This Catalog is a dynamic document; EPA will update it to reflect the continuing rapid advances in field screening methods. Suggestions for methods to be added or revisions to methods included in the current version also may be provided to EPA through Carla Dempsey.

FIGURE 1--CURRENT CONTENTS OF FIELD SCREENING METHODS CATALOG

Headspace Technique Using an OVA (FID) for Volatile Organic Compounds
Headspace Analysis Using HNu (PID) for Total Volatile Organics
Headspace Technique Using a Mobile GC for Volatile Organics
Immunoassays for Trace Organic Analysis
Total PNA Analysis Using an Ultraviolet Fluorescence Spectrophotometer
Use of Fiber Optic Sensors in Environmental Monitoring
Air Monitoring for VOCs Using Programmed Thermal Desorber and GC
Pesticide Analysis Using a GC with ECD--Hexane/Methanol Extraction
Phenol Determination by Liquid-Liquid Extraction and GC Analysis
Use of Bonded Sorbents for Semi-Volatile Analysis
Use of Bonded Sorbents for Pesticide Analysis
VOC Analysis Using GC with Automated Headspace Sampler
PCB Analysis Using a GC in an On-site Laboratory--Hexane Extraction
PCB Analysis Using a GC in an On-site Laboratory--Hexane/Methanol/Water Extraction
PCB Analysis Using a GC in an On-site Laboratory--Hexane/Acetone Extraction
PCB Analysis Using a GC in an On-site Laboratory--Hexane/Methanol Extraction
Pesticide Analysis Using Isothermal GC with ECD--Hexane Extraction
PAH Analysis Using GC (FID) with Heated Column
X-Ray Fluorescence in Laboratory for Heavy Metals
X-Ray Fluorescence for Heavy Metals (On Site)
Field Atomic Absorption Analysis
Trace Atmospheric Gas Analyzer (TAGA)--MS/MS
Soil Gas Sampling Using a Perforated Tube
Soil Gas Sampling Using Mini-Barrel Sampler
Soil Gas Sampling Using Industrial Hygiene Samplers
Soil Gas Sampling for Downhole Profiling
Soil Gas Sampling Using Direct Injection--Stopper
Soil Gas Sampling Using Direct Injection--Auger
Soil Gas Sampling Using a One-Liter Syringe
Soil Gas Sampling Using Tenax Tubes

A FIELD DEPLOYABLE ANALYTICAL INSTRUMENT FOR ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS OF SUPERFUND SITES

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ABSTRACT

This presentation discusses the single instrument thermal extraction from solid samples of semivolatile organic substances, such as the base/neutral priority pollutants, and their subsequent analysis by high resolution gas chromatography (GC) and/or gas chromatography mass-spectrometry (GCMS), and the application of this type of instrumentation to environmental analysis.

Site investigations and cleanup activities under Superfund often require rapid analysis of samples for trace volatile and semivolatile organic compounds as well as heavy metals. The analytical data are used by response officials for decision making in characterizing and cleaning up sites. Traditional analytical techniques require laboratory facilities to extract samples, cleanup extracts, and instrumentally analyze the extracts. This process is time consuming and expensive. Analytical data obtained from field instruments can supplement data obtained from laboratory analysis of samples. Field instrumentation that allows for the rapid analysis of samples enables response officials to perform site investigations and cleanup activities in a more efficient and cost-effective manner. Field deployable analytical instrumentation for analysis of volatile organic substances will be discussed elsewhere in this symposium.

In this presentation we discuss the potential for the use of a single field deployable instrument, the Pyran Level 2 Analyzer, for the thermal extraction of solid samples with analysis of the extracts by combined GCMS techniques. The instrumentation was originally developed for use in petroleum exploration for analysis of various source rock samples for trace levels of high molecular weight petroleum hydrocarbons and NSO compounds. It consists of a chemically inert all quartz thermal extractorpyrolyzer interfaced to an all quartz cold trap-injector and cross-linked liquid phase coated capillary GC column which elutes into either a flame ionization detector or an ion trap detector (mass spectrometer). The unit requires only compressed gas (helium and carbon dioxide) and electrical power, and has been designed for use on oil rigs and in seismic fans.

We believe that this instrument represents one of the few devices that can be used for the analysis of environmental samples in the

field, at reasonable cost per sample, and that has a wide range of analytical capabilities. The Pyran instrument will be described in detail and data from the analysis of several types of environmental samples will be presented. Its applications and limitations in field analysis will be reviewed.

INTRODUCTION

Effective chemical hazard assessment and mitigative actions for hazardous waste site evaluations are dependent on a number of considerations. With regard to a specific site, the following information is needed:

1) identities and quantities of specific chemicals involved at the site;

2) the toxic and reactive properties of specific chemicals at the site;

3) knowledge concerning routes of, and probability of, exposure to specific chemicals at or from the site;

4) environmental fates and transport mechanisms of the toxic chemicals at the site.

Virtually all efforts associated with assessing hazards and developing mitigative plans for chemical releases at Superfund sites involve both identification and quantitative evaluation of specific compounds at the sites. This implies a need for analytical techniques that can provide useful chemical information, in a timely fashion, from analysis of the various types of samples that are encountered at hazardous waste sites. Ideally, the analytical device that is the heart of this "problem solving" instrument system would have the following capabilities (Overton 1986):

1) portability or field deployability;

2) ability to identify and quantitate a wide variety of specific chemical substances;

3) application for analyses of vapors, liquids and solid samples;

4) sensitivities to one-tenth the toxic concentrations;

5) rapid analytical response times compared to those available by sending samples to a laboratory;

6) ruggedness and reliability;

7) readily available, and simple to operate and interpret;

8) requires utilities that are readily available in field situations.

Unfortunately, this "idealized" field analytical instrument does not presently exist. Currently available analytical instruments are simply unable to provide field deployable compound-specific detection in a configuration that has all of the capabilities described above. After due consideration for the information needs associated with chemical hazard assessments and mitigative actions, and the analytical capabilities that are realistically achievable in a timely fashion with field deployable instrumentation, we have developed the following guidelines for a field deployable analytical instrument. They include:

- identify primarily organic chemical contaminants;
- primary capability is associated with identifying and quantitating toxic chemicals in a timely fashion with field deployable equipment;
- analytical instruments should be broadly applicable without on-site modifications or methods development for analysis of vapor, liquid and solid samples;
- chemical data should be equivalent (or nearly so) to data obtained from laboratory analysis of samples.

Based on these guidelines, we believe a compound-specific analytical instrument system is needed for use in the field to provide information on which to base environmental chemical hazard assessments and mitigative actions. This analytical instrument system should have the following capabilities:

1) sensitivities to one-tenth the toxic levels;

2) accuracies in compound identification equivalent to analyses obtained from laboratory-bound instruments;

3) capability to be rapidly deployed at or near the hazardous waste sites;

4) analytical response times in hours rather than days;

5. ability to be operated by specially trained technicians rather than graduate chemists;

6. can be used to analyze waste materials and contaminants in containers, soils and sludges, water and air.

A great amount of research is being conducted to develop more sophisticated, small, rugged analytical devices for a variety of field applications. Much of this work is being conducted for purposes related to U.S. Department of Defense activities. This research seems to be divided into two basic efforts. One effort is attempting to miniaturize existing analytical instruments such as the gas chromatograph-mass spectrometer (Analytical Chemistry 1987). The other effort is aimed at developing new solid state sensors, and arrays of solid state sensors, whose data outputs are examined by powerful multivariate statistical routines designed to identify "patterns" in the data (Setter 1986). Virtually all of these research efforts are aimed toward analysis of volatile compounds in air samples.

A new field deployable analytical instrument has recently been developed for the analysis of semivolatile, high molecular weight marker compounds in source rock samples from petroleum exploration activities. The instrument uses thermal extraction of semivolatile organic compounds into an inert, all quartz apparatus followed by integrated gas chromatographic-mass spectrometric analysis of the thermal extracts. This unit, called a Pyran Analyzer, was developed by Ruska Instruments of Houston, Texas. We believe that this device has great potential for application at hazardous waste sites to analyze base-neutral and acid extractable types of semivolatile organic compounds. Additionally, using suitable trapping techniques, the device should also be able to analyze volatile organic compounds. The unit is rugged, potentially field deployable in a van, and can have analytical turn-around times of approximately one hour for most types of analyses.

After a thorough review of field deployable analytical instruments that have evolved over the past several years, we have reached the following conclusions:

1) Aside from transportable field laboratories, there is no readily available, field deployable, analytical capability for analyzing a wide variety of base-neutral and acid extractable type organic compounds. Even the expensive Sciex MS-MS analytical device has not proven useful as a general analytical instrument for analysis of the variety of samples commonly encountered at Superfund sites (Collins 1986). The prohibitive cost and complexity of the Sciex further limits its usefulness for most routine Superfund applications.

2) Virtually all conventional analyses of environmental samples, for base-neutral and acid-extractable type organics compounds, involve extraction with organic solvents, followed by GCMS analysis using conventional instrumental techniques. All volatile analyses are based on purge and trap procedures

except for those that are being developed for NOAA-EPA by our Instrument Development Group (Overton 1986).

3) The Pyran Thermal Chromatographic System has great potential for field deployable analysis of most of the sample types that are encountered at Superfund sites.

4) The Pyran Instrument must be evaluated and, perhaps, modified to meet the unique requirements for analytical application at Superfund sites.

5) New procedures may be required in order to convert the Pyran device into a field deployable, analytical instrument for Superfund applications.

The Pyran Thermal Chromatograph is an instrument that was specifically designed and developed to meet the analytical need of petroleum exploration and development activities. It is a self-contained extraction system and analyzer that is relatively compact, rugged and designed for field applications. Figure 1 shows the essential components of the Pyran Analyzer. It is constructed of quartz to provide the chemical inertness and stability that is needed for reproducible thermal extraction and pyrolysis of organic compounds from source rock samples. Since quartz does not absorb radiant energy, the quartz construction allows precise temperature control at both subambient and elevated temperatures using a computer controlled combination of cyrogenic cooling (liquid CO_2) and radiant heating. The Level I analyzer includes a thermal extraction and pyrolyzer unit that is interfaced directly to a flame ionization detector. The Level II unit includes a thermal extractor and pyrolyzer module that is interfaced, with all quartz components, to a specially designed capillary column gas chromatograph that has no moving parts. Again, all quartz construction of the chromatographic oven and column allows precise and reproducible temperature control and programming from subambient to several hundred degrees centigrade. The chromatographic effluents are detected by an Ion Trap Mass Spectrometer and analyzed by conventional data treatment software. Figures 2 and 3 show data from analyses of a spiked synthetic sediment sample that was thermally extracted and analyzed by both the Pyran Level I and II units. These data confirm our belief that the Pyran Analyzer has great potential for analysis of base/neutral and acid extractable type compounds at Superfund sites.

The Level I analyzer thermally extracts organic components and detects the substituents without any chromatographic separation using flame ionization detection. It is designed to permit rapid screening of samples and has analysis times of less than fifteen minutes. The Level II analyzer has a thermal extraction module that is interfaced to a GCMS analyzer. The GCMS unit has the capability

to identify and quantitate specific substances that are thermally extracted from the sample. The analyses times, including extraction, are generally on the order of one hour. The Level II analyzer is designed to identify specific chemicals in a sample and to measure their concentrations with analytical turn around times that are significantly shorter than are available from conventional laboratory GCMS analysis of environmental samples. The Pyran Level I and II analyzers have great potential to provide analytical data, in a timely fashion, for use at Superfund hazardous waste sites. This potential, however, has not been totally proven or substantiated.

The Pyran unit was originally designed for the automated analysis of solid or liquid samples. In addition to these types of samples, we believe the unit can be used for the analysis of gaseous samples as well. Gaseous samples could be analyzed by adsorption onto solid adsorbents and subsequent thermal extraction/GCMS analysis. Milligram quantities of solid and liquid samples can be screened by Level I analysis or analyzed directly by the Level II unit. Special mass spectral techniques, such as the use of combined electron impact-chemical ionization procedures, may be useful for use in the analysis of the thermal extracts (Broadbelt 1987). Also, enhanced "target compound" data treatment algorithms will undoubtedly be necessary since the Pyran unit analyzes samples without any chemical clean-ups.

The analytical potential of the Pyran Level I and II Thermal Chromatograph must be fully evaluated and characterized from a stand-point of its application to Superfund analytical needs. This process involves determining the precision, accuracy, recoveries, detection limits and potential interferences for organic priority pollutant type compounds in a variety of sample matrices (sludges, sands, silts, clays, etc. with varying TOC content). This validation procedure is necessary because the Pyran unit uses methods of analysis that are significantly different from those used in conventional laboratory analyses. Conventional laboratory analyses, described in EPA methods 624 and 625 (Environmental Protection Agency 1980), involve time consuming liquid-liquid extractions, optional clean-up of the extracts with liquid-solid chromatography (silica gel, alumina, fluorosil, etc.), and instruments analysis with GCMS techniques. The clean-up procedures are designed to remove interfering compounds, from naturally occurring sources, before the extracts are submitted to analysis by GCMS techniques. The Pyran unit, on the other hand, is a fully automated unit that thermally extracts and analyzes samples in a single step. It therefore has much greater sample through-put capacity than conventional EPA analytical procedures. However it does not use any type of extract clean-up procedure. Consequently, all organic compounds, not just the analytes of interests, will be subjected to its capillary GCMS analysis. The implication of this

fact on the analytical results from Pyran Analysis will have to be fully elucidated. It is obvious that total extraction and analysis of all components in complex environmental samples will place a substantial burden on the mass spectral procedures and data treatment techniques that are needed to turn analytical data into the identities and quantities of specific sample analytes.

Figure 4 shows data from the Pyran analysis of a "penta" contaminated coal tar sludge that also contained low ppm levels of octa and hepta chlorinated dioxins and furans. Examination of the mass spectral data reveals the presence of numerous polynuclear aromatic hydrocarbons but only barely detectable levels of pentachlorophenol. Virtually the entire sample was composed of organic material. These large quantities of polynuclear aromatic compounds, and other organic components, made detection of trace quantities of the chlorocarbons very difficult. Additional methods must be developed before the Pyran unit can be used to completely characterize these "difficult to analyze" types of samples.

In conclusion, we believe the Pyran Thermal Chromatographic Analyzer has great potential for use in many Superfund analytical applications. This potential should be evaluated more fully because of the short analysis times and cost savings associated with its field deployable analyses. Enhanced instrumental techniques, such as chemical ionization GCMS analysis or daughter ion mass spectral analysis, may be needed to fully exploit the analytical advantages of the Pyran analyzer.

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Figure 1 - Schematic diagram of the Pyran Levels I and II Thermal Extractor and Analyzer. Level I analysis involves thermal extraction of milligram quantities from solid samples that are placed in small quartz crucibles (8mm OD) in an all quartz pyrolysis vessel. The extracted organic material is then detected by a flame ionization detector. Level II analysis involves thermal extraction of solid samples in an all quartz pyrolysis vessel, cold trapping of the extracted analytes, and flash evaporation of the analytes onto a fused silica capillary gas chromatographic column. The capillary column is then temperature programmed, using a combination of radiant heating and cryogenic cooling, to produce the capillary gas chromatogram. Eluting analytes are detected by an Ion Trap mass spectrometer.

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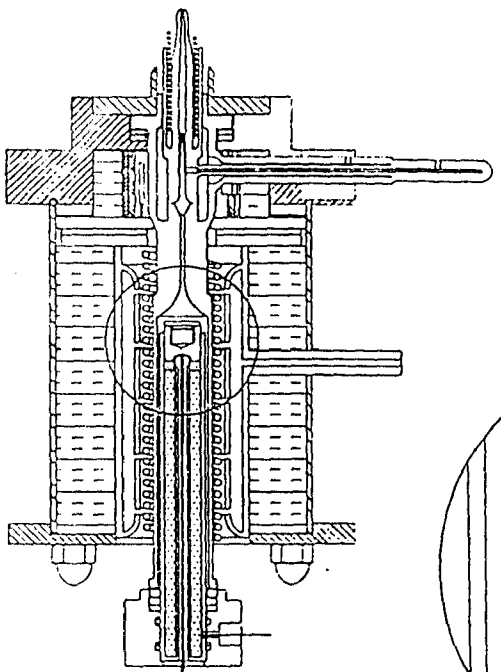
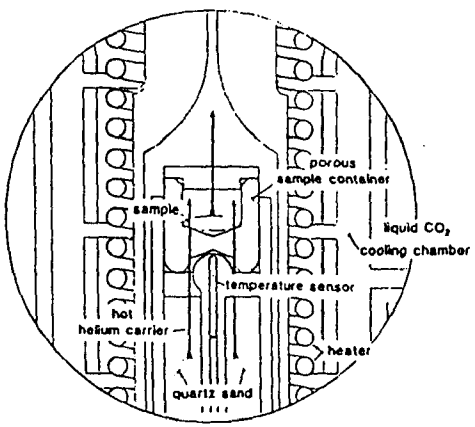
PO BOX 747(60, HOUSTON, TEXAS 77274
713 975-0547
TELEX 762 404

Level I – FID

Quartz Analyzer





LEVEL II TC/MS™

QUARTZ ANALYZER

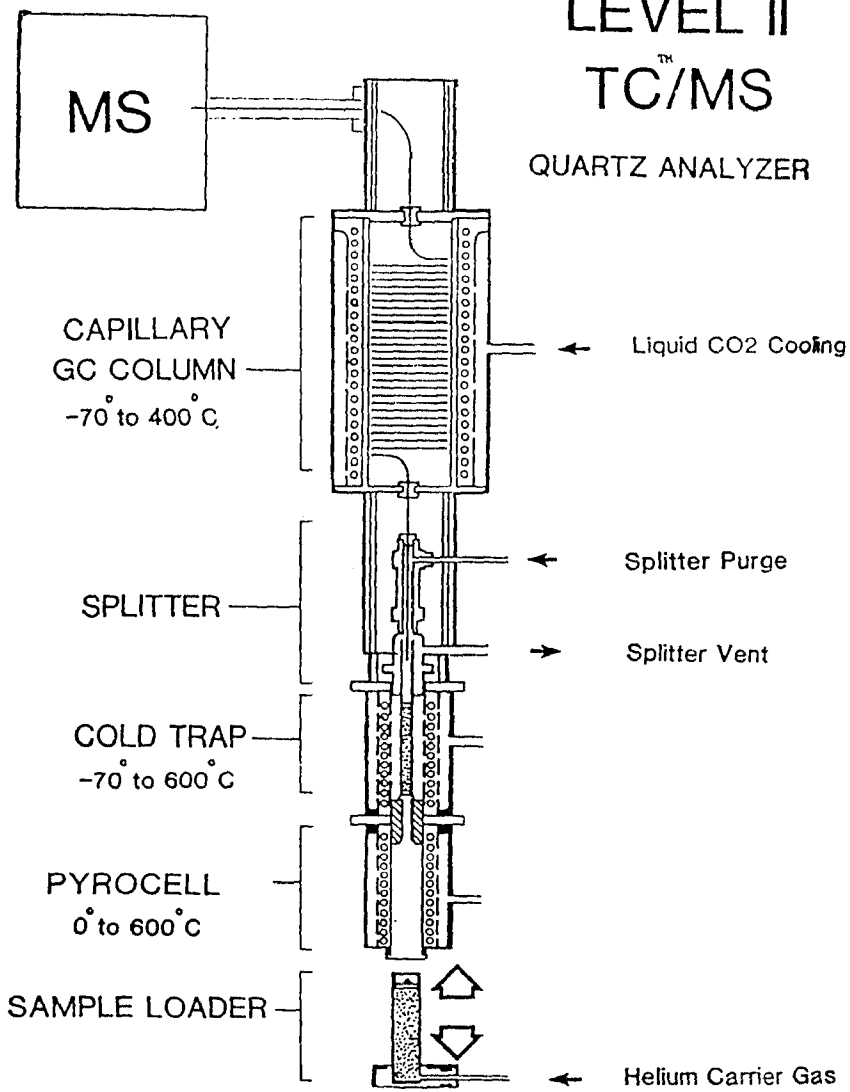
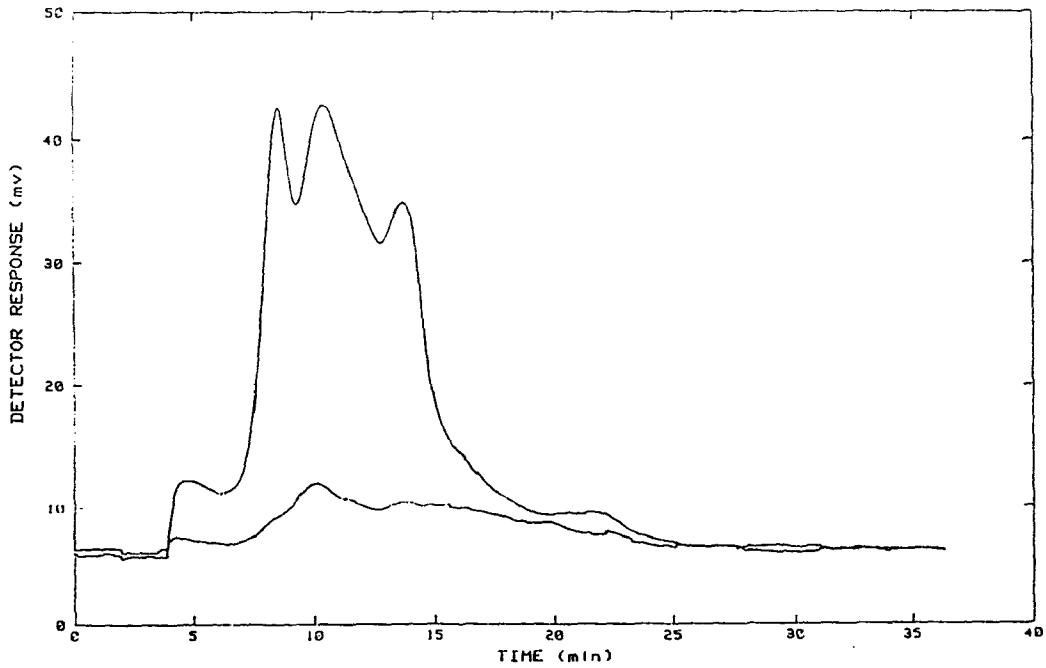


Figure 2 - (top) Level I thermal extraction profile (FID) from the Pyran analysis of two spiked synthetic sediment samples supplied by EPA; (middle) Total Ion Chromatogram, from scan 700 to 1200, from the Level II Pyran Analyses of the EPA #1 spiked synthetic sediment sample; (bottom) Total Ion Chromatogram, from scan 1200 to 2000, from the Level II Pyran analysis of the EPA #1 spiked synthetic sediment sample.


DETECTOR RESPONSE (mv)
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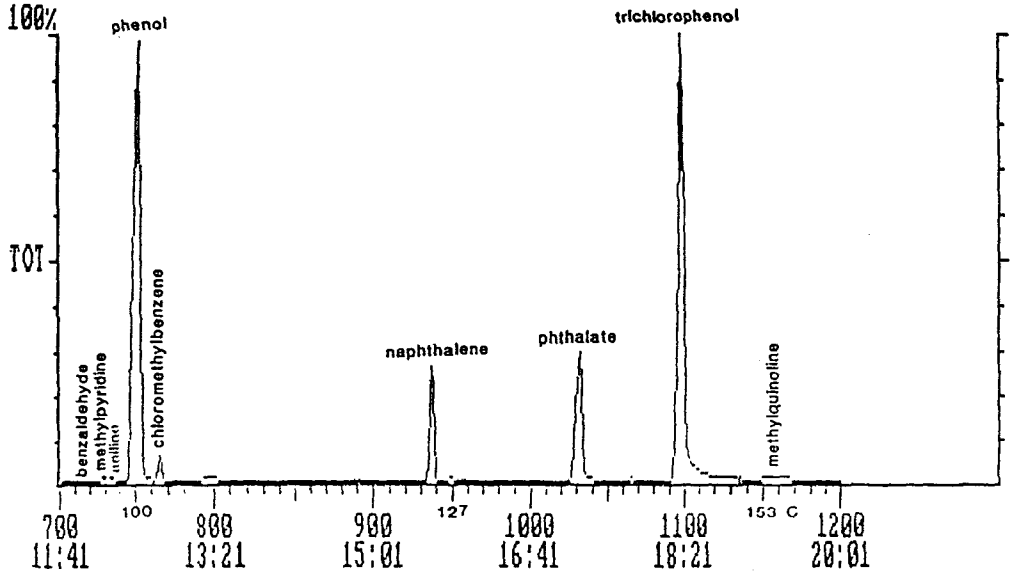
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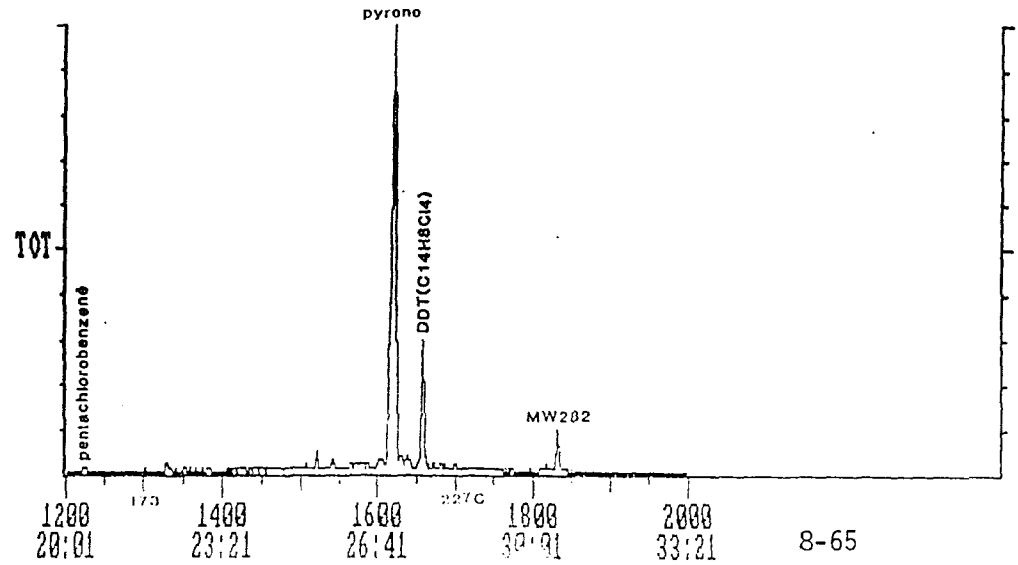
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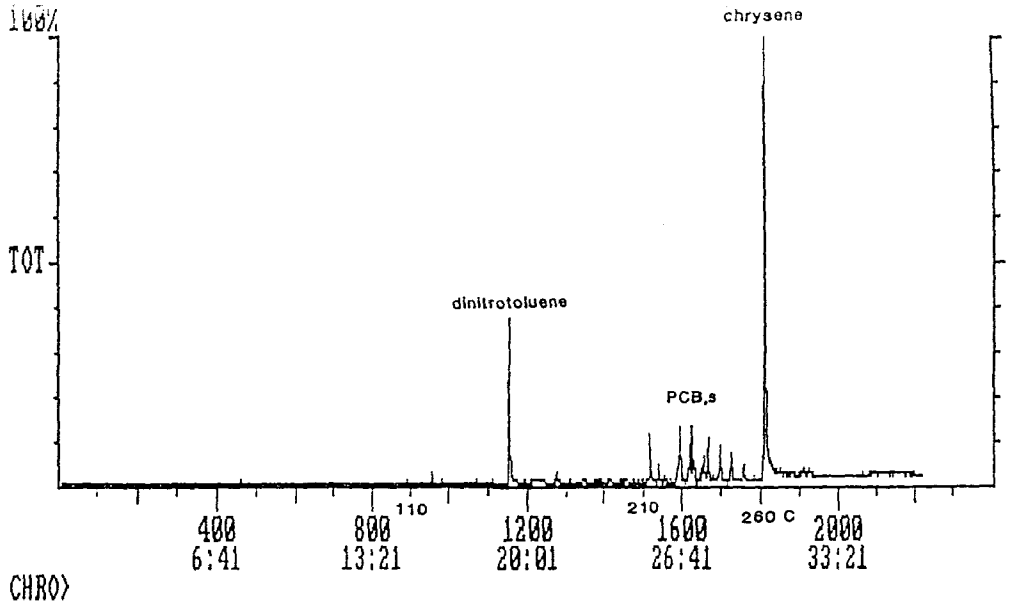
Figure 3 - (top) Total Ion Chromatogram from the Level II Pyran analysis of EPA #2 spiked synthetic sediment sample; (middle) Total Ion Chromatogram from the Level II Pyran Analysis, from scan 1500 to 1800, of EPA #2 spiked synthetic sediment samples; (bottom) Extracted Ion Current Profiles (M/e = 290 to 294, 324 to 328, and 258 to 362) from the Level II Pyran analysis of the same spiked sediment sample. These data show detection of PCB's in the sample.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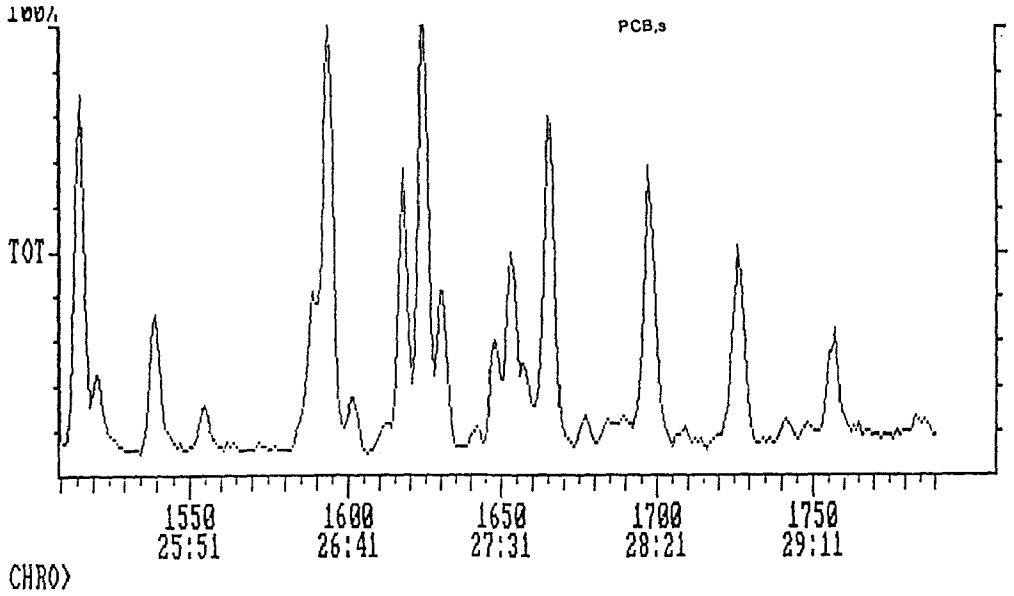
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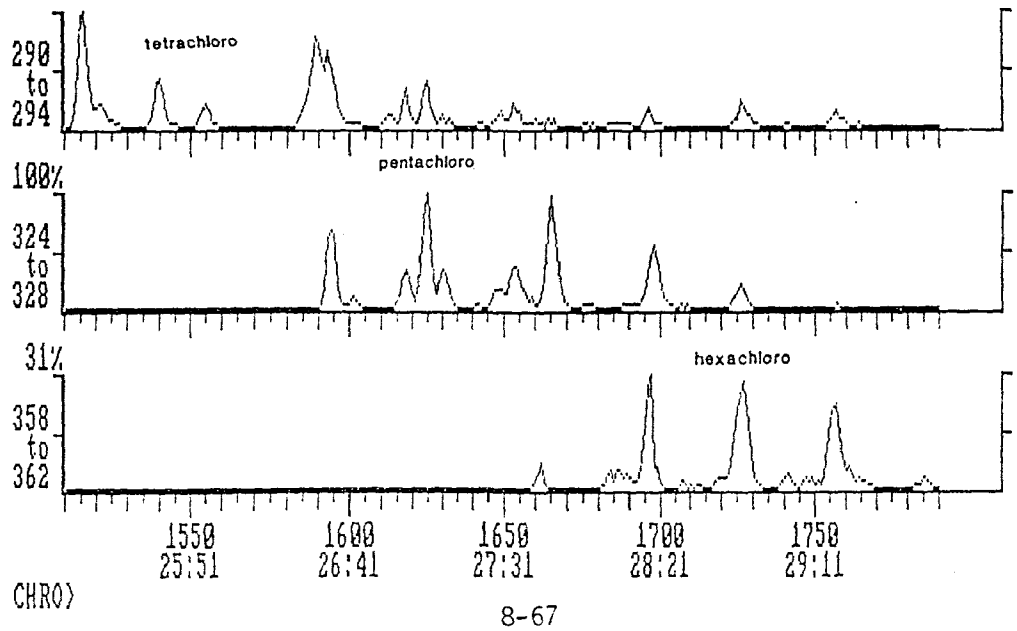
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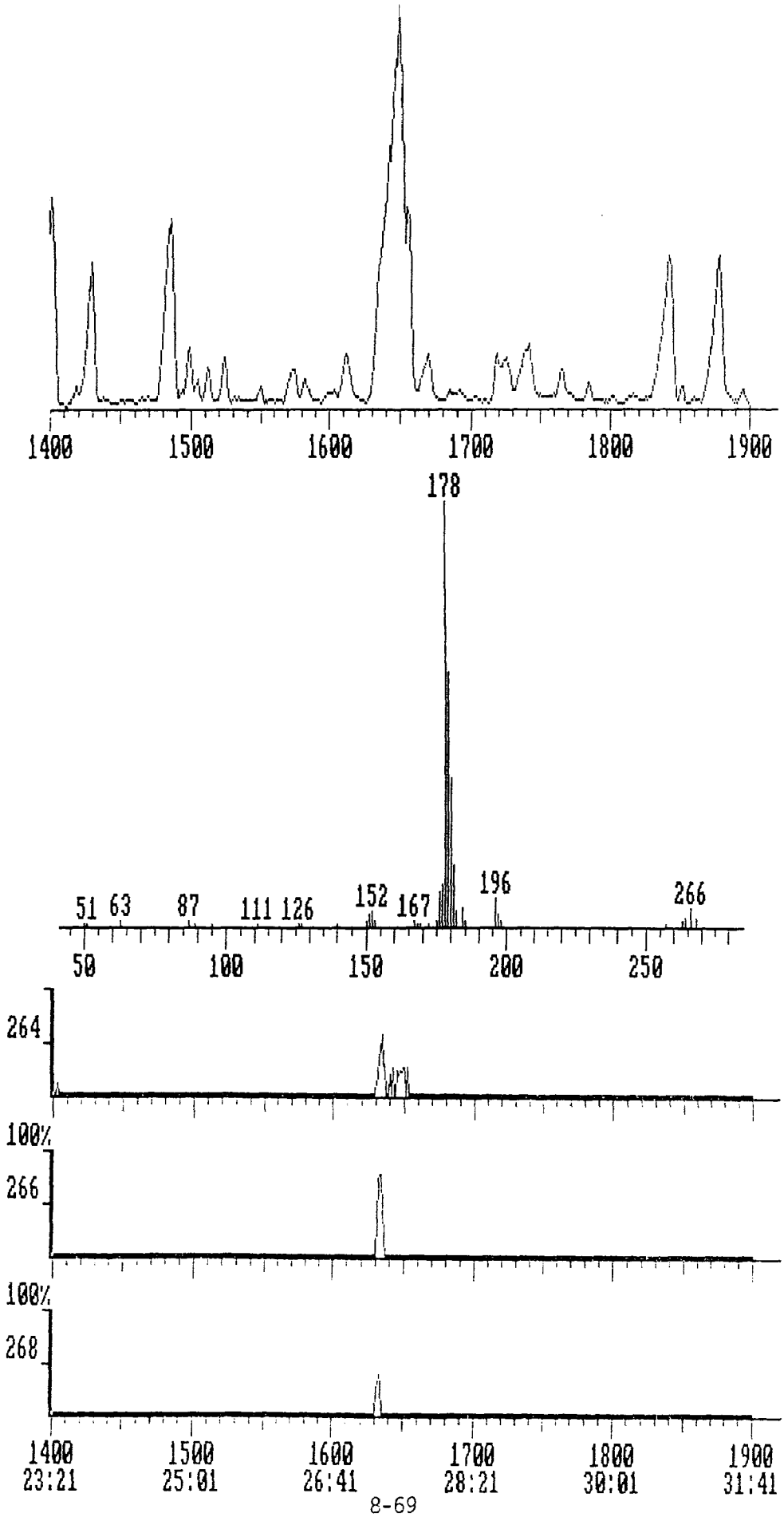
Figure 4 - (top) Total Ion Chromatograph, from scans 1400 to 1900, from the Pyran Level II analysis of a "penta" contaminated coal-tar sludge sample; (middle) mass spectrums of the large peak at scan 1640 (note presence of ions at 268, 266 and 264 from low levels of pentachlorophenol that coeluted with phenanthracene and anthracene; (bottom) Extracted Ton Current Profiles (M/e 268, 266 and 264) from the Pyran Level II GCMS analysis of the contaminants sludge samples shown in top and middle portion of this figure.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DEVELOPMENT OF SAMPLING/MONITORING GUIDANCE FOR THE RCRA HAZARDOUS WASTE REGULATORY PROGRAM

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ABSTRACT

Under the RCRA Hazardous Waste Regulations, it is the responsibility of waste generators to evaluate the wastes that they generate to determine whether their wastes exhibit any of the hazardous waste characteristics, and whether the concentration of toxic constituents exceeds any regulatory thresholds established within the revised hazardous waste listings. Wastes generated by industrial processes are variable in their composition and volume, depending on the nature of the product, the process, and various operational factors. As a result, one sampling and analysis of a waste is not sufficient to permanently identify a waste as hazardous or non-hazardous. Rather, it is essential that a continuing sampling and analysis, or monitoring, program be implemented by industrial waste generators to identify whether specific wastes are hazardous or non-hazardous over the lifetime of their generation.

This paper presents the results of an investigation into statistical methods for determining the number and frequency of samplings needed to adequately identify a waste as hazardous or non-hazardous over the lifetime of its generation. These statistical methods were supplemented with judgement factors and practical limitation to develop a recommended approach for EPA/OSW to adopt as guidance within the SW-846 Manual. The variability of industrial processes and the associated waste that they generate are considered as an integral part of this recommended approach. Other aspects of sampling/monitoring programs designed to fulfill regulatory requirements, such as grab versus composite sampling, are also discussed.

INTRODUCTION

Under the RCRA Hazardous Waste Identification Regulations (40 CFR 261), it is the responsibility of the waste generator to evaluate the wastes that he generates to determine whether these wastes are hazardous. Specifically, he must test each waste to determine whether it exhibits any of the hazardous waste characteristics or whether the concentration of toxic constituents in the waste exceeds any concentration-based regulatory thresholds which may be established within the hazardous waste listings.

Wastes generated by industrial processes are variable in their composition and volume, depending on the nature of the product, the process and various operational factors. Additionally, the measurement of waste characteristics or components is subject to the unavoidable measurement variability inherent in the sampling and analysis methods employed. As a result, one sampling and analysis of a waste is not sufficient to permanently identify a waste as non-hazardous. Rather, it is essential that a continuing sampling and analysis program be implemented by industrial waste generators to identify specific wastes as non-hazardous over the lifetime of their generation.

The ultimate objective of this investigation was to provide guidance to industrial waste generators to assist them in designing and optimizing their monitoring programs. This objective was met by developing an effective statistical method for estimating how frequently a waste must be sampled to adequately characterize it as non-hazardous. The statistical method was then supplemented with judgement factors and practical limitations to form a preliminary recommended approach for EPA/OSW to adopt as guidance within the SW-846 Manual.

Refinement of the method is continuing based on input and comments by EPA and others; the final guidance is scheduled for completion in September, 1987.

REQUIREMENTS OF THE GUIDANCE AND GENERAL ASSUMPTIONS

To facilitate the selection of an appropriate statistical method for estimating sampling frequency and the development of the associated sampling/monitoring guidance, it was first essential to list the general requirements and desirable elements of the guidance. These were listed as follows:

- The guidance should be oriented towards defining how frequently a generator must sample to confirm that their waste is non-hazardous. There is no minimum frequency for identifying a waste as hazardous.

- The sampling frequency should be designed to establish that a waste is non-hazardous with a high level of confidence.Therefore, greater waste variability should lead to a requirement for more frequent sampling.

- Proximity to regulatory thresholds is an important consideration in the establishment of an appropriate sampling frequency (i.e., wastes near a regulatory threshold need to be sampled more frequently).

- Volume of waste generated may be an element worthy of consideration in estimating an appropriate sampling frequency

(i.e., it may not be reasonable to request small-quantity generators to sample as frequently as large quantity generators).

- Statistical procedures for determining sampling frequency should be simple in their presentation and may need to be supplemented with judgment factors. The ability of the regulated community (industry) to implement the approach is an important consideration.

In order to narrow the scope of this investigation and make the development of the required guidance a manageable task, it was essential that a series of general assumptions be adopted with respect to the nature of industrially-generated wastes and the hazardous waste regulatory framework. The general assumptions that were adopted include:

- A waste should be managed as hazardous only when the mean waste value exceeds a regulatory threshold (a sequential or weighted mean would be appropriate for a time series of measurements).

- Industrially-generated wastes follow an approximate normal distribution in the variability of their characteristics and constituent concentrations under routine or continuous operating conditions. Start-up or changeover conditions can only be considered as separate events for the design of an appropriate sampling/monitoring program.

- Each waste has a principal potentially hazardous characteristic or constituent concentration for which a regulatory threshold is established in the hazardous waste regulations.

- It is not practical to separate measurement (sampling and analysis) variability from process variability in the statistical approach to estimating sampling frequency. The variability of any sampling/monitoring data must be considered as combined process and measurement variability.

GENERAL ELEMENTS OF THE STATISTICAL METHOD

Based on the requirements and desirable characteristics of the method previously developed and explained, the following additional criteria were developed as guidelines for defining frequency of sampling within the statistical method:

- For the statistical method to be useful, it must cause an increase in sampling frequency in response to (a) the mean

waste concentration approaching or surpassing a regulatory threshold or (b) large variability within the data set.

- Frequency of sampling should be based on trigger values that signal an increase in sampling frequency (i.e., reduction in the sampling interval). For instance, a trigger might be the point at which the probability is 90% that the sample mean is greater than 75% of a regulatory threshold.

- A conclusion that a waste is hazardous should not be based on a single concentration in excess of a regulatory threshold. Such an event should, however, trigger more frequent sampling, at least until sampling results return to a safe zone.

- Cumulative averaging should be employed to focus on the recent behavior of the waste generating process. This procedure also reduces the probability of the pertinent sample parameter exceeding a threshold by chance alone. However, the autocorrelation among neighboring sample means needs to be accounted for in any statistical tests.

- The method for determining sampling frequency should take into account recent advances in understanding of sampling variance components in the region of thresholds. This is a different problem from approaching a method detection threshold where measurement values are constrained or truncated by the logical impossibility of values less than zero.

DETAILED STATISTICAL METHOD

The above description of the desirable characteristics of the statistical method could lead to any of a large number of statistical techniques. The following techniques were considered for determining sampling frequency:

- A modified Shewhart Chart (Control Chart) with the entries normalized for sampling variance and based on at least two consecutive means out of the safe zone to trigger increased sampling beyond a calculated base level;

- Prediction intervals based on standard linear least squares regression techniques;

- Time series based on Box and Jenkins methods, lag k-sample autocorrelation analysis, semivariograms, or systems feedback control models;

- Non-parametric methods such as trend analysis, contingency analysis, concordance, or runs tests.

The method that was selected is based on a modified Shewhart Control Chart. Methods used to construct the control chart are related to linear least squares prediction intervals and incorporate certain aspects of Box-Jenkins time series methods as applied to systems feedback control. A complete mathematical description of the method is presented in Appendix 1. A brief summary of the method is provided below along with a description of the logic (see Figure 1).

The method is based on the calculation of a sequential mean of all sample results that is weighted toward the most recent result. This weighted mean, $\bar{X}_{w,t}$ is calculated at each sampling time and used in direct comparison to the pertinent regulatory threshold, L, to determine whether the waste is hazardous or non-hazardous (see Figure 1).

The heart of the method incorporates two statistical t-tests (at significance level α) to evaluate whether:

a) the weighted mean exceeds a defined percentage, P, of the regulatory threshold (test of approach to the regulatory threshold), or

b) the change in the weighted mean from the previous sampling, $\bar{X}_{w,t} - \bar{X}_{w,t-1}$, is greater than a preset maximum, c (test of excessive variance).

If either these two tests are not passed, then the sampling interval is reduced by a constant factor. If both of these tests are passed in consecutive time, then the sampling interval is increased by a constant factor.

METHOD PARAMETER VALUES AND LIMITING CONDITIONS

Prior to applying the method, it is first necessary to establish the value of various parameters of intended constant value that are contained in the method and to set boundary conditions with respect to minimum and maximum sampling intervals. The large number of parameters in the method provides for a high degree of flexibility in application to specific requirements but also requires the application of well-founded judgement to establish appropriate values for these parameters. Practical limitations dictate the requirement for a minimum and maximum sampling interval to avoid the potential extremes of a purely mathematical equation.

Suggested values for the parameters in the equations are provided below. (See Appendix 1 for a description of the development of

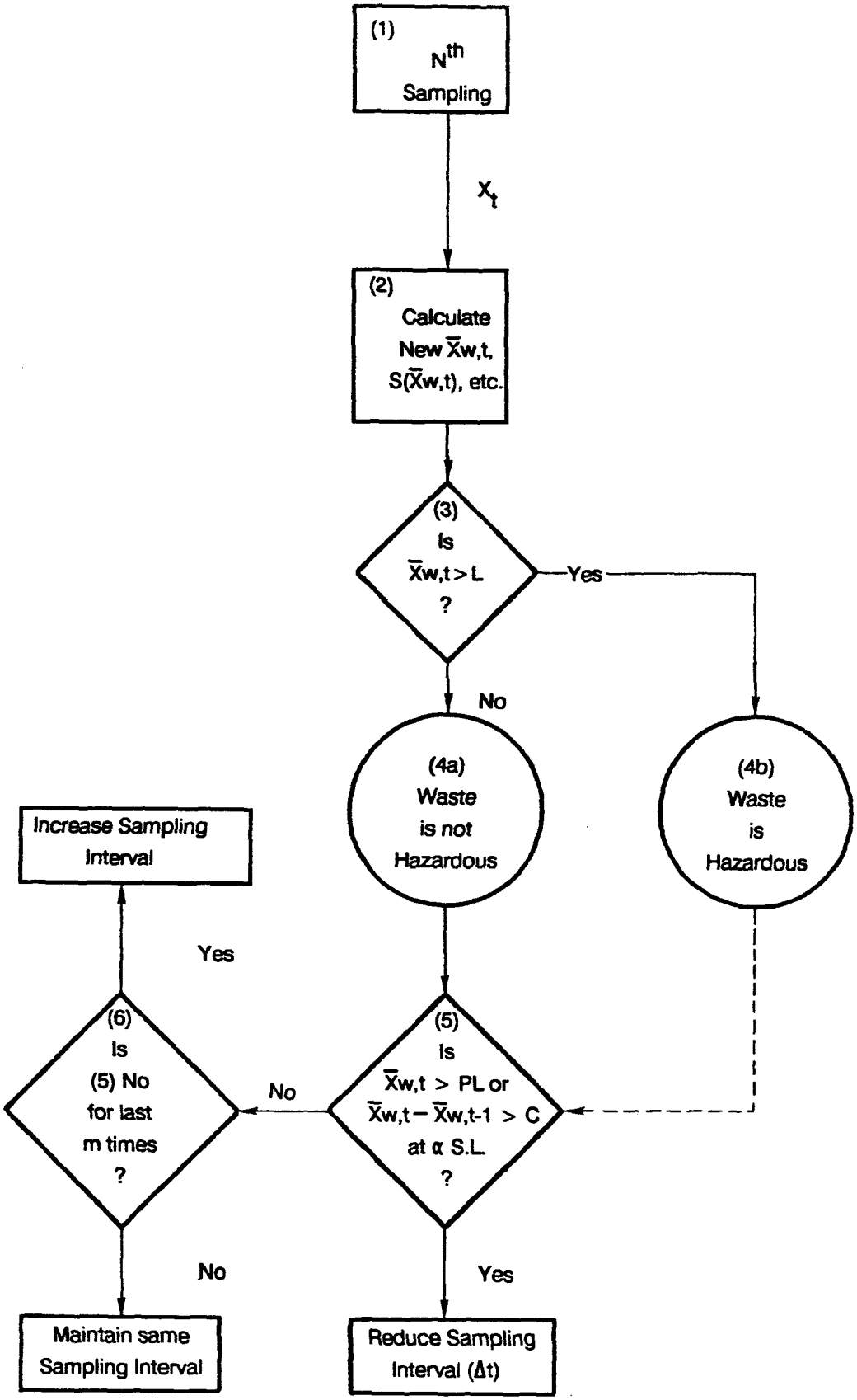


FIGURE 1. Logic Diagram for the Statistical Method

these parameters and the associated equations). These suggested values have been selected based on limited numerical simulation of the method, real world practicality, and engineering judgement.

Symbol	Description	Suggested Value
L	Regulatory Threshold	-
P	% of Regulatory Threshold (action trigger level)	0.68
m	Number of repeated values which triggers a decrease in sampling frequency	5
λ	Mean weighting factor	0.5
c	Maximum acceptable deviation in sequential sample means.	0.1L
h	Sampling frequency regulating factor	0.25

The diversity of waste generators makes it impractical to propose one set of maximum/minimum sampling intervals or significance levels that would fairly apply to all generators. What is reasonable for a high volume waste generator may be too stringent for the low volume generator. Recognizing this fact, we propose breaking down the world of waste generators into four categories based on volume of waste generated. Each generator category would have associated with it specific minimum and maximum sampling intervals as well as a specific significance level to apply within the two t-tests. The table below lists the authors suggested values for the four recommended waste categories:

Waste Volume Category (Kg./Mo.)	Sampling Interval Min.	Max.	Significance Level (α)
< 100	2 Yr.	2 Yr.	NA
100 - 1000	3 Mo.	2 Yr.	0.05
1000 - 10,000	1 Mo.	1 Yr.	0.10
10,000 - 100,000	1 Wk.	3.Mo.	0.2

Under this system the small volume waste generator (< 100 kg/mo.) is exempted from the rigors of the statistical method. The low

volume of waste represented by this category does not justify a sophisticated monitoring program. The remaining categories and their sampling intervals are self explanatory.

In considering the suggested significance levels above, it is important to understand that the intent of the system is to reduce the burden on the smaller generator. Thus, for example, it must be demonstrated to a higher level of confidence that the smaller generators weighted average waste value is in excess of the trigger value. This higher confidence level requirement makes it less likely that a given sample will force the smaller generator to increase his sampling frequency. Conversely, the lower confidence level (higher significance level) specified for the larger generator makes it more likely that a given sample result will trigger an increase in sampling frequency.

Before any statistical analyses may be performed, it is also necessary to have some minimum quantity of data with which to work. In order to allow use of this method as quickly as possible, the authors suggest that at a minimum three samples be collected at the minimum applicable sampling interval. The mean of these three samples can than be used to initiate the statistical method. If the generator has valid historical data, it may be used. This three-sample minimum is also applicable in the case of start up of a monitoring program or for remonitoring a waste stream after a significant process change.

METHOD PERFORMANCE

To test the method that was developed on a preliminary basis and to evaluate tentative optimum values for the various parameters within the method, a number of computer data simulations were run. The results of these simulations, involving thousands of data points, suggested the parameter values previously listed. The results of two of these simulations are presented graphically in Figures 2-4 and 5-7, respectively to illustrate the functioning of the method and to present the control chart concept for graphing the two test statistics. Both examples were calculated based on a high volume generator. In both simulations, it is assumed that the regulatory threshold is 10 PPM and PL is 7.5 PPM. The graphs also depict only every fourth data point to improve graph readability.

The first example (Figures 2-4) is of a steady state process that demonstrates a low degree of variance and a relatively stable mean as shown in Figure 2. As can be seen, the mean is generally below the PL of 7.5. As long as the mean is below PL, any data points in excess of PL can be attributed to random variability and are not statistically significant.

Using this data to perform the two T tests described in the statistical method produces the graph shown in Figure 3. This figure graphs the T statistic (T1) for the hypothesis that the mean value of X is greater than PL and that the weighted average of the previous data is significantly different from the weighted average generated from the most recent data. The confidence levels shown on the graph correspond to the critical values of T, appropriate for a high volume generator. The T-statistic graph indicates that in all but three cases the mean does not exceed PL with any degree of statistical significance. The three cases over the 95% confidence limit signify that a generator who produced this data would have to increase his sampling frequency.

The graph of the second T-statistic (T2) indicates that the sequential sample means do not differ significantly in most cases. The graph shows 1 case where the difference in sequential sample means may have been significant. This data point would trigger an increase in sampling frequency based excess sequential sample mean variability.

The third graph (Figure 4) shows the change in sampling interval in response to each new sample. From Figure 2 it can be seen that initially most of the data is below PL, thus no decrease in sampling interval is required, rather as sets of 5 samples below PL are collected the sample interval increases to the maximum allowable interval. As the sample mean and the individual data points start to exceed Pl, the T-statistic triggers a corresponding decrease in sample interval.

The second example data set is shown in Figure 5. The first half of this graph shows a data set with a gradually increasing mean and a high degree of variability that eventually exceed PL. The second half of the graph illustrates a data set with gradually decreasing mean and variability.

Figure 6 provides the graph of the T-statistics associated with this data set. As can be seen from the graph there are 6 T-statistic data points that indicate with a high degree of probability that PL has been exceeded. These 6 points correspond to the region in Figure 5 where the mean does rise above PL. In only one case does Figure 6 indicate that the sequential means varied significantly. From this graph one would expect the 6 points that exceeded PL and the 1 point indicating high variability in the sequential mean should trigger a reduction in sampling interval. Indeed, as shown in Figure 7, this is the case, as the mean exceeds PL, the sample interval does drop. As the sample mean and variability decrease the sample lengthens until it stabilizes at the maximum interval.

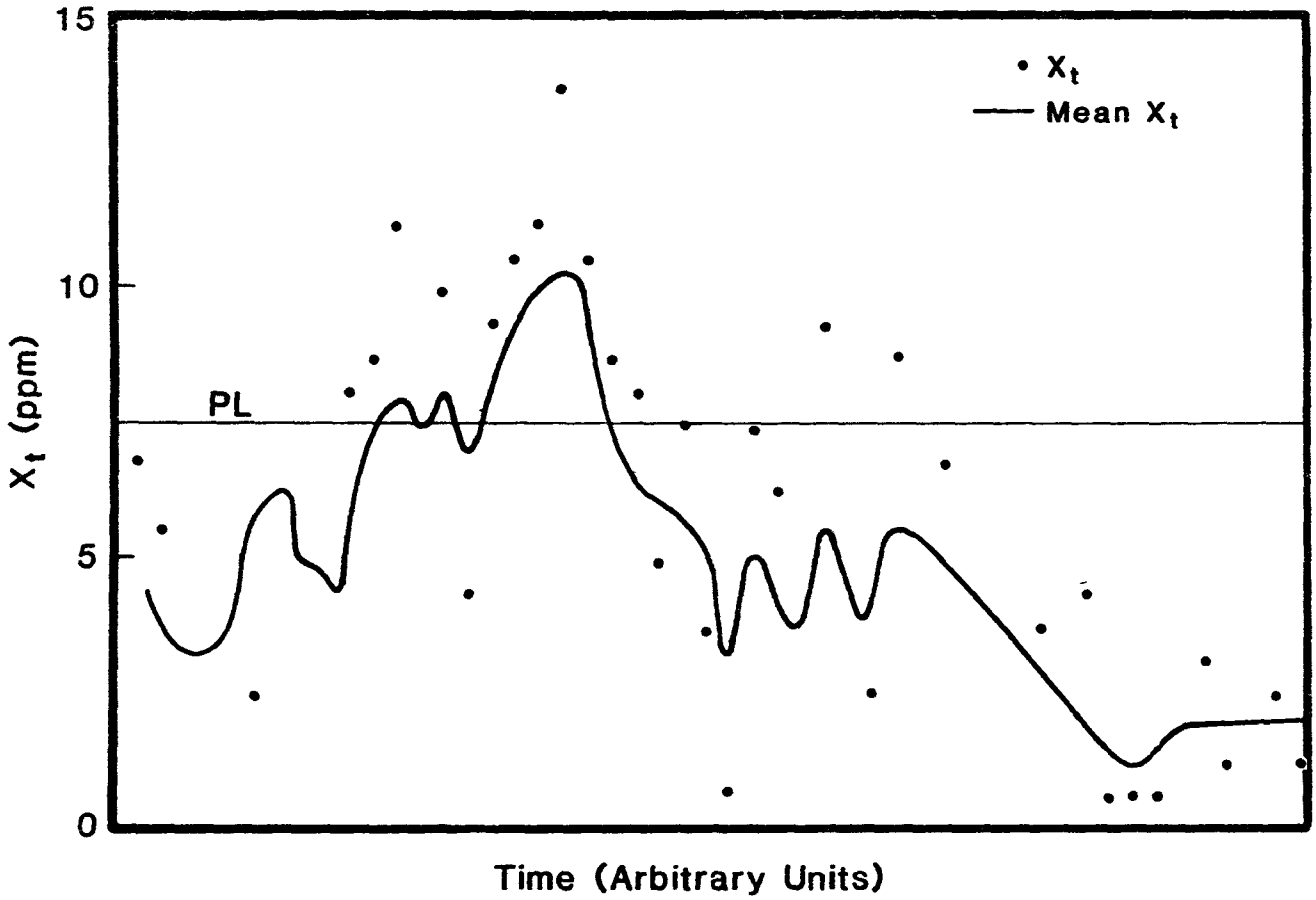


FIGURE 2. Example 1, x_t and Mean x_t Versus Time.

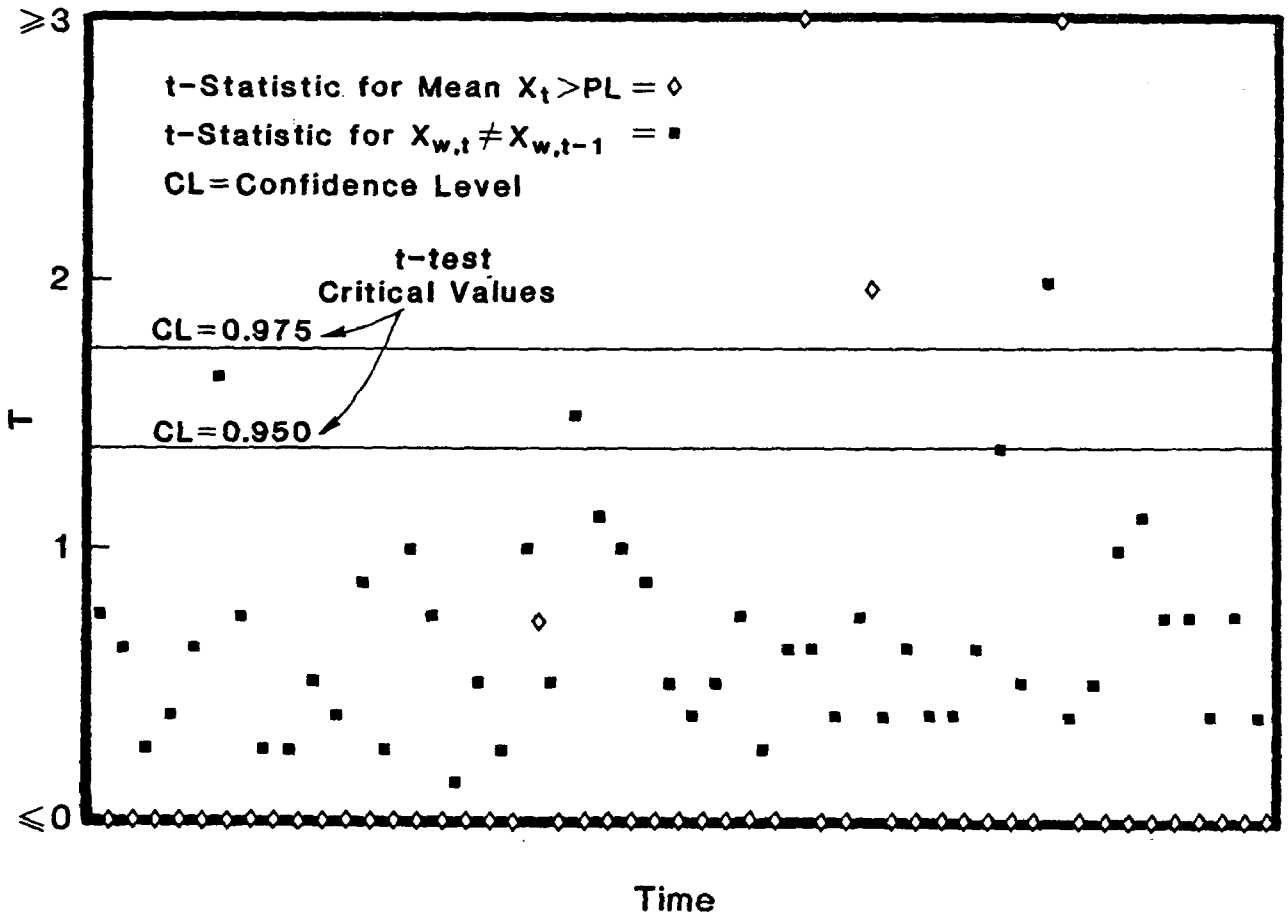


FIGURE 3. Example 1, T-Statistic Versus Time.

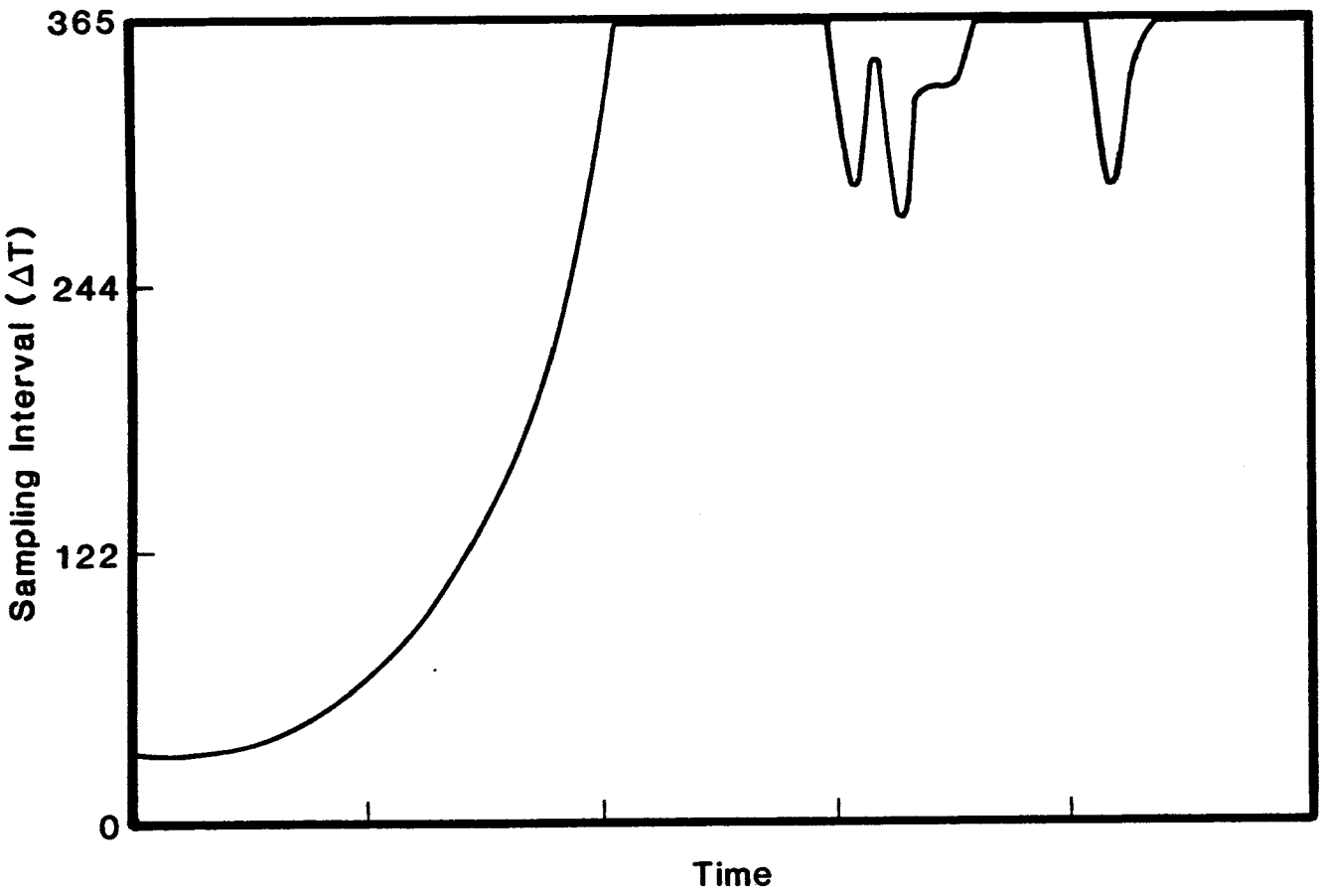


FIGURE 4. Example 1, Sampling Interval Versus Time.

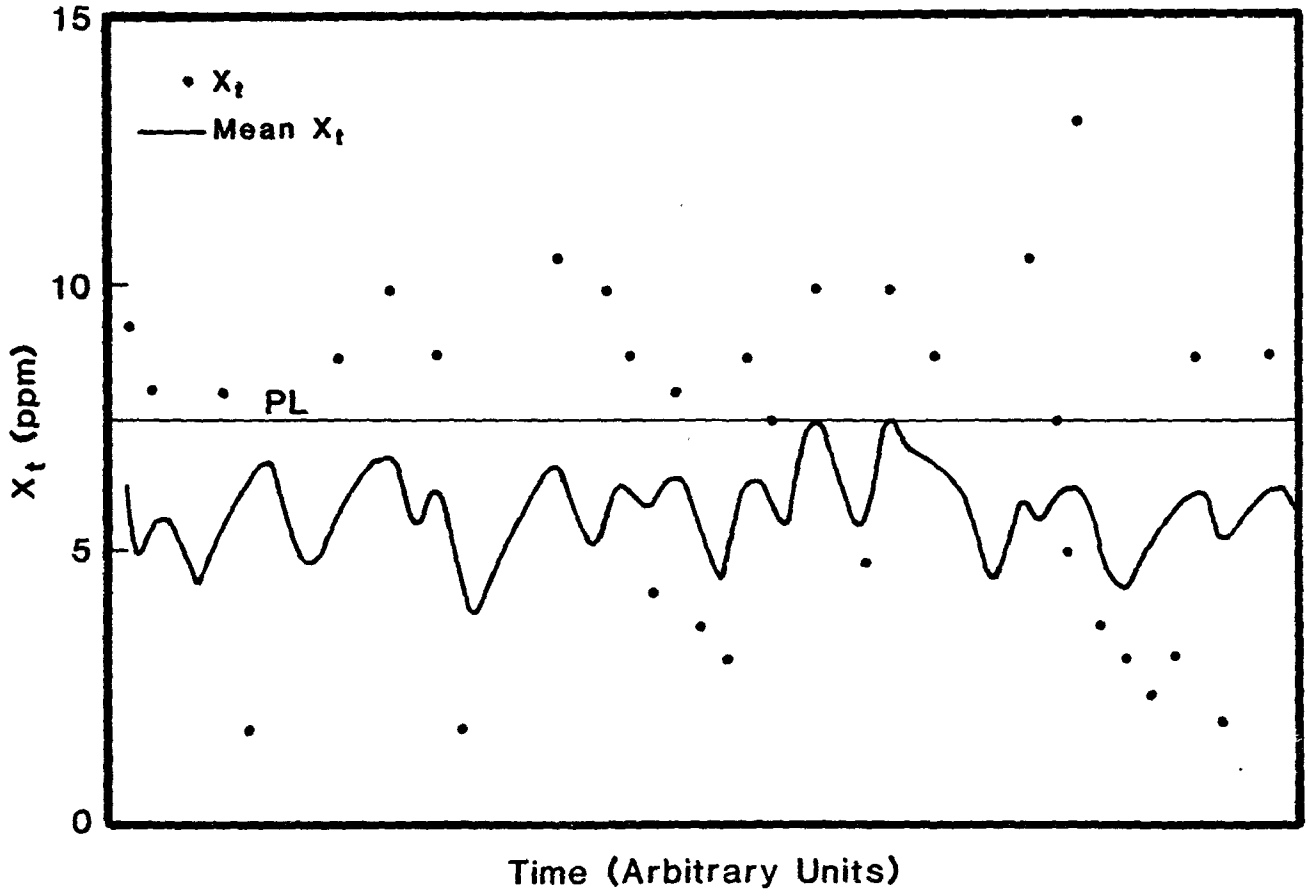


FIGURE 5. Example 2, x_t and Mean x_t Versus Time.

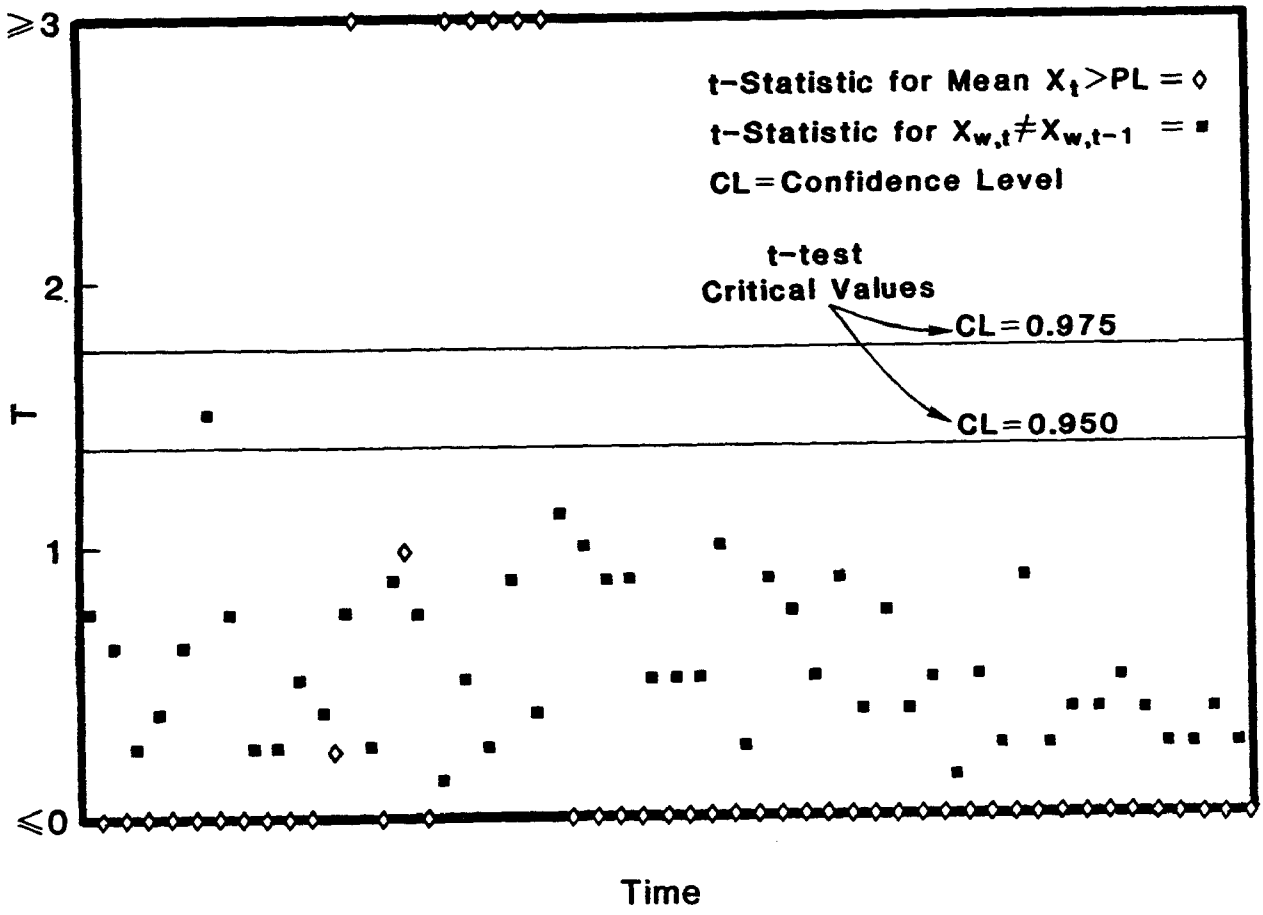


FIGURE 6. Example 2, T-Statistic Versus Time.

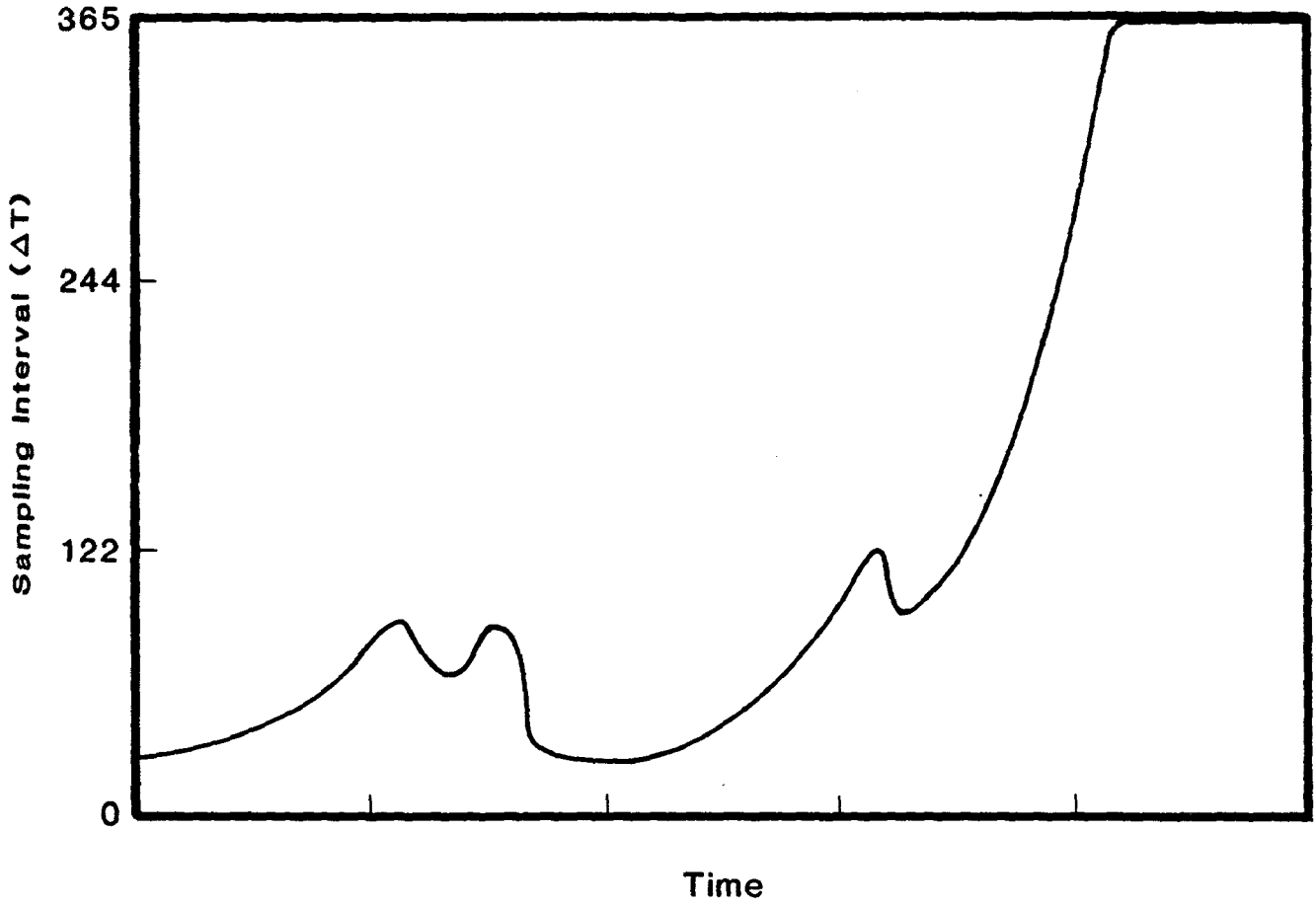


FIGURE 7. Example 2, Sampling Interval Versus Time.

APPENDIX I

Mathematical Description of the Statistical Method

In the method, we specify the regulatory threshold (L) and the percentage of the threshold that may not be exceeded (P). We also select a parameter λ (λ:$0 < \lambda < 1$) specifying how far back in the time series of sampling results (x_t) to average. We suggest $\lambda = 0.5$. After obtaining the sample result of time t (the nth Sampling), the method then proceeds as follows:

1. Calculate the weighted average waste concentration:

$$\bar{x}_{w,t} = \lambda x_t + (1 - \lambda)\, \bar{x}_{w,t-1}. \qquad (1)$$

   * NOTE that this is a recursive calculation based on the previous average. The calculation damps the effect of single extranneous values of x_t.

2. Calculate the unweighted mean and variance of x_t:

$$\bar{x}_n = \frac{1}{n} \sum_{t=1}^{n} x_t \qquad (2)$$

$$S^2(\bar{x}_n) = \frac{1}{n-1} \sum_{t=1}^{n} (x_t - \bar{x}_n)^2 \qquad (3)$$

3. Calculate the following variance, covariance, and auto correlation coefficients:

$$r_0 = \frac{1}{n} \sum_{t=1}^{n} (x_t - \bar{x}_n)^2 \qquad (4)$$

$$r_1 = \frac{1}{n} \sum^{n-1} \left[x_t - \bar{x}_n\right] \left[x_{t+1} - \bar{x}_n\right] \quad (5)$$

$$r = r_1 / r_0 \quad (6)$$

4. Calculate the sequential variance.

$$S^2\left[\bar{x}_{w,n}\right] = S^2\left[\bar{x}_n\right]\left[1 + \frac{2(n+1)}{n} r\right] \quad (7)$$

5. Calculate the following test statistic.

$$T_1 = \frac{\left[\bar{x}_{w,t} - PL\right]}{\sqrt{S^2\left[\bar{x}_{w,n}\right]/n}} \quad (8)$$

If T_1 > the one-sided critical value for the student t-statistic at significance α, then it is inferred that $\bar{x}_{w,n}$ exceeds PL.

We now calculate a parameter (θ) that will be used for a statistical test of excess variability in the time series of x_t.

6. Calculate $z = (r_0 + 2r_1)/r_1$. (9)

7. θ can be obtained by solving for the roots θ of the equation

$$(1 - \theta - z(1 - \theta) + z = 0 \quad (10)$$

or

$$\theta^2 + (Z - 2)\ \theta\ + 1 = 0 \quad (11)$$

*This is done by setting a = 1, b = z − 2, c = 1 and then choosing the root.

$$\theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{12}$$

for which $-1 < \theta < 1$.

8. Calculate the following variables based on deviations in $\bar{x}_{w,t}$ between time step n and n − 1.

$$a_t = \left| \bar{x}_{w,t} - \bar{x}_{w,t-1} \right| \tag{13}$$

$$s^2 \left[a_t \right] = - r_1 / \theta \tag{14}$$

where r_1 was calculated in equation 7.

9. Calculate the following test statistic.

$$T_2 = \frac{a_t - c}{\sqrt{s^2 \left[a_t \right] / n}} \tag{15}$$

Where c = a maximum acceptable deviation ($|\bar{x}_{w,t} - \bar{x}_{w,t-1}|$). If T > the two-sided critical value for the student - t statistic at significance $\alpha/2$ then it is inferred that the change from $\bar{x}_{t-1}$ to $\bar{x}_t$ is excessive.

10. If $\bar{x}_{w,n}$ exceeds PL (step 5) or a_t exceeds c (step 9) then

$$(\Delta t)_{n+1} = (1-h)(\Delta t)_n \tag{16}$$

where $(\Delta t)_{n+1}$ is the time interval between the n and n + 1 sampling periods and 0 < h < 1.

11. If neither test statistic (steps 5 and 9) exceeds its critical value for m time steps, the time interval between sampling periods in lengthened by defining $(\Delta t_{n+1}) = (1+h)(\Delta t)_n$.

12. The process is iterative and is performed after each sampling period. Therefore, first update the following variables:

$$t_n + (\Delta t)_{n+1} \rightarrow t_{n+1}$$

$$1 - \theta \rightarrow \lambda$$

then return to step 1.

RAPID FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ENVIRONMENTAL SAMPLES UTILIZING A MICROCHIP GAS CHROMATOGRAPH

Edward B. Overton, Professor and Director, Tom H. McKinney, Charles F. Steele, Edward S. Collard, Robert W. Sherman, Research Associates, Institute for Environmental Studies, Louisiana State University, Baton Rouge, Louisiana

ABSTRACT

A microchip gas chromatograph with high resolution capillary columns has been linked to an external personal computer allowing for rapid analysis of environmental samples in the field. The instrument can be used for the analysis of volatile organic compounds in air, water, and soil samples during site investigations and cleanup activities. The time required for analysis is approximately two minutes. A modified, temperature independent Kovats index system in which the retention times of the reference compounds are calculated at ambient temperatures rather than measured eliminates the need for standard gases in the field and minimizes the need for temperature control. Telemetry techniques allow the microchip gas chromatograph to be operated in the field by a technician while the chromatographic data are analyzed by a chemist in a central laboratory if necessary.

A portable sorption tube concentration device has been developed to increase the overall sensitivity of the analytical procedure. The concentrator may be used to analyze water samples for volatile organics using a "purge and trap" technique.

The microchip gas chromatograph has been interfaced with an Ion Trap Detector. This allows the speed and resolution of the microchip gas chromatograph to be combined with the compound identification capability of a mass spectrometer.

INTRODUCTION

Cleanup activities under Superfund involving both emergency removals and remedial actions require the analysis of samples for volatile organic compounds. Analytical data obtained from field instruments can supplement data obtained from laboratory analysis. Field instrumentation that allows for rapid analysis of air and water samples enables officials to perform site investigations and cleanup activities in a more effective and cost-efficient manner. Field instruments in common use today, such as the portable flame ionization and photoionization detectors, are capable of vapor detection but lack inherent analytical powers that can be found in more sophisticated instruments.

DISCUSSION

The Micromonitor 500 (MM500), manufactured by Microsensor Technology Inc., Fremont, California, possesses the inherent analytical capability to greatly enhance the rapid acquisition of reliable chemical data in field situations (Sadat and Terry 1984). The analytical capabilities of the instrument are based on compound separation with high resolution capillary columns and detection with non-specific thermal conductivity detectors. The Micromonitor 500 contains several high resolution gas chromatographic modules with different column lengths. Vapor samples are drawn into the instrument by an internal vacuum pump. The sample gas is then routed to the appropriate gas chromatographic modules and specific volatile components are separated, detected, and then identified by the instrument's internal computer system.

We have made modifications to the instrument to increase its effectiveness for field environmental analysis and to overcome some of its limitations as it comes from the factory. In addition, we have developed a portable concentrator to increase the overall analytical sensitivity. As it comes from the factory, the MM500 is designed to be portable and has the capability to detect and identify several dozen preselected chemical vapors (Wohltjen 1984). The instrument is completely self-contained with an internal battery and carrier gas supply. The compounds which each commercial version of the instrument can identify are selected by the user and preset during construction at the factory. The instrument will detect up to 10 of the preselected volatile chemicals during any one analytical cycle. If one of these 10 gases is detected, the results of the analysis will be displayed on a LCD readout in a manner such as "BENZENE DETECTED 85 PPM." The instrument detects volatile chemical by first predicting their retention times at the ambient temperature and then integrating chromatographic peaks which elute at the anticipated retention times.

Even considering the powerful analytical capabilities inherent in the MM500's design configuration utilizing microchip gas chromatographic modules with high resolution capillary columns, the instrument has several limitations that impact its ability to be used during responses to chemical releases. These limitations are as follows. Commercial versions of the devise can only detect compounds which have been preselected and can be identified by parameters stored in its internal ROM library. Large quantities of other vapors could be present but would go undetected by the MM500. Further, the presence of common fuels which contain many individual components, such as gasoline, will confuse the MM500's computerized interpretation of data. Also, large quantities of a preselected vapor will go undetected because when the capillary columns become overloaded the retention times of the preselected compounds will be outside of expected retention time windows. Finally, detection

limits are too high by factors of ten to one hundred for commercial versions of the device when they are used to detect toxic levels of hazardous chemicals at or below TLV concentrations.

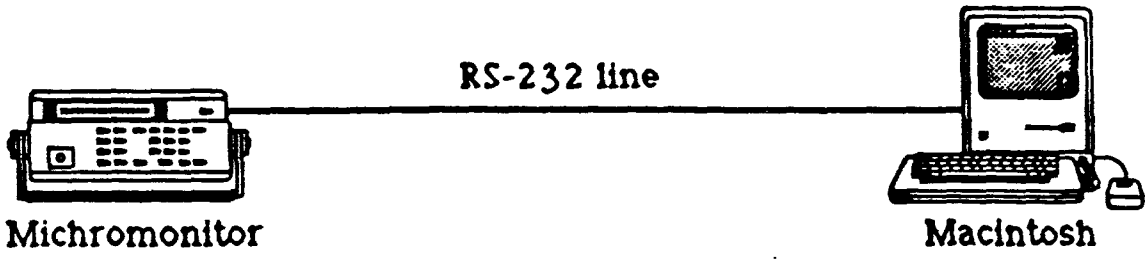
In order to circumvent these technical limitations and to take full advantage of the considerable analytical capabilities resident in the MM500, we have developed methods to control the instrument and retrieve raw chromatographic data with an external microcomputer. The acquired data are processed by special software that allows for rapid chemical analysis of vapor samples.

Our development efforts take advantage of the unique and considerable computational powers of the Apple Macintosh™ microcomputer linked, through a RS232 interface, to the MM500. The software we have developed provides three basic modes of operation for the MM500-Macintosh™ ensemble. Initial versions are designed primarily for qualitative analysis while subsequent software will provide capabilities for both qualitative and quantitative analysis. All of these operational modes rely on the MM500 as the analytical probe with data treatments and reductions done in the Macintosh™. The connection between the devices is bidirectional bit serial giving the capability for the instrument control and data transmission. The RS232 ports can be linked by a variety of methods including twisted pair cables, modems using telephone lines, radiofrequency modems, or any combination of these. Figure 1 is a schematic diagram showing the various connections that have been used to link the MM500 to a Macintosh™. These various connections can be used to allow data to be collected in the field using a MM500 as the analytical probe and, shortly thereafter, to be interpreted by a chemist at an analytical laboratory situated anywhere in the country. This capability means that the analytical sensor can be operated by a field technician with minimal training in chemical analytical methods. The data can be interpreted as sites remote to the analytical device by scientists with special training in the use of chromatographic analytical methods.

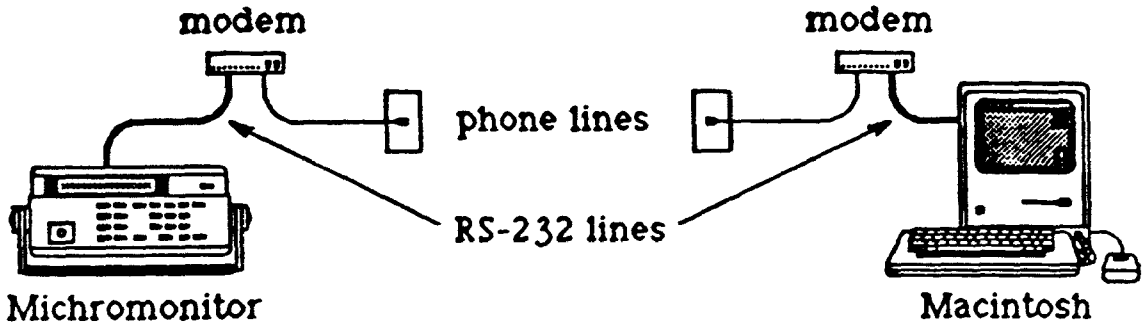
The first of the three analytical modes of operation provides access to all of MM500's standard procedures using the external microcomputer. A picture of the front panel, similar to that shown in Figure 2, is displayed on the computer's CRT. By moving the cursor over buttons on the front panel's display and clicking the mouse, the operator can perform the same functions that could be performed by actually pushing buttons on the front panel. However, use of the Macinstosh™ external to the MM500 allows for the analysis to be performed by a trained scientist situated at locations remote to the analytical sensor. For example, the MM500 can be placed in the field, convenient to sampling locations, and be operated from a command post or analytical laboratory.

Michromonitor telemetry

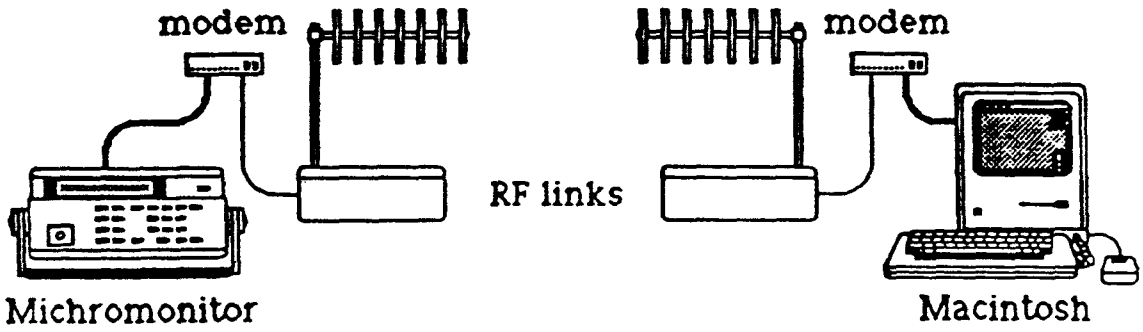
1. Conventional



2. Phone lines



3. RF links



4. Phone lines and RF links

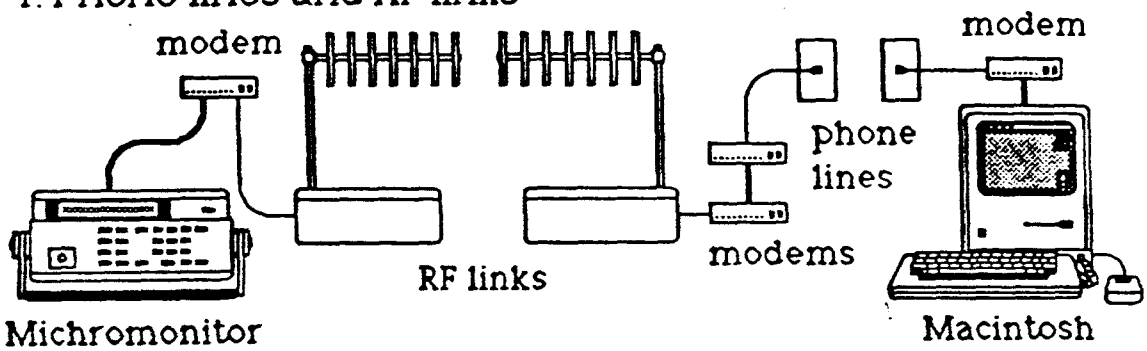


Figure 1. Various ways to connect the MM500 with an external microcomputer.

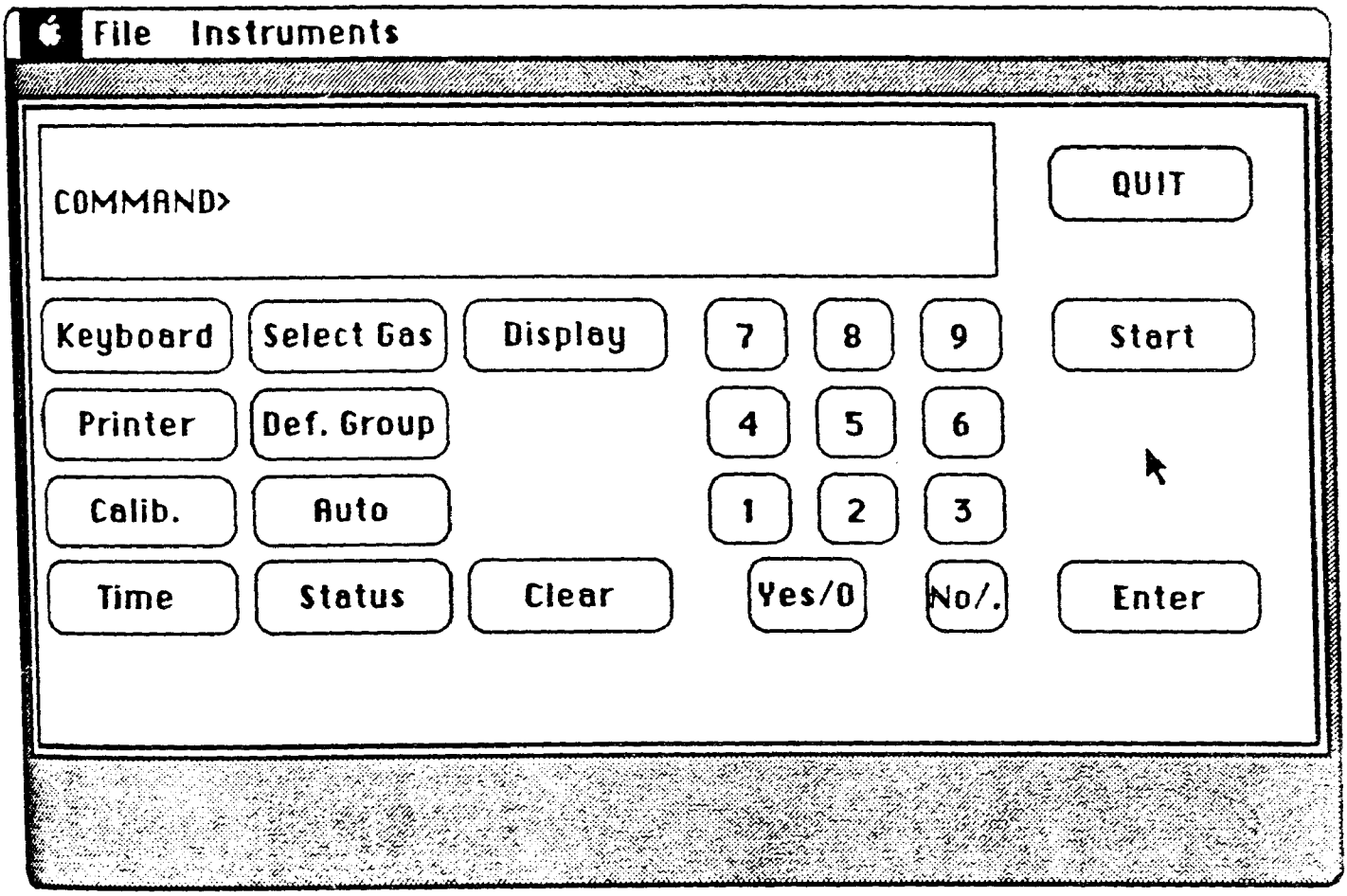


Figure 2. CRT display of MM500's front panel.

The second mode of operation for the MM500 package allows the devise to analyze samples and dump raw digitized chromatographic data to the Macintosh™. The data are converted into displays of the gas chromotograms that were produced by the instrument's analytical modules. These types of displays allow peak shapes, elution profiles, peak areas and instrument drift to be evaluated. Figure 3 shows copies of the CRT display for the chromatographic profiles obtained from the analysis of the same sample by two different analytical modules. The displays show the outputs from the high, medium, and low gain amplifiers of the signal from the thermal conductivity detector on each analytical module.

The third mode of operation is the most useful analytical package but also the most complex. The MM500 analyzes a sample with a user selected analytical module and stores data on the retention times and peak areas of all peaks in the chromatogram. The ambient temperature is also measured and stored. These data are transmitted to the Macintosh™. The software uses information on the retention times of the reference peak (air peak) and ambient temperature to calculate expected retention times for normal hydrocarbon standards as if they had been analyzed concurrently with the actual sample. Using these calculated retention times, for ethane (C_2) through undecane (C_{11}), the software then calculates Kovats retention indices (Kovats, 1958) for all peaks in the analytical run. A report, similar to that shown in Figures 4 and 5, is then displayed on the Macintosh™. The report tabulates retention times, retention indices, peak areas, and the name of compounds in the retention library that have the closest index to the calculated index for each peak. A second part of the report shows a display of the compounds in the library that have retention indices within 10% of the retention index for each peak with compound names highlighted if the retention index is within 1% of the peak's index. A histogram, resembling 9 gas chromatograms with very narrow peaks, is also displayed as an aid for interpreting the analytical data. This mode of operation provides data that can be used primarily for qualitative identifications although peak areas are also given. It is important to emphasize that identifications based on gas chromatographic retention time or index comparisons are limited by the resolution of the chromatographic columns. Care must be exercised when interpreting gas chromatographic analytical data to include as much information as possible concerning the origin of the sample as well as any other facts that may aid accurate qualitative interpretation of chromatographic data.

Each chromatographic module in the MM500 is designed to analyze chemicals within a certain range of volatities. The most volatile components are separated and detected with a module which uses a four meter capillary column. The least volatile components are analyzed on a module using a 0.5 meter capillary column. The range of volatilities for compounds appropriate for analysis with the

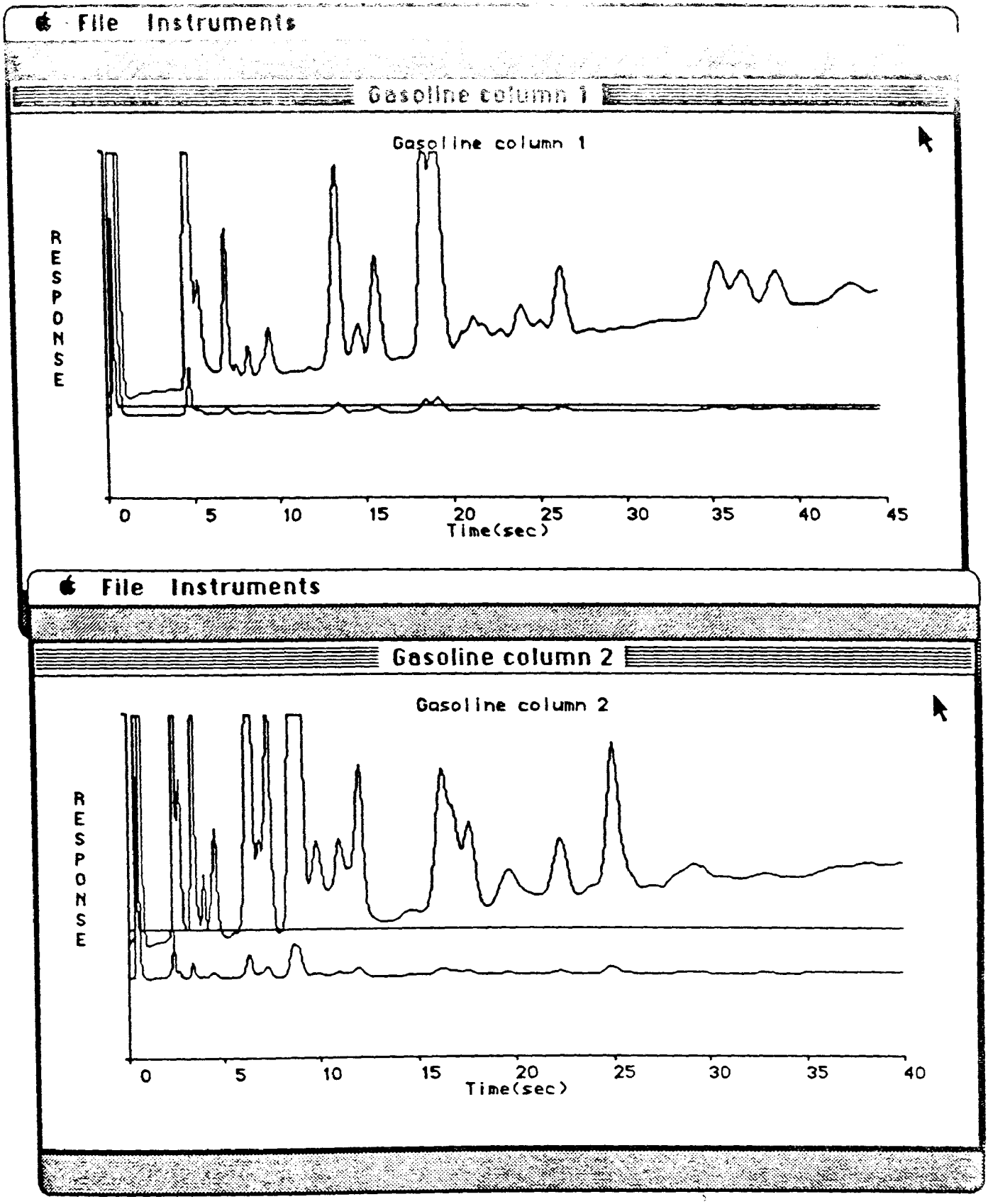


Figure 3. CRT displays from the MM500's analysis of a gasoline sample using a 4 m by 0.1 mm ID DB 1701 column with 0.5 micron film thickness (top), and a 2 m by 0.1 mm ID DB 1701 column with 0.5 micron film thickness (bottom).

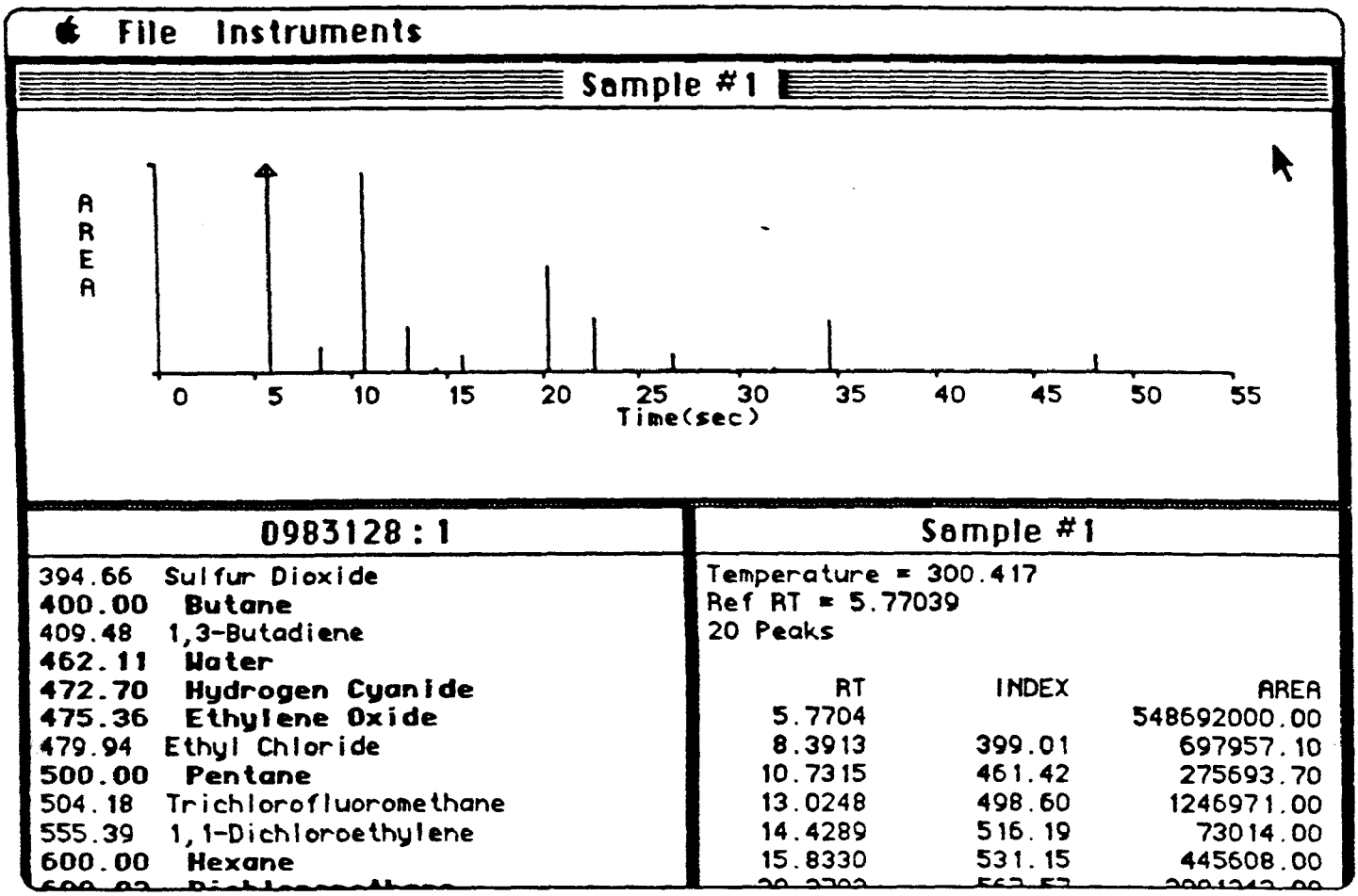


Figure 4. CRT display from MM500's analysis of a sample of unknown content with bar plot shown in the foreground, using a 4 m by 0.1 mm ID DB 1701 column with 0.5 micron film thickness.

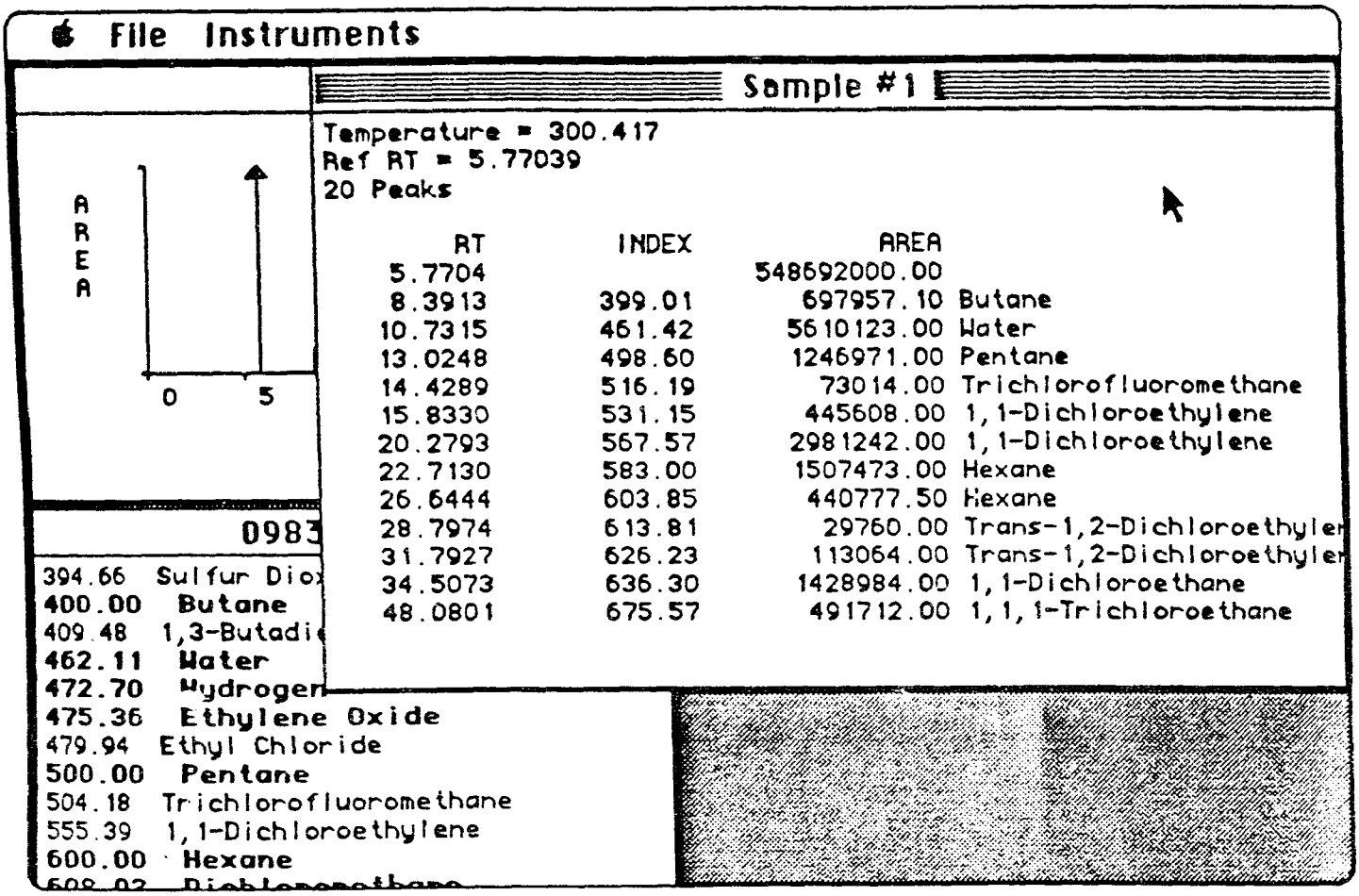


Figure 5. CRT display from MM500's analysis of a sample of of unknown content with analytical report window shown in the foreground, using a 4 m by 0.1 mm ID DB 1701 column with 0.5 micron film thickness.

MM500 encompasses chemicals that have a room temperature vapor pressure of approximately 1 mm of Hg and higher. This range includes all of those compounds that are classified by the EPA as volatile priority pollutants.

Table 1 contains the retention times and retention indices for several representative vapors that were analyzed with a single analytical module at three different temperatures. These temperatures included room temperatures plus and minus 20°C. Examination of this data reveals that retention times can change by a factor of 200% for every 20°C change in operational temperature. This means that retention times cannot be reliable used to provide qualitative information on the identities of specific peaks. On the other hand, retention indices change by less that 3% for every 20°C change in operation temperature. These temperature independent retention indices can be readily converted to meaningful qualitative information about the volatile components in air samples.

Because the MM500 uses an extremely small sample loop (80 nanoliters) to collect vapors for analysis, its minimum detection limit is approximately 10 ppm for most compounds. These detection limits are too high for many environmental applications. However, we have circumvented this limitation by designing a field deployable sorption tube concentration device. This device is used to concentrate volatile organic chemicals in large sample volumes (200-400 ml) on ambient temperature sorption traps and desorb the volatile organics at 250°C into much smaller volumes (2 ml). The device is outlined schematically in Figure 6.

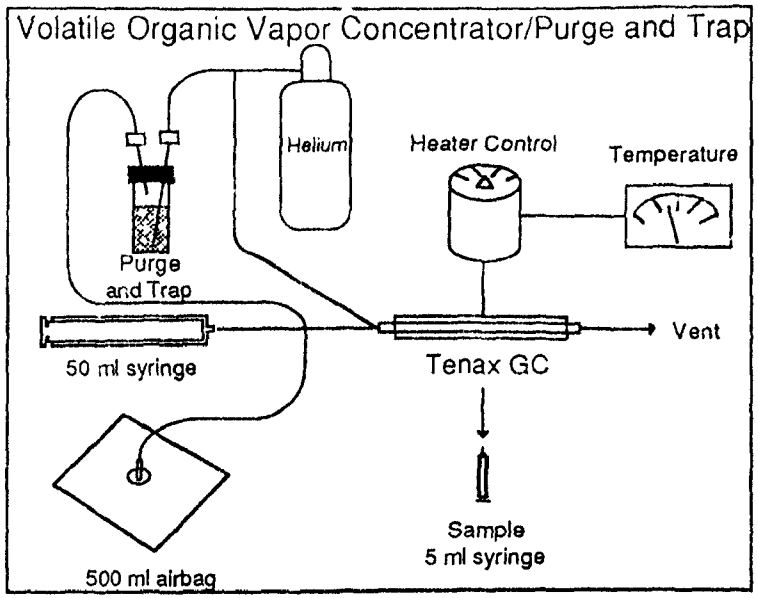
This concentrator differs from others which are commercially available in that the same very small Tenax traps are used repeatedly, providing reproducible trapping characteristics. The time required for sample concentration is on the order of five minutes. The recoveries of several volatile components are given in Figure 7 and Table II.

In addition to concentrating volatile components in air samples, we have developed a technique to concentrate volatile components in water and sediment samples (purge and trap technique) in the field using the same portable concentrator. This technique and some preliminary data are shown in Figures 8 and 9 and Table III.

The microchip gas chromatograph has been interfaced with the Finnigan Model 700 Ion Trap Detector (Finnigan MAT, San Jose, CA) allowing the speed and resolution of the microchip gas chromatograph to be combined with the compound identification capability of a mass spectrometer as shown in Figure 10. The two instruments were interfaced by using a short length (2-5 meters) of capillary column (DB 1701, 0.1 micron film thickness) to connect the gas chromatograph module to the open split interface of the Ion Trap

Table 1. Retention Indexes calculated at three temperatures

Gas Temp (°K)-->	RT low 280	RI low	RT med 300	RI med	RT high 320	RI high
HEXANE	2.991	600.00	2.106	600.00	1.673	600.00
CARBON TETRACHLORIDE	5.434	684.76	3.235	695.90	2.196	706.27
HEPTANE	6.166	700.00	3.314	700.00	2.147	700.00
CHLOROFORM	6.157	699.82	3.454	707.46	2.257	716.03
BENZENE	6.626	708.26	3.699	719.26	2.380	731.60
1,2-DICHLOROETHANE	7.878	727.56	4.144	737.79	2.541	749.27
TRICHLOROETHYLENE	8.883	740.51	4.505	750.69	2.674	762.11
OCTANE	15.898	800.00	6.396	800.00	3.166	800.00
TOLUENE	17.471	811.08	7.460	820.81	3.725	829.15
NONANE	38.124	900.00	14.079	900.00	5.944	900.00


Volatile Organic Vapor Concentrator/Purge and Trap
Helium
Heater Control
Temperature
Purge
and Trap
Vent
50 ml syringe
Tenax GC
Sample
5 ml syringe
500 ml airbag

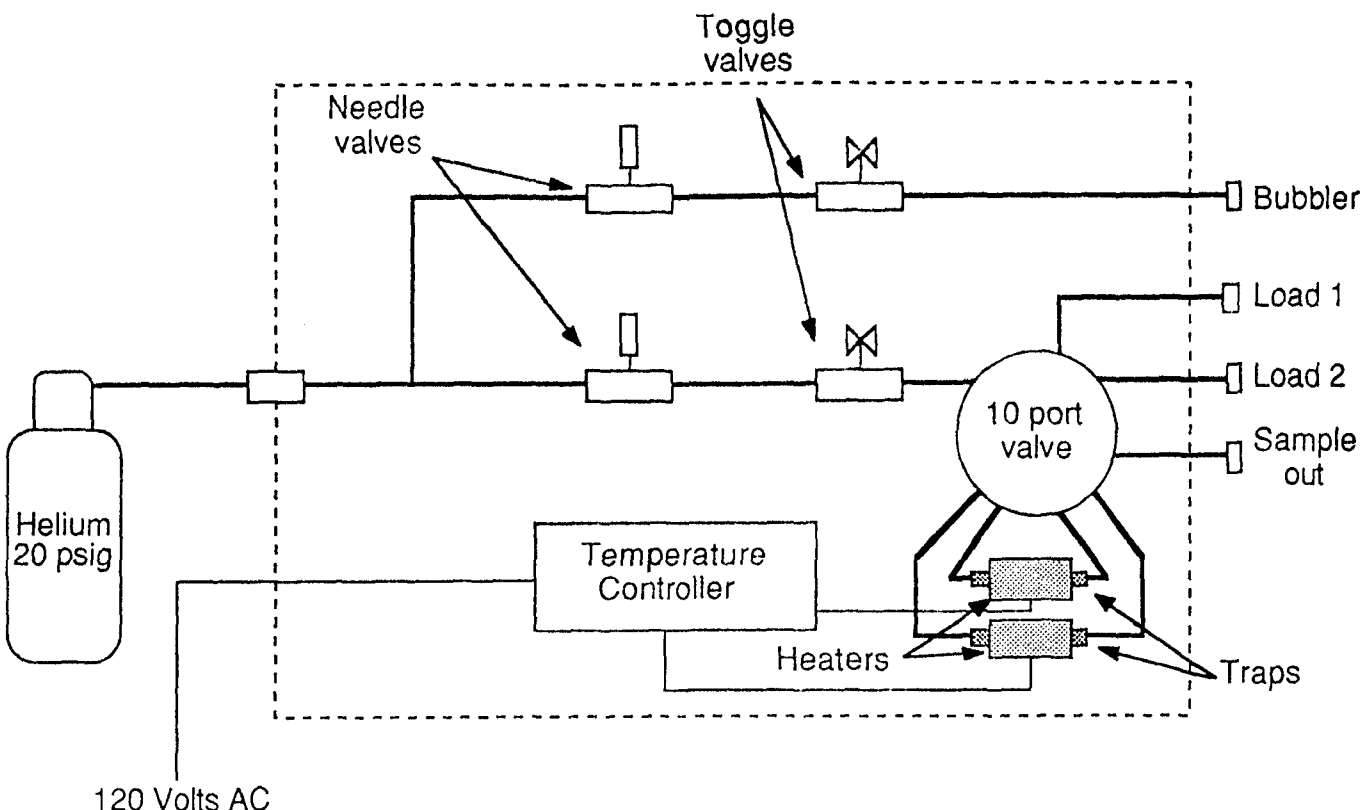

Toggle
valves
Needle
valves
Bubbler
Load 1
Load 2
Sample
out
10 port
valve
Helium
20 psig
Temperature
Controller
Heaters
Traps
120 Volts AC

Figure 6

VOLATILES IN AIR
1ppm v/v
BEFORE CONCENTRATION
AFTER CONCENTRATION
(100:1)
1- CHCl3
2- BENZENE
3- 1,2-DCP
4- BrCHCl2
5- TOLUENE
6- C2Cl4
1
2
3
4
5
6
2
4
6
8
seconds

FIGURE 7

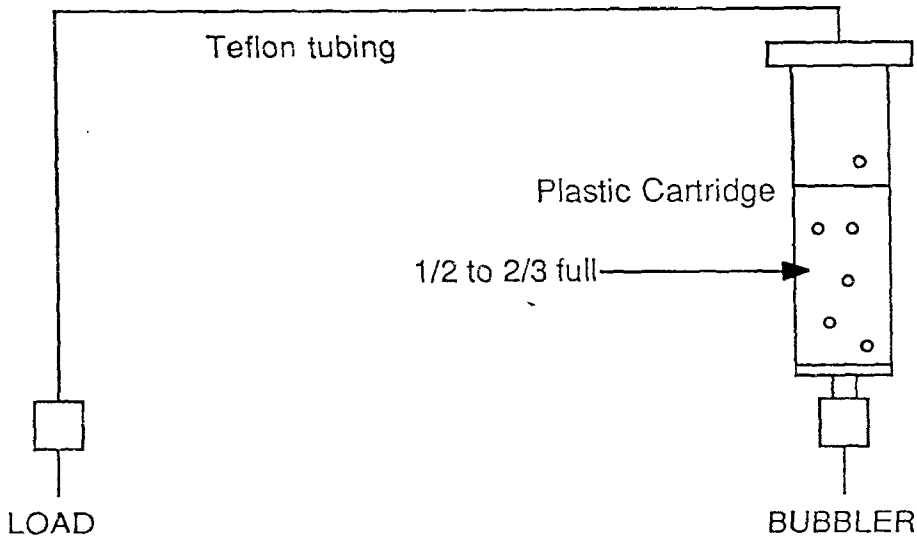
RECOVERY OF VOLATILE COMPONENTS
150ppb (v/v), 200 ml air sample

CCl4	CHCl3	Benzene	1,2-DCP	BrCHCl2	Toluene	CCl4	Br2CHCl
36.1	64.5	74.8	91.8	89.5	86.5		120.7
38.1	62.6	66.5	91.3	86.9	95	84.1	110.8
36.7	62.3	67.1	72.4	86.3	92.4	80.8	
36.9	63.1	69.5	85.2	87.6	91.3	82.4	115.7
.1	1.2	4.6	11	1.7	4.3	2.3	7

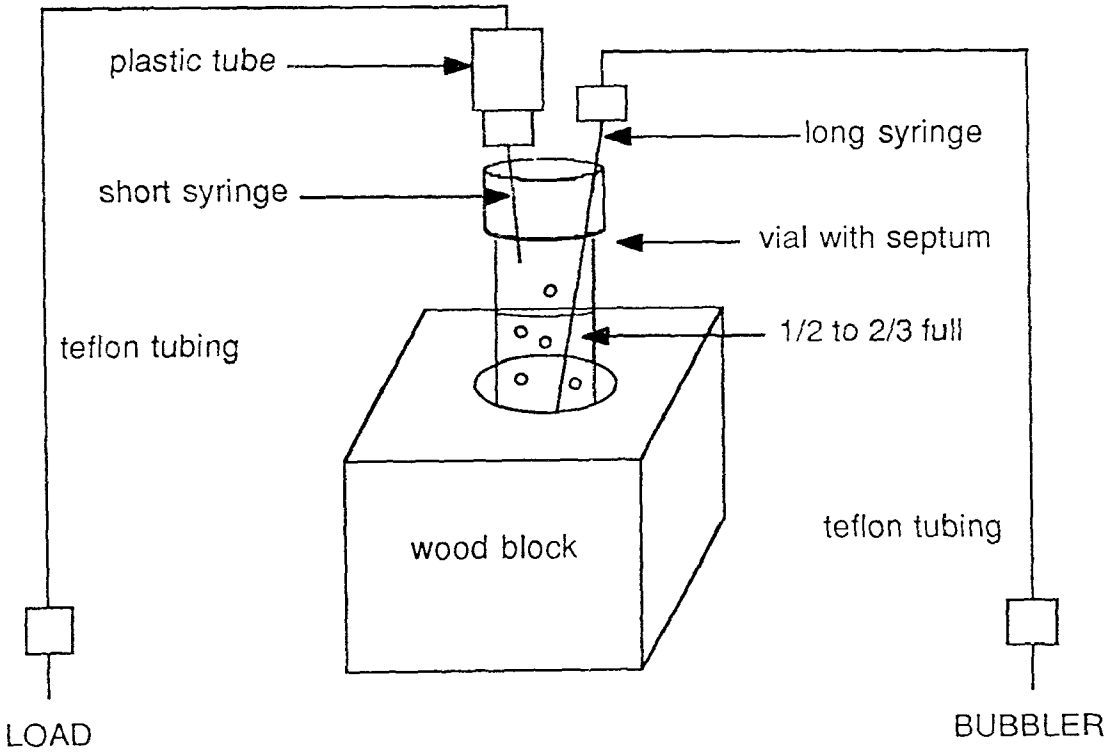
Table 2

FIGURE 8

Plastic Cartridge



Glass Vial



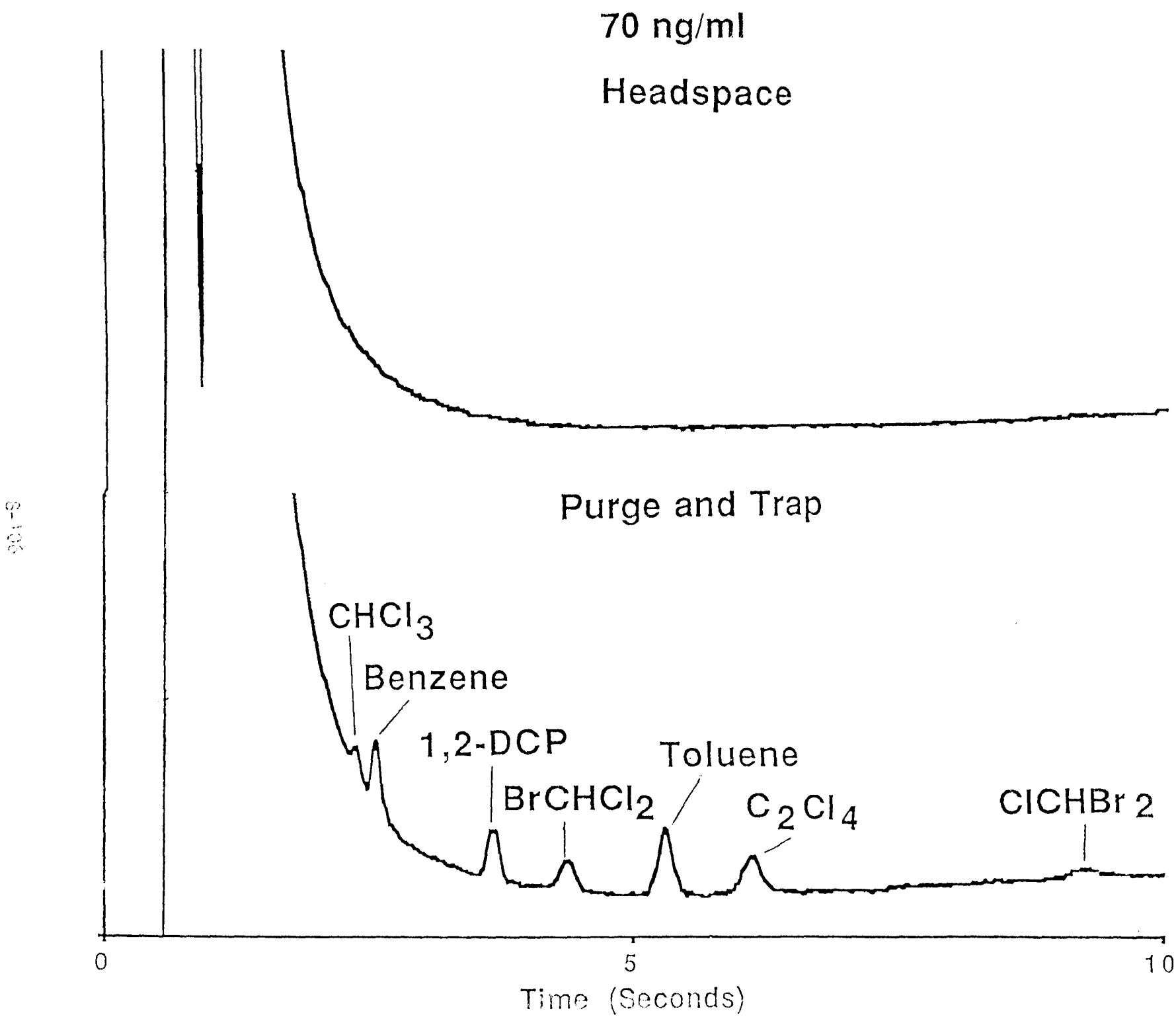

70 ng/ml
Headspace
Purge and Trap
CHCl3
Benzene
1,2-DCP
BrCHCl2
Toluene
C2Cl4
ClCHBr2
0
5
10
Time (Seconds)

FIGURE 9

60 ng/ml

% Recovery

$CHCl_3$	Benzene	1,2-DCP	$BrCHCl_2$	Toluene	C_2Cl_4	Br_2CHCl
76.6	59.0	74.7	88.4	97.0	114.7	107.6
	62.0	79.1	96.0	108.3	108.8	113.9
	56.7	73.9	89.1	105.8	102.3	109.2
76.6	59.2	75.9	91.2	103.7	108.6	110.2
	2.7	2.8	4.2	5.9	6.2	3.3

Purge and Trap
Lower Detection Limits (ng/ml)

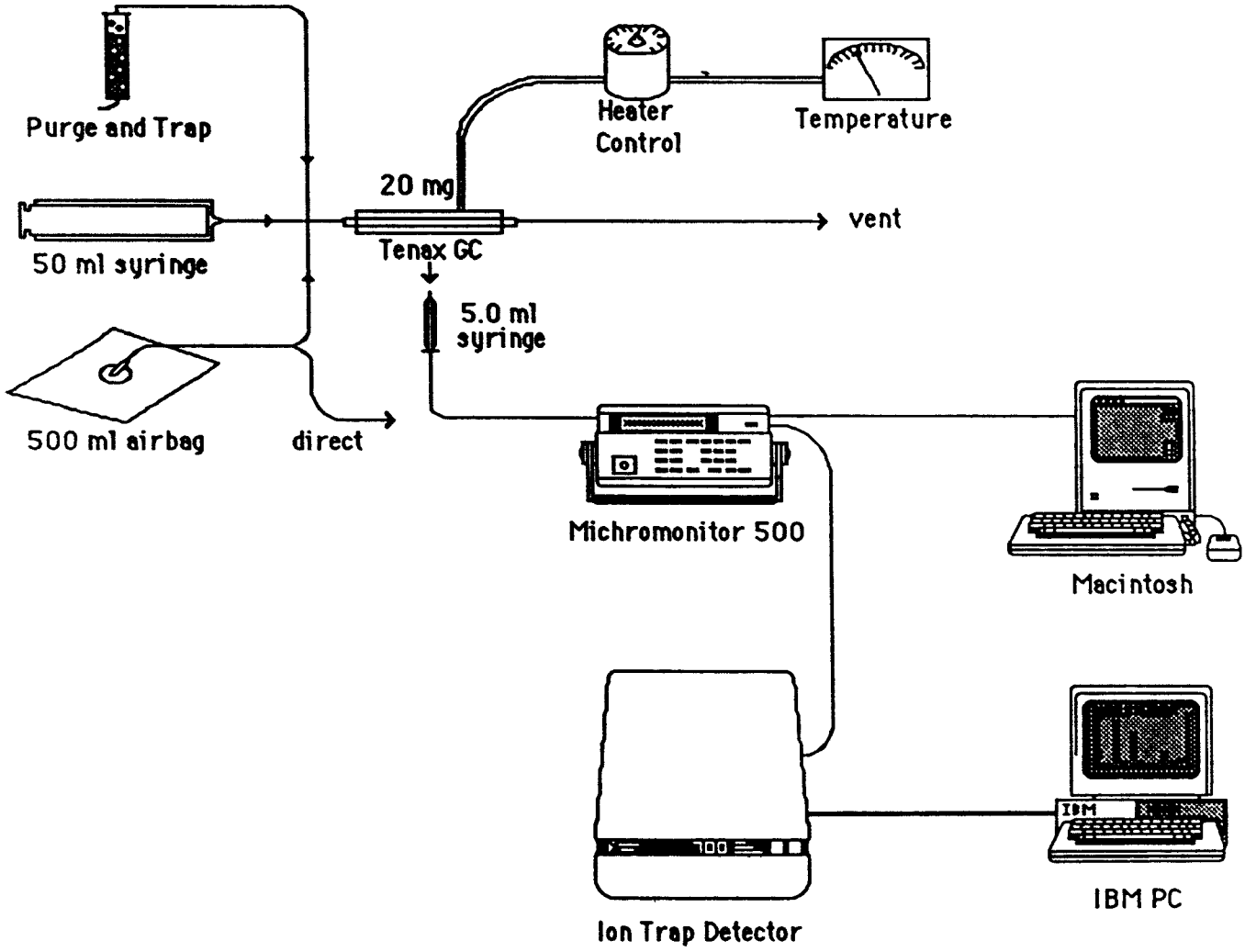
Chloroform	70
Benzene	10
1,2-Dichloropropane	20
Bromodichloromethane	20
Toluene	10
Tetrachloroethylene	20
Chlorodibromomethane	60

Table 3

FIGURE 10

Concentrator/Purge and Trap - Michromonitor/ITD

10 - 15 minutes



Detector (ITD). The interfacing column also serves as a separating column. Figures 11, 12, and 13 schematically show the ITD and the interfacing with the microchip gas chromatograph.

The ITD is a relatively small mass spectrometer (compared to conventional mass spectrometers) capable of producing electron impact spectra of compounds introduced into its source region. The ITD is fundamentally different from conventional quadrapole instruments in the manner in which the mass spectral information is produced. Resulting mass spectra are similar to those obtained with quadrapole instruments. However, the ITD is a mechanically simple and rugged device when compared to quadrapole units which is important for its application to field analysis of environmental samples.

Figure 14 shows a gas chromatograph/mass spectrometer analysis of a mixture of seventeen different volatile priority pollutants. The total run time for the analysis was slightly over two minutes.

CONCLUSION

By modifying off-the-shelf chemical instrumentation and designing a field deployable concentrator we have developed analytical tools that allow for the rapid acquisition of reliable chemical data in the field. The instrumentation can be used to characterize air, water, and soil samples for volatile organic compounds during hazardous waste site investigations and cleanup activities. Field use of the instrumentation is currently being carried out by the U.S. EPA, the U.S. Coast Guard, and Hazardous Materials Response Branch of the National Oceanic and Atmospheric Administration.

ACKNOWLEDGEMENTS

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FIGURE 11

ION TRAP DETECTOR

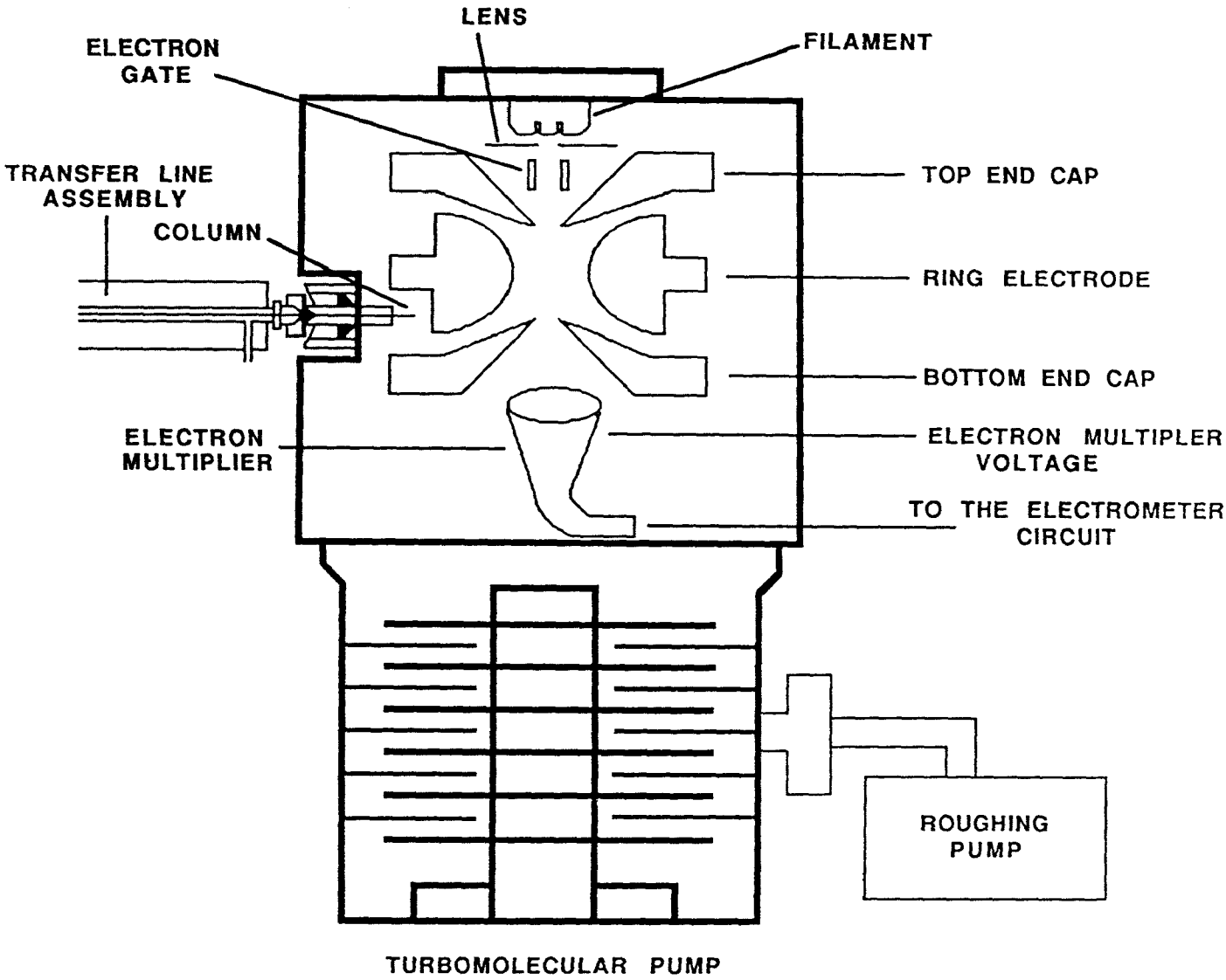


FIGURE 12

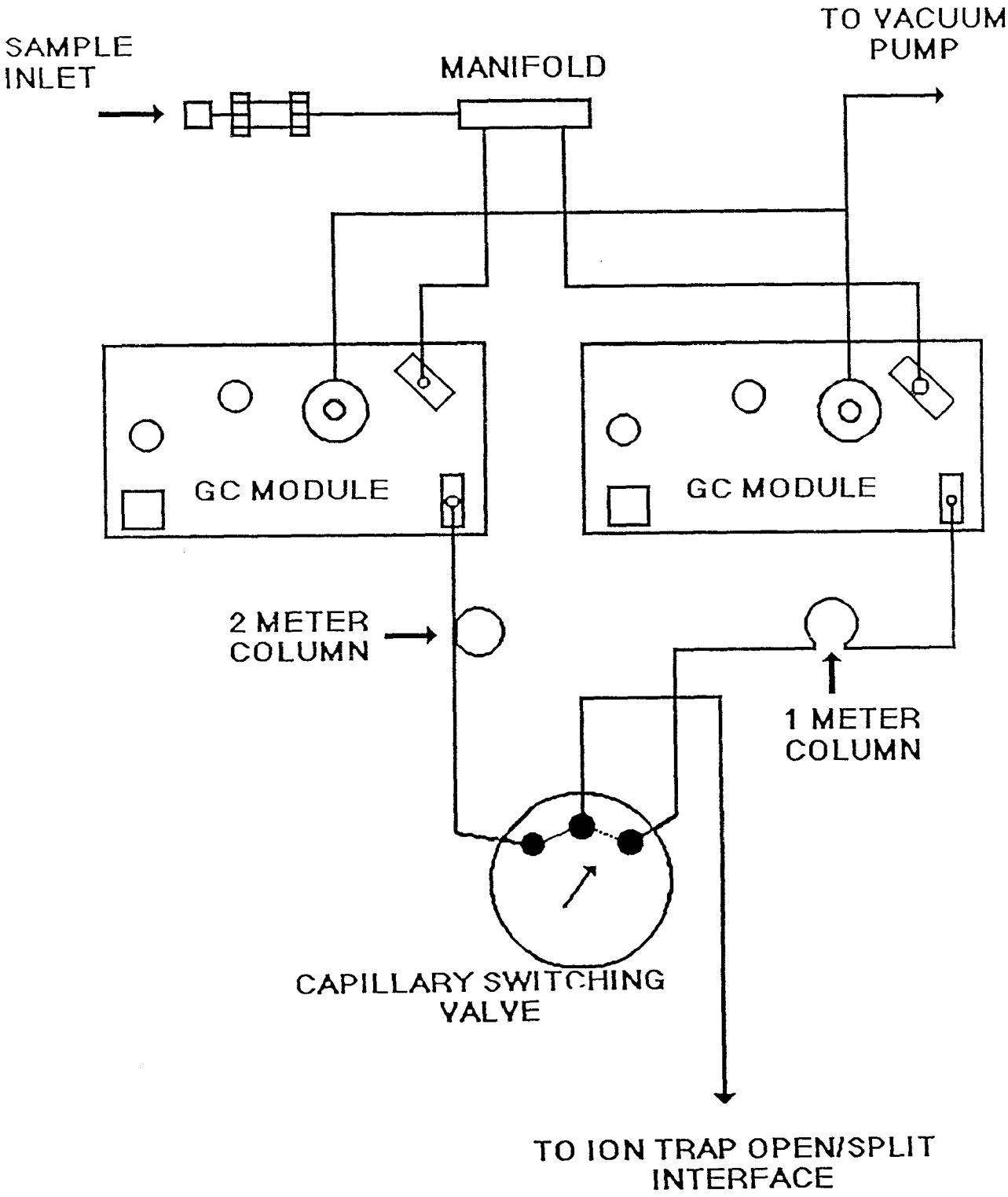
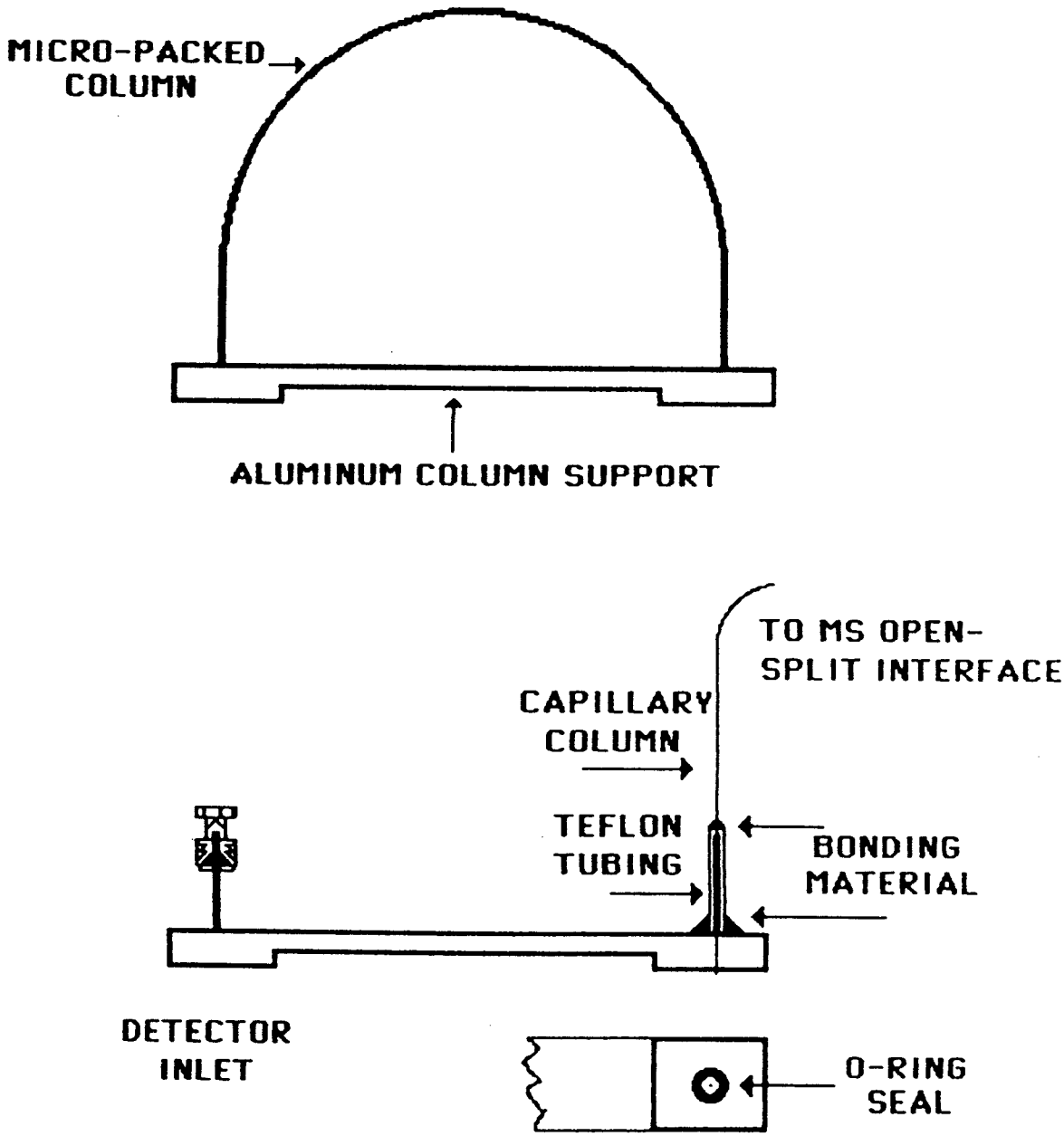

SAMPLE
INLET
MANIFOLD
TO VACUUM
PUMP
GC MODULE
GC MODULE
2 METER
COLUMN
1 METER
COLUMN
CAPILLARY SWITCHING
VALVE
TO ION TRAP OPEN/SPLIT
INTERFACE

FIGURE 13


MICRO-PACKED COLUMN
ALUMINUM COLUMN SUPPORT
TO MS OPEN-SPLIT INTERFACE
CAPILLARY COLUMN
TEFLON TUBING
BONDING MATERIAL
DETECTOR INLET
O-RING SEAL

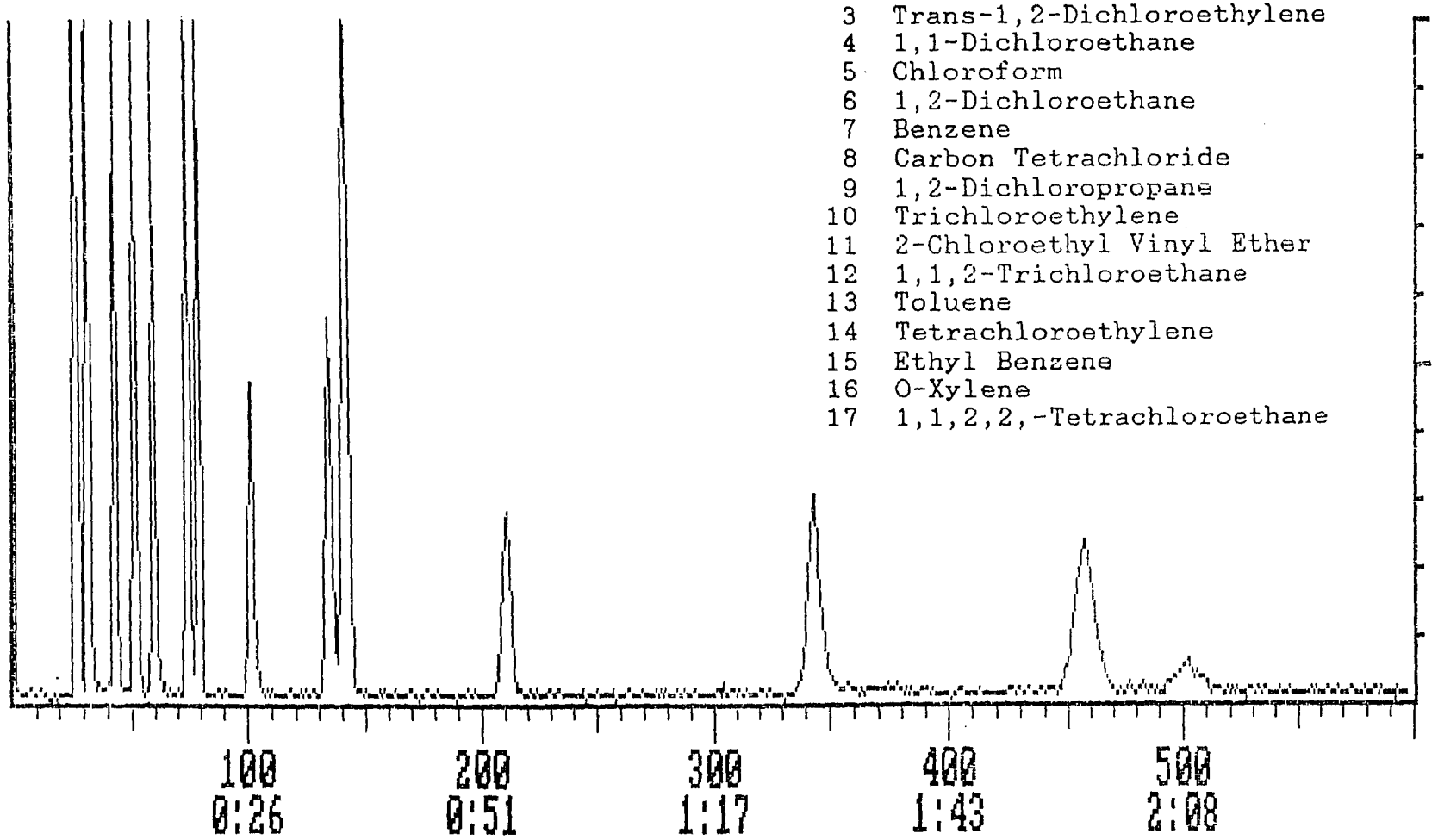

1 1,1-Dichloroethylene
2 Methylene Chloride
3 Trans-1,2-Dichloroethylene
4 1,1-Dichloroethane
5 Chloroform
6 1,2-Dichloroethane
7 Benzene
8 Carbon Tetrachloride
9 1,2-Dichloropropane
10 Trichloroethylene
11 2-Chloroethyl Vinyl Ether
12 1,1,2-Trichloroethane
13 Toluene
14 Tetrachloroethylene
15 Ethyl Benzene
16 O-Xylene
17 1,1,2,2,-Tetrachloroethane
100
0:26
200
0:51
300
1:17
400
1:43
500
2:08

Figure 14

SAMPLING TECHNIQUES FOR EVALUATION OF TARRY WASTE IMPOUNDMENTS

Roger A. Dhonau, Senior Environmental Engineer, C. John Ritzert, Manager-Technical Services; Environmental Services Division, Lancy International, Inc., Zelienople, PA

ABSTRACT

A 26 million gallon unlined industrial waste lagoon was investigated with the intent of characterizing the waste's general composition and suitability for reclamation as an alternative fuel. Physical characteristics of the waste varied considerably, providing unique challenges to sample acquisition. The tar-like nature of the waste did not lend itself to traditional sampling techniques and numerous practical problems had to be overcome. The highly stratified nature of the lagoon contents required development of a sampling approach that would allow the identification of specific vertical and lateral areas. The determination of an average composition for each strata was also required. The sampling plan developed incorporated both statistically random as well as intentionally subjective placement of sample locations in order to accomplish these objectives. Results of this investigation allowed the division of lagoon wastes into areas usable as alternative fuels for cement kilns or incinerators, and those that would not.

This paper discusses the logic of sample location selection and parameters chosen to characterize this waste. Difficulties encountered in sampling this type of waste will be discussed in conjunction with techniques found to be successful in obtaining representative samples.

INTRODUCTION

An investigation was performed on an inactive lagoon which had received wastes from a large coking facility and adjoining chemical plant over many years. The intent of this investigation was to provide basic characterization data for the preliminary economic evaluation of two alternatives deemed to be most economically and environmentally feasible for remediation of the site. These alternatives, reclamation as a waste fuel and incineration at a commercial facility, were selected for initial evaluation on the basis of the general characteristics of the waste streams known to have been directed to the lagoon over its years of operation. Physical characteristics of the lagoon contents presented unique challenges to acquisition of the waste samples needed for this investigation. A combination of several techniques were required in order to both access the sampling sites and to obtain the designated samples.

The lagoon was originally constructed in the early part of this century when plant wastes were discarded in a swampy depression. As this depression was filled, additional capacity was created by raising the

elevation of the surrounding area via the placement of ash, coal, and coke. Numerous expansions and contractions of the lagoon occurred over the ensuing years, each raising the elevation of the surrounding area. As was common practice at the time, no records of these activities were maintained and consequently, depth of the lagoon was unknown. At the time of the investigation the lagoon surface was 87,000 ft^2.

Although there were no records of quantities and types of wastes placed in the lagoon over most of its active life, it was known that the vast majority of wastes were various tars and sludges generated during the coking operations. In addition, several other waste streams, such as ammonia still lime sludges, scrap oven bricks and general plant wastes were also placed into the lagoon. At the time field activities were initiated the lagoon surface consisted of a two to six inch rubbery crust overlain by one to six inches of water. This water layer was found to be highly dependent upon recent weather conditions, as it completely evaporating during dry periods. Beneath the crust was a viscous tarry waste.

Obtaining representative samples of the material in the lagoon presented several obstacles primarily related to the physical state of the contents. The tar-like material would not support a normal drill rig and the rubbery consistency of the crust make discrete samples difficult to obtain. In that this was a preliminary investigation, available techniques were also severely limited by economic constraints.

SAMPLING LOCATIONS

The surface area of the lagoon was divided into twelve grid areas averaging approximately 7,250 ft^2 each with one boring designated for each area. This number of borings was determined to be sufficient to properly discern variability in the lagoon contents while remaining within the economic confines of the preliminary nature of this investigation. Due to the irregular perimeter of the lagoon and restrictions of the sampling technique, there was unavoidable variation in the size of the grid areas.

The restrictions of the sampling technique were due primarily to the mounding of coke, coal, and soil around portions of the lagoons banks. Because of this physical obstacle, tow winches for the sampling platform could not be properly placed to maneuver the sampling platform into certain small regions of the lagoon. In order to access these regions, it would have been necessary to move several thousand cubic yards of material. Again, such an effort would not have been in keeping with the preliminary nature of this investigation.

The purpose of the investigation dictated that spatial variations in the wastes be established. As a means of vertically characterizing the lagoon, random samples were identified through each core column. This was accomplished with the use of random number tables utilizing a sufficient number of elements to include all one-foot segments of an individual core. In order to ensure that sample points would be

distributed throughout the entire core length, random numbers were selected from each five foot increment of the anticipated core length (30 feet) plus additional numbers in the event that the lagoon was found to be deeper, as was the case. This procedure also alleviated the problem of obtaining an excessive number of samples in shallow regions and too few samples in very deep locations. A fixed grid was rejected as overly biased and risking the omission of significant waste layers.

SAMPLE ACQUISITION

The chemical composition and tar like consistency of the waste made sampling considerably more difficult than what is normally encountered. Most of the waste was too viscous for equipment and procedures normally utilized in liquid investigations and structurally too weak to be retained by equipment used for sampling solid wastes. To complicate the situation further, there were inclusions of very hard materials, such as refractory bricks, dispersed throughout the lagoon.

In order to access the selected boring locations, a small floating platform was constructed and equipped with a small skid mounted drill rig. The platform was approximately ten feet by twelve feet with two rows of sealed 55 gallon drums mounted beneath the platform to provide buoyancy. Since the water layer was far too thin to provide any significant buoyancy the platform was constructed to rest directly on the rubbery crust rather than float above it. This situation provided both advantages and disadvantages to the sampling efforts. By having the platform in contact with the wastes, considerable stress was placed upon the platform during moves between locations. As the platform was pulled from one location to another, the lagoons rubbery crust would often be stretched in the process. It was therefore necessary to maintain tension on all tow and guide lines to the platform at all times, in order to keep it from drifting as the crust returned to its original position. On the other hand, direct contact with the waste significantly increased the stability of the platform during the sampling.

The rubber-like consistency of the upper layer of the lagoon contents prevented use of a standard split spoon type sampler. It was, therefore, necessary to use a piston type sampler where the waste could be drawn into the sampler in a manner similar to a syringe. A split spoon type sampler with a basket retainer was most successful in lower zones of the lagoon contents where the waste had a more soil like consistency. A split spoon with other inserts types was also utilized in the sampling program with the type of insert depending upon the consistency of waste encountered.

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The selection of sampler type was based upon the consistency of the previous sample within a given column. In most instances the change in waste consistency was gradual enough to allow proper selection of the sampling device for a given depth. However, in several instances the waste consistency changed so quickly that they could not be adequately anticipated. Unfortunately, this resulted in the collection of only partial samples or complete loss of a given sample.

In order to obtain the samples the selected sampling device was driven two feet into the waste, removed, and immediately followed with a section of casing to the same depth. This casing section was then cleaned out. The sampler was then passed down the casing to obtain the next sample. This procedure was repeated with the sampler driven in advance of the casing for the entire length of the sampling column. The sampling column was extended to a depth at which natural soils were encountered.

After each sampler was retrieved from the boring, the contents were inspected and logged and a sample was taken for laboratory analysis according to the randomly selected sample locations. Samples of specific materials or interest were also identified and collected by the field supervisor based on technical judgment. The samples were placed in 500 ml wide mouth glass containers and refrigerated immediately at the site. Samples were coded on-site as to boring number, sample depth, date of collections, and field supervisor's initials. This information was also recorded, along with other notes and observations, in a field log.

Samplers were steam cleaned after each use. No solvents or detergents were used. In order to keep sampling and coring running smoothly, up to four (4) samplers of each type were required: one for use on the rig; one containing sample material being inspected by the field supervisor; one in cleaning; and one in transportation to or from the sampling platform to the inspection/cleaning location.

Each segment of every boring was inspected by the field supervisor prior to either placement in a sample container or returning it to the lagoon. Inspection included the following steps:

- Determination of percentage recovery
- Examination for color, texture, adhesion and inclusions. Colors were referenced Munsell Color standards
- Inclusions were noted as to type, size, and approximate percentage by volume

These observations were used as a basis for selection of supplementary samples within a given boring and to assist in estimating the possible origin of various types of wastes noted.

FINDINGS

Physical characteristics of the wastes varied through a wide spectrum of combinations. Color was generally absent, with most samples black to grey and occasionally ranging to almost pure white (spent lime slurry). The small percentages of samples that did show color contained mostly dark hues of greens, browns, and reds. Texture varied from honey like to that of a crumbly soil. Inclusion content varied from one visible to 20 percent or more. These inclusions generally appeared to be limestone, sand, coal, coke, and/or brick.

Subsequent chemical analysis determined a much wider range of characteristics. As indicated earlier, the purpose of this investigation was to obtain sufficient data to evaluate incineration and waste fuel options. Under this guidance, analytical parameters included the following:

Heat Content (BTU/lb)	Sulfer (%)
Moisture (%)	Viscosity (centipoise)
ASH (%)	pH

These parameters are indicative of general composition and are of primary importance for evaluation of incineration and waste fuel options. Evaluation of the resultant analytical data allowed the lagoon contents to be classified into three categories: materials suitable for use as a waste fuel (cement kiln); materials suitable for incineration; and materials not suitable for either of these options.

Typical analyses of waste samples for each category are as follows:

	Possible Waste Fuel	Possible for Incineration	Other
ph	2.4	6.9	11.7
Heat Value (BTU/lb)	9010	5,790	3,650
Sulfur (%)	5.6	3.1	1.2
Moisture (%)	15.2	22.0	15.4
Ash (%)	10.5	25.4	40.5
Viscosity (centipoise) @ 90°C	3,100	22,500	100,000

As can be seen by these values, a wide range of wastes were encountered during this investigation. The most significant of these with respect to sampling methodology was viscosity. At the upper range of

viscosity, the waste had a soil like consistency and could be sampled in a similar manner. At the lower range a piston sampler or split spoon with a flap value retainer was needed.

In summary, the chosen combination of commercially available soil sampling equipment was found to be both efficient and cost effective in the collection of tarry waste samples. The use of custom made or complex and expensive equipment was not required. The devices selected for this program not only allowed for acquisition of more than 80 percent of the targeted samples, but could be quickly and inexpensively replaced when a device was damaged or lost through the course of the program.