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Volume I

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QUALITY ASSURANCE

1 QUALITY ASSESSMENT THROUGH THE USE OF A QUANTITATIVE DATA BASE

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ABSTRACT

The evaluation of data quality is today a fundamental component of hazardous waste analysis. The primary focus of the quality assessment activity is to determine the confidence levels that can be assigned to real sample data. How confident can the data user be that the data is correct within some pre-established limits of acceptability. At CWM, an integrated QA/QC program has been implemented that combines many different components into an overall quality assessment of the corporate analytical systems and data.

One of the fundamental parts of any QA/QC program is the quantitative evaluation of the quality of the data. CWM has developed a simple, practical, and functional program that uses the most basic quantitative QA/QC components. It is the simplicity of the design that allows for improved control and implementation of the program and, in turn, defines the data validity and defensibility in a straightforward manner. The interrelationship of the separate components is the key to establishing the quality of data for such complex and diverse materials as hazardous waste.

The CWM QA/QC program components include policies, procedures, and data assessment models. Quality goals are established in the program, and assessment activities are specified that evaluate the quality of the laboratory and the data that is produced there. The QA/QC program is centrally controlled at the corporate level in order to better promote objectivity in this internal company program. Several important features of this program are:

(1) uniform corporate goals for data validity and defensibility

(2) quality assessment performed at the analytical bench

(3) internal audit program including self-audit mechanism

(4) quantitative evaluation of the analytical system from a variety of viewpoints.

Quantitative assessment is accomplished by reviewing a data base which includes information from round robin samples (analyzed quarterly), parallel analysis (analyzed monthly for all tests quarterly), and QC analysis (check samples, duplicates, and fortifications). The mechanisms used to determine the level of quality derived from this quantitative data base will be presented.

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TECHNIQUES FOR OVERALL DATA QUALITY ASSESSMENT

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ABSTRACT

Data quality assessment is the systematic and independent verification of data quality. Data quality assessment is an iterative two tier process. The second tier of the assessment involves overall evaluation of the quality of the data. This paper describes techniques and methods used to perform the overall data assessment in a timely manner. Using computer tools to format the data for evaluation, the overall assessment can be simplified. The overall assessment process includes: 1) evaluation of the data inventory, 2) evaluation of trends, 3) evaluation by mapping and graphics, and 4) evaluation from the historical comparison.

INTRODUCTION

The purpose of quality assessment is to 1) determine the validity of the data, 2) determine if quality objectives were met for the project, 3) determine if all the pieces of data "make sense," 4) determine usability of the data for making decisions, and 5) determine the anomalies present in the data. Data validation is an iterative two tier process. This process includes an initial review of the sampling and geological data which is performed by personnel responsible for sample collection. Parallel to the assessment of the field data is the assessment of the laboratory data. This includes detailed review of the laboratory's quality control methods. Data validation procedures have been published by many of the EPA Regions and by the Hazardous Site Evaluation Division. The second tier of the assessment process involves the overall evaluation of the quality of the data. The overall assessment includes: 1) a review of quality control results which require the integration of laboratory and field data, 2) a comparison of actual statistical limits with those targeted in the data quality objectives, and 3) an evaluation of anomalies.

This paper describes techniques and methods used to perform the overall data assessment in a timely manner. Using computer tools to format the data for evaluation, the overall assessment can be simplified. The overall assessment process includes: 1) evaluation of the data inventory, 2) evaluation of trends, 3) evaluation by mapping and graphics, and 4) comparison of historical information.

INVENTORY

The inventory is a summary of total samples and data records, locator and log numbers and text for a single site by sampling location as shown in Table 1. A second inventory of information by site, summarizes the total number of results and locations for specific parameters, Table 2. From this information one can assess if the frequency of field and laboratory quality control was per the sampling plan and methods. This inventory can also be used to assess 1) whether sample data is missing, and 2) to evaluate the uniformity from round to round.

The next inventory assessment shown in Table 3 involves a comparison of the data records by site,location, and sampling date. The information provides the number of values greater than zero, number of values greater than the method detection limit, the number of values greater than zero with no method detection limit present, and the values missing method detection limits. For each category the percentage of occurrences compared to the entire data set is presented. This information is also presented for the QC samples. With this information it is easy to determine if positive hits are presented without the appropriate method detection information. This data can be sorted by site, location, laboratory and sampling event to assist in comparisons to project quality objectives.

TRENDS

In order to successfully determine whether trends exist it is useful to evaluate historical information. Table 4, includes a report which outlines the most current sampling event versus the historical mean, maximum, minimum, and standard deviation. Other statistical evaluations may be used. The total number of records by parameter is presented so that population size may be addressed. The number of non-detected occurrences is also presented. This information allows evaluation of consistency of positive responses between the historical data and the most current results.

By manipulating the data into graphic formats, trends and anomalies can easily be spotted. The concentrations of benzene and three chlorinated benzenes from a single ground water well are graphed over time in Figure 1. By viewing the data in this manner it is evident that a relationship between benzene and chlorobenzene exists. It is also evident that some data is missing. By evaluating the data in this manner one can rapidly determine missing data and anomalies and proceed to verify the associated laboratory and sampling details. This means that evaluation time can be spent where it is most crucial.

A second example is from a site where the regulators and community insisted that the site undergo remediation. By looking at the paper data on a sample by sample basis, it was impossible to determine the frequency of positive responses for the benzenes.

TABLE 1

Automated Compliance Systems
Node: Superfund Demo Data Base (DEMO)
DATA INVENTORY SUMMARY (EDS01) for: Sleepy Hollow Solvents, Inc.

April 19,1989

Site	Locator	Total Samples	Data Records	Sample Text	Locator Numbers	Locator Text	Log Numbers	Log Text	Sample Dates
SHSIGW	Site Numbers:								820124 thru 880707
	Site Text:								
	Locators: 54								
SHSIGW	388 BLANK	1	31						830404
SHSIGW	48	1	38		6	6		16	880412
SHSIGW	52	1	18		6	6		4	880411
SHSIGW	522 BLANK	1	31						830404
SHSIGW	54	1	27		6	6		5	880411
SHSIGW	56	1	28		6	6		6	880411
SHSIGW	58	1	31		6	6		5	880411
SHSIGW	61	1	16		6	6		5	880413
SHSIGW	62	1	28		6	6		5	880411
SHSIGW	64	1	37		6	6		5	880412
SHSIGW	67 BLANK	1	31						830404
SHSIGW	81-R	1	25						880412
SHSIGW	92-R	1	20						880412
SHSIGW	92-RDUP	1	17						880412
SHSIGW	AAZ	1	32						880413
SHSIGW	BLANK1	1	31						830404
SHSIGW	CCZ	1	26						880413
SHSIGW	DUPL1	1	109						880706
SHSIGW	EEZ-R	1	20						880413
SHSIGW	FBLNK1	1	108						880707
SHSIGW	FBLNK2	1	108						880707
SHSIGW	FBTB	2	178						820124 820429
SHSIGW	FIELDBLANK	24	1416						840718 840819 841024 850109 850417 851017 860128 860416 860716 861023 870115 870415 870416 870716 870716 871015 871016 880118 880119 880406 880407 880411 880412 880413
SHSIGW	GCMS BLANK	1	31						830404
SHSIGW	IIZ	1	24						880413
SHSIGW	JAMES-BROWN	30	1214						820124 820429 820721 821019 830125 830406 830714 830714 831013 840111 840424 840718 841024 850202 850417 850710 851017 860128 860417 860716 861023 870116 870416 870717 871016 880118 880127 880407 880408 880706
SHSIGW	JAMES-BROWN-FB	1	31						830406
SHSIGW	JAMES-BROWN-TB	1	31						830406
SHSIGW	KKZ	1	22						880413
SHSIGW	METHBLNK	4	167						880706 880707 880707 880707
SHSIGW	OOO	1	28		7	6			880412
SHSIGW	PROD-36	39	2636						820124 820429 820722 820805 821020 830125 830406 830714 830714 831013 840111 840425 840718 840814 841024 850202 850417 850513 850710 851017 860128 860416 860716 860716 861023 861023 870115 870115 870415 870415 870716 870716 871015 871015 880118 880127 880407 880408 880706
SHSIGW	PROD-36-FB	4	200						820721 820805 830125 830406
SHSIGW	PROD-36-TB	4	125						820805 830125 830406 850417
SHSIGW	PROD-37	39	2582						820124 820429 820721 820721 820721 821020 830125 830406 830714 830714 831013 840111 840425 840718 840814 841024 850109 850417 850710 851017 860128 860416 860716 860716 861023 861023 870115 870115 870415 870415 870716 870716 871015 871015 880118 880127 880407 880408 880706
SHSIGW	PROD-38	37	2564						820124 820429 820721 820721 820908 821020 830125 830406 830714 830715 831013 840111 840425 840802 841024 850109 850417 850710 851017 860128 860416 860716 861023 861023 870115 870115 870416 870717 870717 871015 871015 880118 880127 880407 880408

TABLE 2

Automated Compliance Systems
Node: Superfund Demo Data Base (DEMO)
DATA INVENTORY GROSS COMPARISONS (EDS03) for: Sleepy Hollow Solvents, Inc.

April 19,1989

Site	Parameter Name	Locations	Results	Date Range
SHSIGW	1,1,1-Trichloroethane	39	374	01/24/82 thru 07/07/88
	1,1,2,2-Tetrachloroethane	37	356	01/24/82 thru 07/07/88
	1,1,2-Trichloroethane	37	356	01/24/82 thru 07/07/88
	1,1-Dichloroethane	40	371	01/24/82 thru 07/07/88
	1,1-Dichloroethylene	37	355	01/24/82 thru 07/07/88
	1,2,4-Trichlorobenzene	27	164	01/24/82 thru 07/07/88
	1,2-Dichlorobenzene	30	167	01/24/82 thru 07/07/88
	1,2-Dichloroethane	40	373	01/24/82 thru 07/07/88
	1,2-Dichloropropane	37	359	01/24/82 thru 07/07/88
	1,2-Diphenylhydrazine	15	111	01/24/82 thru 10/15/87
	1,2-Trans-dichloroethylene	37	409	01/24/82 thru 07/07/88
	1,3-Dichlorobenzene	20	157	01/24/82 thru 07/07/88
	1,3-Dichloropropylene	27	117	01/24/82 thru 10/13/83
	1,4-Dichlorobenzene	23	160	01/24/82 thru 07/07/88
	2,3,7,8-TCDD	13	25	07/21/82 thru 04/25/84
	2,4,6-Trichlorophenol	20	121	01/24/82 thru 07/07/88
	2,4-Dichlorophenol	20	121	01/24/82 thru 07/07/88
	2,4-Dimethylphenol	27	128	01/24/82 thru 07/07/88
	2,4-Dinitrophenol	20	121	01/24/82 thru 07/07/88
	2,4-Dinitrotoluene	20	128	01/24/82 thru 07/07/88
	2,6-Dinitrotoluene	20	128	01/24/82 thru 07/07/88
	2-Chloroethylvinyl ether	37	356	01/24/82 thru 07/07/88
	2-Chloronaphthalene	22	130	01/24/82 thru 07/07/88
	2-Chlorophenol	23	134	01/24/82 thru 07/07/88
	2-Nitrophenol	20	121	01/24/82 thru 07/07/88
	2-methyl-4,6-dinitrophenol	16	17	07/06/88 thru 07/07/88
	3,3'-Dichlorobenzidine	20	128	01/24/82 thru 07/07/88
	4,4'-DDD	13	30	10/13/83 thru 02/02/85
	4,4'-DDE	13	30	10/13/83 thru 02/02/85
	4,4'-DDT	13	30	10/13/83 thru 02/02/85
	4,6-Dinitro-o-cresol	13	104	01/24/82 thru 10/15/87
	4-Bromophenyl phenyl ether	20	128	01/24/82 thru 07/07/88
	4-Chlorophenyl phenyl ether	20	128	01/24/82 thru 07/07/88
	4-Nitrophenol	20	121	01/24/82 thru 07/07/88
	4-chloro-3-methyl phenol	16	17	07/06/88 thru 07/07/88
	Acenaphthene	27	145	01/24/82 thru 07/07/88
	Acenaphthylene	20	128	01/24/82 thru 07/07/88
	Acrolein	31	337	01/24/82 thru 10/16/87
	Acrylonitrile	31	337	01/24/82 thru 10/16/87
	Aldrin	13	30	10/13/83 thru 02/02/85
	Alpha-BHC	13	30	10/13/83 thru 02/02/85
	Aniline	16	303	01/24/82 thru 10/16/87
	Anthracene	20	128	01/24/82 thru 07/07/88
	Antimony	15	16	01/11/84 thru 07/07/88
	Arsenic	26	27	01/11/84 thru 07/07/88
	Barium	23	31	01/18/88 thru 07/07/88
	Benzene	50	419	01/24/82 thru 07/07/88
	Benzidine	20	128	01/24/82 thru 07/07/88
	Benzo(a)anthracene	20	128	01/24/82 thru 07/07/88
	Benzo(a)pyrene	20	128	01/24/82 thru 07/07/88
	Benzo(b)fluoranthene	17	46	04/16/86 thru 07/07/88
	Benzo(b)fluoroanthene	15	82	01/24/82 thru 01/28/86
	Benzo(ghi)perylene	20	128	01/24/82 thru 07/07/88
	Benzo(k)fluoranthene	20	128	01/24/82 thru 07/07/88
	Beryllium	15	16	01/11/84 thru 07/07/88
	Beta-BHC	13	30	10/13/83 thru 02/02/85

TABLE 3

Automated Compliance Systems
Node: Superfund Demo Data Base (DEMO)
DATA INVENTORY DETAILS (EDS02) for: Sleepy Hollow Solvents, Inc.

April 19,198

Page 1

Site	Locator	Sample Date	Data Records	Values > 0.0	%	Values > MDL	%	Values > 0.0 No MDL	%	Missing MDLs	%	ACS Sample Number	Lab Sample Number	Data Generated By (entry#)
SHSIGW	388 BLANK	830404	31		.0		.0		.0	31	100.0	DEMO132	XB98813	LATE Labs (1)
SHSIGW	48	880412	38	38	100.0		.0	38	100.0	38	100.0	DEMO454		TERRA-Bull Test (5
SHSIGW	52	880411	18	18	100.0		.0	18	100.0	18	100.0	DEMO455		TERRA-Bull Test (5
SHSIGW	522 BLANK	830404	31		.0		.0		.0	31	100.0	DEMO131	XB97036	LATE Labs (1)
SHSIGW	54	880411	27	27	100.0		.0	27	100.0	27	100.0	DEMO456		TERRA-Bull Test (5
SHSIGW	56	880411	28	28	100.0		.0	28	100.0	28	100.0	DEMO457		TERRA-Bull Test (5
SHSIGW	58	880411	31	31	100.0		.0	31	100.0	31	100.0	DEMO458		TERRA-Bull Test (5
SHSIGW	61	880413	16	7	43.8		.0	7	43.8	16	100.0	DEMO459		TERRA-Bull Test (5
SHSIGW	62	880411	28	28	100.0		.0	28	100.0	28	100.0	DEMO460		TERRA-Bull Test (5
SHSIGW	64	880412	37	37	100.0		.0	37	100.0	37	100.0	DEMO461		TERRA-Bull Test (5
SHSIGW	67 BLANK	830404	31		.0		.0		.0	31	100.0	DEMO130	XB95259	LATE Labs (1)
SHSIGW	81-R	880412	25	23	92.0		.0	23	92.0	25	100.0	DEMO453		TERRA-Bull Test (5
SHSIGW	92-R	880412	20	18	90.0		.0	18	90.0	20	100.0	DEMO451		TERRA-Bull Test (5
SHSIGW	92-RDUP	880412	17	17	100.0		.0	17	100.0	17	100.0	DEMO452		TERRA-Bull Test (5
SHSIGW	AAZ	880413	32	32	100.0		.0	32	100.0	32	100.0	DEMO538		TERRA-Bull Test (6
SHSIGW	BLANK1	830404	31		.0		.0		.0	31	100.0	DEMO128	XB91705	LATE Labs (1)
SHSIGW	CCZ	880413	26	26	100.0		.0	26	100.0	26	100.0	DEMO539		TERRA-Bull Test (6
SHSIGW	DUPL1	880706	109	5	4.6	1	.9	3	2.8	26	23.9	DEMO541	672080	TERRA-Bull Test (7
SHSIGW	EEZ-R	880413	20	18	90.0		.0	18	90.0	20	100.0	DEMO540		TERRA-Bull Test (6
SHSIGW	FBLNK1	880707	108	5	4.6	1	.9	3	2.8	25	23.1	DEMO542	682077	TERRA-Bull Test (7
SHSIGW	FBLNK2	880707	108	6	5.6	1	.9	4	3.7	25	23.1	DEMO543	682078	TERRA-Bull Test (7
SHSIGW	FBTB	820124	89	2	2.2		.0	2	2.2	89	100.0	DEMO6	XG98399	LATE Labs (1)
SHSIGW	FBTB	820429	89	2	2.2		.0	2	2.2	89	100.0	DEMO17	XA12889	LATE Labs (1)
SHSIGW	FBTB	Totals -->	178	4	2.2		.0	4	2.2	178	100.0			
SHSIGW	FIELDBLANK	840718	79		.0		.0		.0		.0	DEMO259	XD73414	LATE Labs (1)
SHSIGW	FIELDBLANK	840819	11		.0		.0		.0		.0	DEMO268	XD96515	LATE Labs (1)
SHSIGW	FIELDBLANK	841024	90	3	3.3	2	2.2		.0		.0	DEMO276	XE13624	LATE Labs (1)
SHSIGW	FIELDBLANK	850109	83		.0		.0		.0		.0	DEMO288	XE34948	LATE Labs (1)
SHSIGW	FIELDBLANK	850417	90	1	1.1	1	1.1		.0		.0	DEMO302	XE59826	LATE Labs (1)
SHSIGW	FIELDBLANK	851017	90	1	1.1	1	1.1		.0		.0	DEMO329	XF17806	LATE Labs (1)
SHSIGW	FIELDBLANK	860128	90	2	2.2	1	1.1		.0		.0	DEMO338	XF40907	LATE Labs (1)
SHSIGW	FIELDBLANK	860416	90		.0		.0		.0		.0	DEMO353	XF64008	LATE Labs (1)
SHSIGW	FIELDBLANK	860716	90		.0		.0		.0		.0	DEMO366	XF87109	LATE Labs (1)
SHSIGW	FIELDBLANK	861023	90		.0		.0		.0		.0	DEMO379	XG20211	LATE Labs (1)

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TABLE 4

Automated Compliance Systems

PERFORMANCE REPORT (PRO1) for: Sleepy Hollow Solvents, Inc.

April 19,1989

Site: SHSIGW
Locator: PROD-36

Sample Numbers ACS: DEMO549
LAB: 672074

24-Jan-82 ---thru--- 08-Apr-88

Page 1

Parameter Group	Parameter	Units	06-Jul-88	HISTORICAL #Recs	ND's	Mean	Maximum	Minimum	Std Dev
SHSI Volatiles - water	1,1,1-Trichloroethane	ug/l	0	24	24	.00	.00	.00	.00
	1,1,2,2-Tetrachloroethane	ug/l	0	24	24	.00	.00	.00	.00
	1,1,2-Trichloroethane	ug/l	0	24	24	.00	.00	.00	.00
	1,1-Dichloroethane	ug/l	0	26	21	1.32	27.00	.00	5.28
	1,1-Dichloroethylene	ug/l	0	24	24	.00	.00	.00	.00
	1,2-Dichloroethane	ug/l	6	32	21	6.24	140.00	.00	24.59
	1,2-Dichloropropane	ug/l	0	24	24	.00	.00	.00	.00
	1,2-Trans-dichloroethylene	ug/l	5	32	17	8.60	80.70	.00	21.51
	Benzene	ug/l	3100	32		2399.61	5350.00	55.00	1507.30
	Bromoform	ug/l	0	24	24	.00	.00	.00	.00
	Carbon tetrachloride	ug/l	0	24	24	.00	.00	.00	.00
	Chlorobenzene	ug/l	1800	32		1029.38	2350.00	52.00	614.40
	Chlorodibromomethane	ug/l	0	24	24	.00	.00	.00	.00
	Chloroethane	ug/l	0	24	24	.00	.00	.00	.00
	Chloroform	ug/l	50	32	6	84.69	1100.00	.00	190.84
	Dichlorobromomethane	ug/l	0	24	24	.00	.00	.00	.00
	Ethylbenzene	ug/l	26	32	7	33.19	360.00	.00	73.35
	Methyl bromide	ug/l	0	24	24	.00	.00	.00	.00
	Methyl chloride	ug/l		32	25	18.38	500.00	.00	88.20
	Methylene chloride	ug/l	5	32	6	58.31	420.00	.00	112.14
	Tetrachloroethylene	ug/l	5	32	18	26.01	555.00	.00	103.34
	Toluene	ug/l	10	32	7	25.76	300.00	.00	60.00
	Trichloroethylene	ug/l	0	32	20	4.54	95.00	.00	16.96
	Trichlorofluoromethane	ug/l	0	26	25	.08	2.00	.00	.39
	Vinyl chloride	ug/l	0	26	25	.08	2.00	.00	.39
	cis-1,3-Dichloropropylene	ug/l	0	16	16	.00	.00	.00	.00
	trans-1,3-Dichloropropylene	ug/l	0	16	16	.00	.00	.00	.00
SHSI Volatiles - water	SUM				494				
SHSI Volatiles - water	MEAN				494				
<single parameter>	1,2-Dichlorobenzene	ug/l	61	32	2	111.91	191.00	.00	51.85

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FIGURE 1

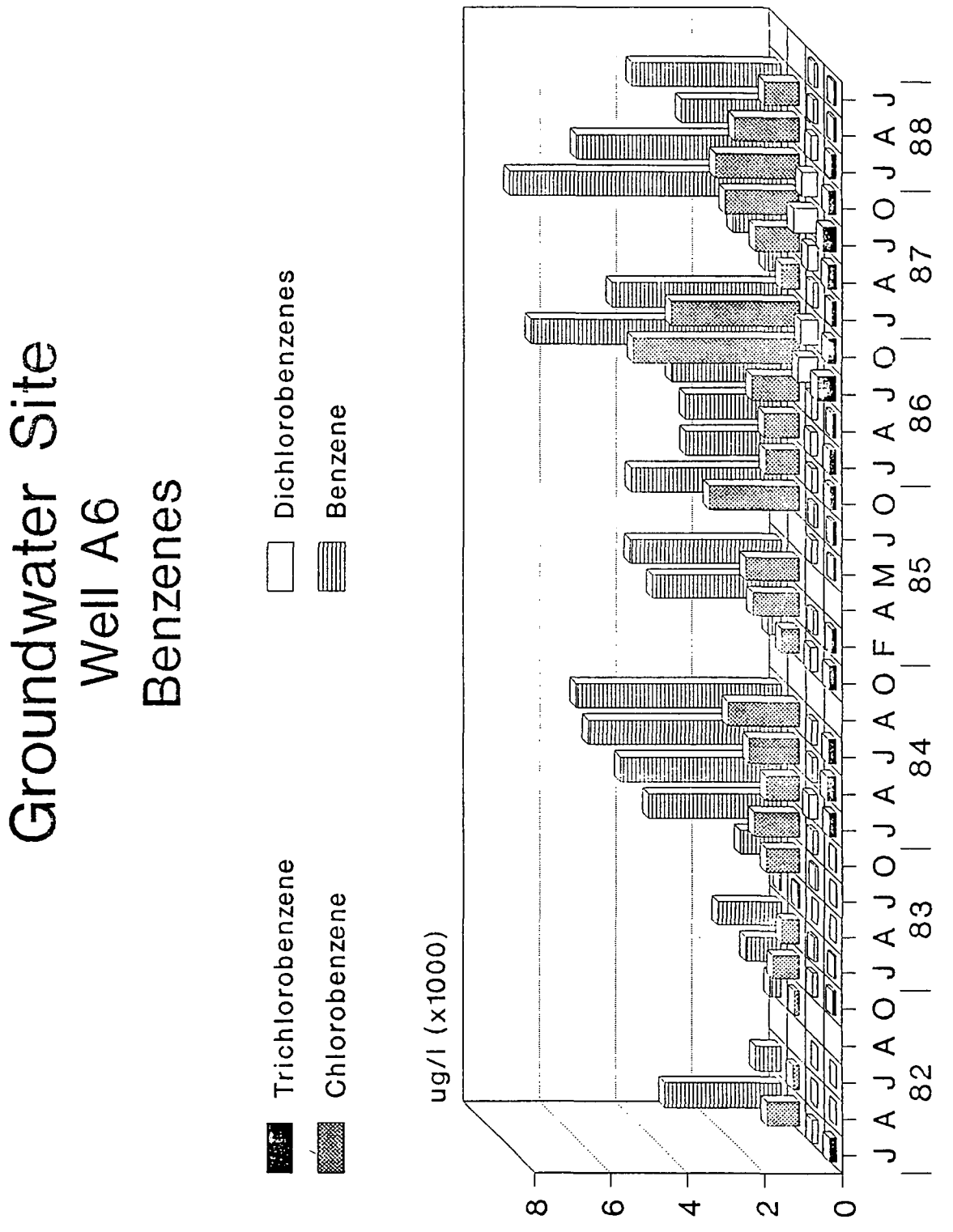
Groundwater Site
Well A6
Benzenes
Trichlorobenzene
Chlorobenzene
Dichlorobenzenes
Benzene
ug/l (x1000)
0
2
4
6
8
J A J A O J A J O J A A O F A M J O J A J O J A J O J A J
82
83
84
85
86
87
88

Figure 2 is a plot of the various concentrations of benzene compounds over time. It is obvious that positive responses occurred only on one sampling round four years ago. With this information the site owner traced the problem back to bottle contamination and other sampling errors.

Simple summaries of information can assist in determining not only the anomalies but the origin of the problem. At one site the occurrence of phthalates was high. Some regulators believed that the site should be remediated because of this problem. Since phthalates are normal laboratory and sampling contaminants, the data was closely evaluated. After seven years of data was input to the data base, the data was evaluated by the laboratory performing the analysis, by the percentage of hits, and by percentage of hits without method detection limits. As is obvious in Figure 3, one laboratory produced a greater percentage of positive responses than the other labs. Upon further examination most of the hits from Lab B were phthalates. It is obvious that the problem was laboratory contamination and not the samples. After presenting this information to the regulators, it was determined that site remediation was not required.

Figure 4 shows a plot of common laboratory solvents over time from a site. During four sampling events there is a significant increase in the solvent content. Again this problem was related to laboratory contamination and makes a significant difference in the final decisions regarding the fate of the site.

It is essential to be able to evaluate analytical data in conjuntion with geographical and geological information. By being able to query information related to the analytical results and combine this with geographical information one can easily reaffirm the validity of results. In Figure 5 the concentration of the sum of benzene, toluene and xylene is contoured in the lower portion of the drawing while the site map is in the upper portion of the drawing. Since the tanks had long been removed from the site when the sampling was performed, this information adds credence to the location of the contamination. The locations of the tanks were estimated from aerial photographs and historical information, input using a Geographical Information System. The data base searched for the compounds of interest and plotted concentration contours.

FIGURE 2

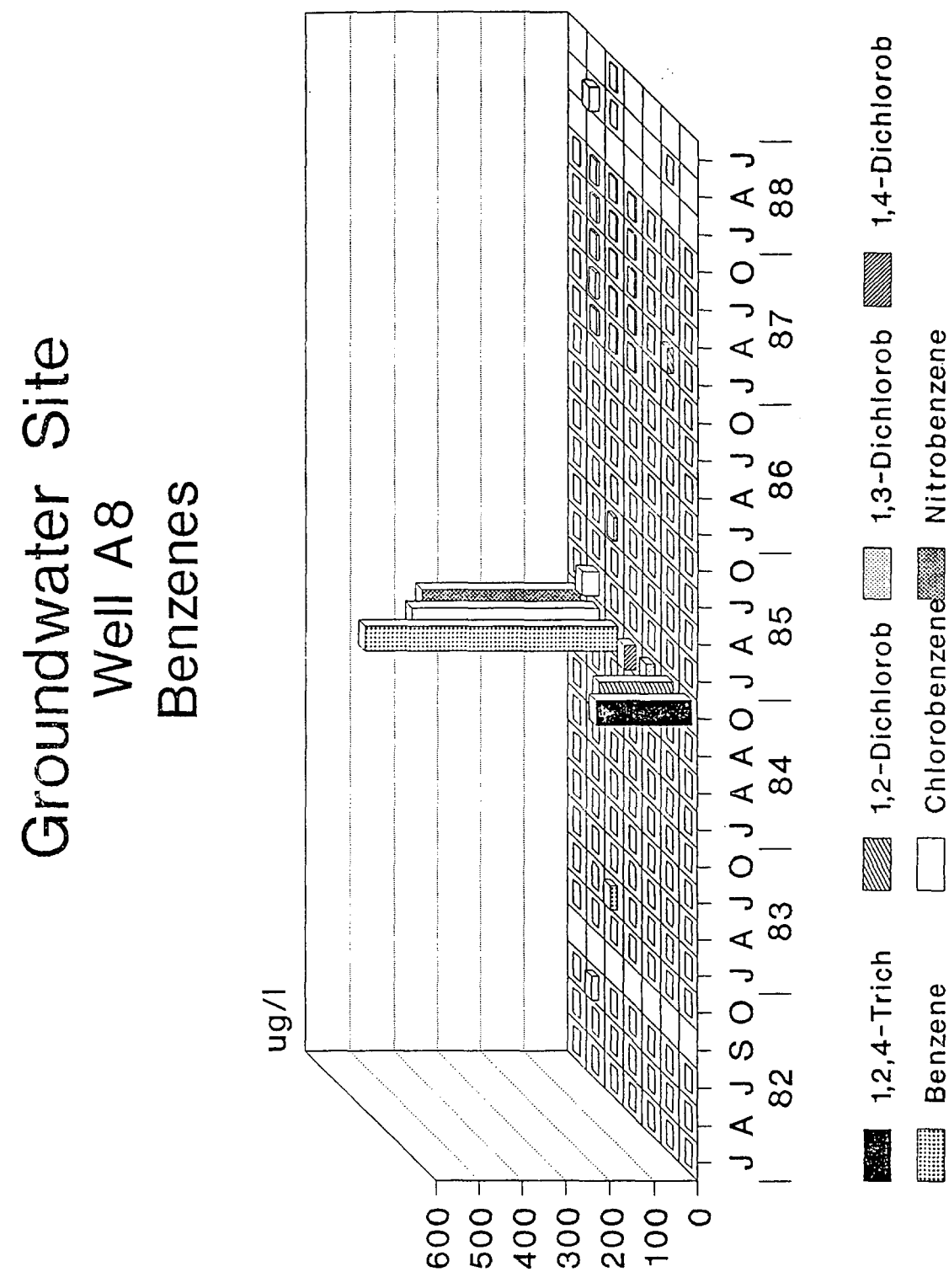
Groundwater Site
Well A8
Benzenes
ug/l
600
500
400
300
200
100
0
J A J S O J A J O J A A O J A J O J A J O J A J O J A J
82
83
84
85
86
87
88
1,2,4-Trich
Benzene
1,2-Dichlorob
Chlorobenzene
1,3-Dichlorob
Nitrobenzene
1,4-Dichlorob

FIGURE 3

Single Facility
7 Years Data
26 Wells

	Lab A	Lab B	Lab C
# Records	42,347	12,501	27,211
% Hits	4.4	13.1	4.7
% Hits w/o MDL's	1.1	5.7	0.5
Entropy	2.3	4.6	2.1

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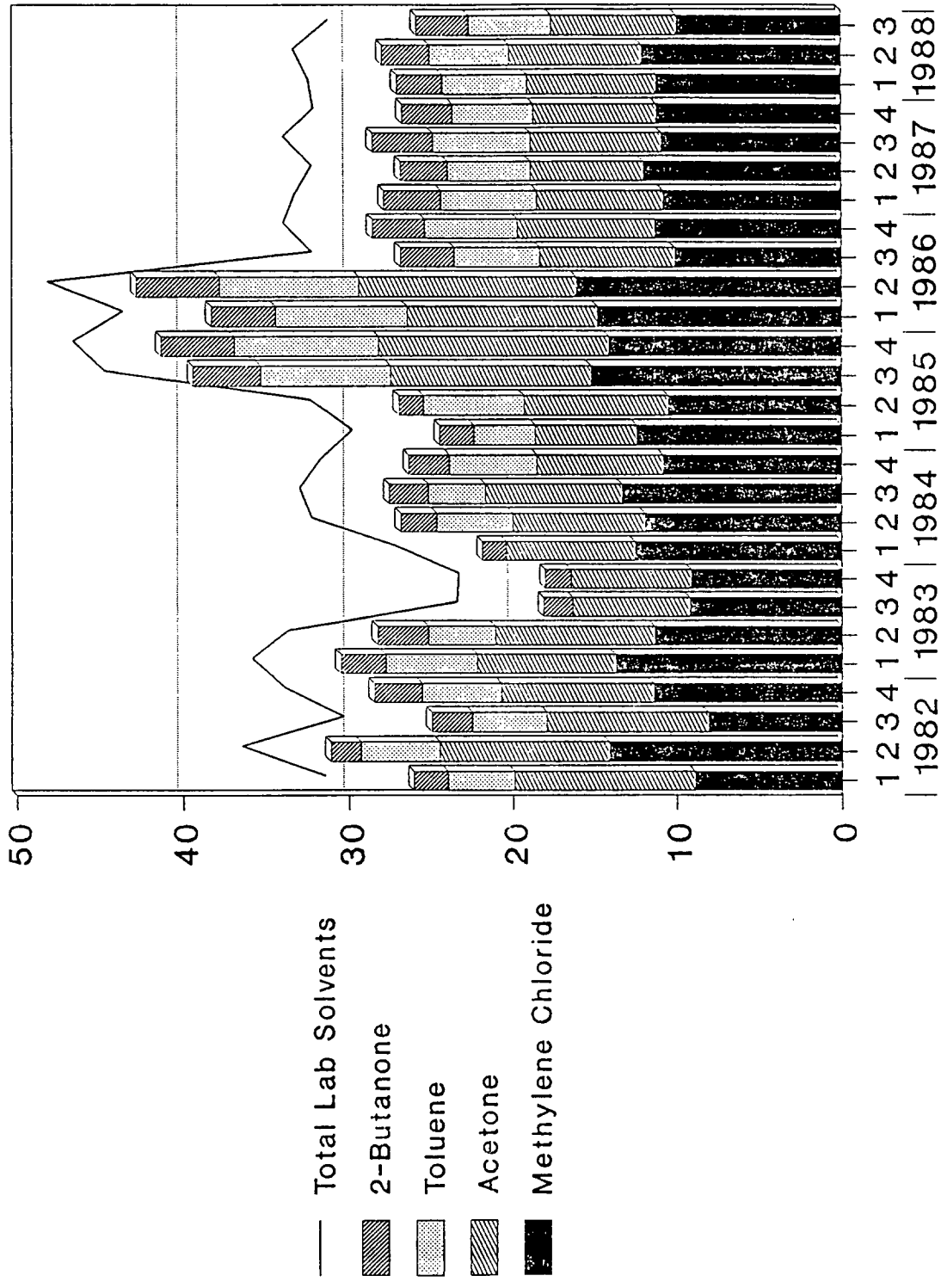
50
40
30
20
10
0
1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4 1 2 3
1982 | 1983 | 1984 | 1985 | 1986 | 1987 | 1988
Total Lab Solvents
2-Butanone
Toluene
Acetone
Methylene Chloride

FIGURE 4

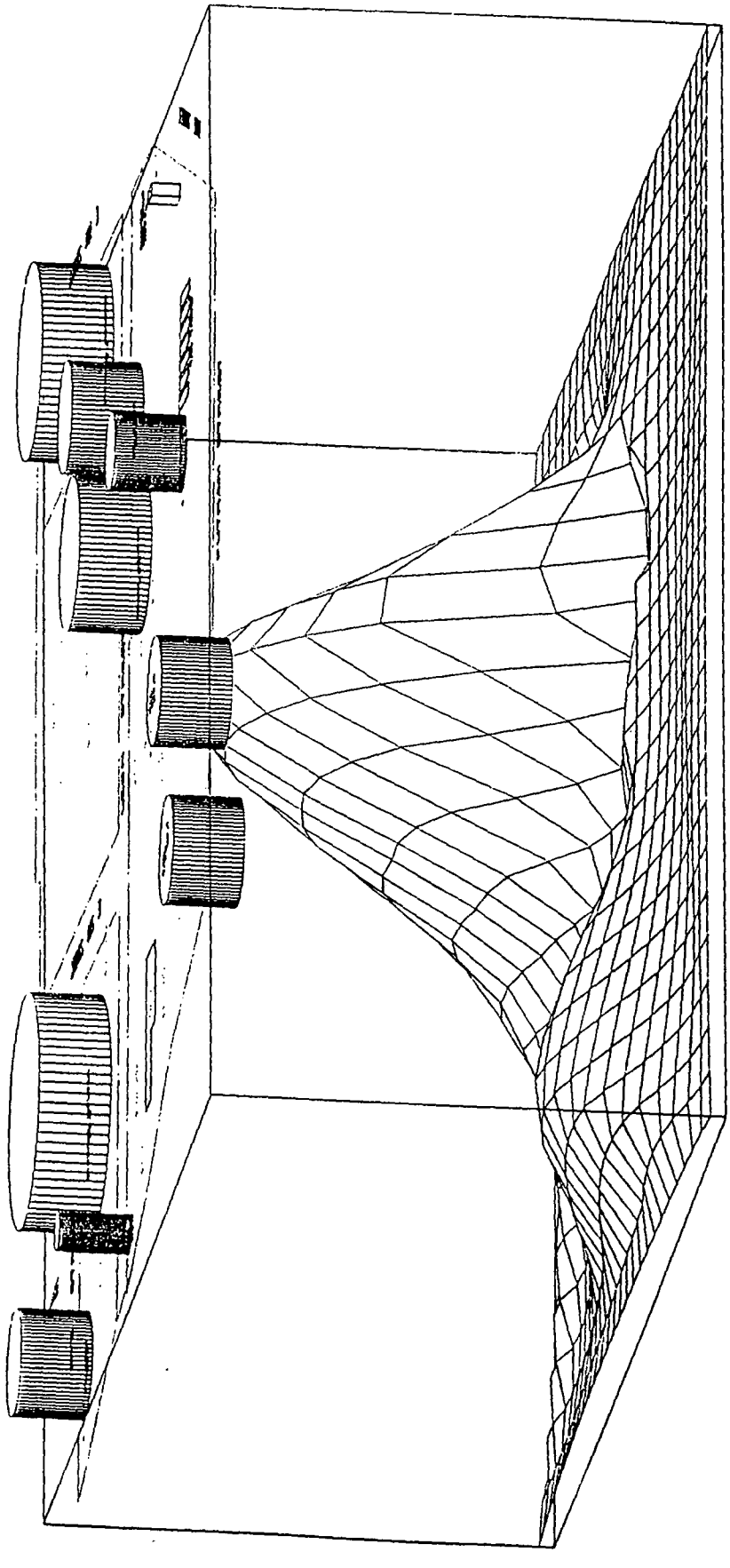

FIGURE 5

SUMMARY

The best way to perform the overall data quality assessment is by the use of statistics, graphs and mapping of all the information. By using these techniques the anomalies in sampling and analysis can be identified. Time can then be spent on the crucial problem areas and on making accurate decisions with the data. This can most easily be accomplished if data is well organized in a central data base. The data base must accept analytical and geological data and allow easy query and transport of the data between different software packages. Once this is accomplished the reviewer of the data quality can make accurate assessment of the data in a reasonable amount of time. Overall assessment of data is critical in making accurate and timely decisions in the environmental arena.

3

QA DIAGNOSTICS
TAKING THE PULSE OF THE RREL QA PROGRAM

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INTRODUCTION

How healthy is your QA program? Does it contribute significantly to project planning and execution, or is it merely a paperwork hurdle to be overcome or subverted? Is it a drain on your budget, or a cost-effective means of achieving a quality product?

One means of evaluating a QA program is to consider its impact on individual projects. This paper presents eight case studies of individual projects carried out by the Risk Reduction Engineering Laboratory (RREL) during fiscal year 1989 which illustrate the effects of the RREL QA program. The first major involvement of the RREL QA program during project planning takes the form of reviews of QA project plans. The case studies which follow provide examples of QAPjPs which contained potentially fatal flaws in project design -- such as incomplete or incorrect sampling strategies, inappropriate analytical and sampling methods, and sample preservation methods that were incompatible with the planned methods of analysis. These errors were corrected prior to the initiation of experimental operations, but had these projects proceeded as originally planned, much or all of the data would have been worthless. During the execution of the field and laboratory phases of these projects, RREL carried out on-site audits. The case studies cited in this paper revealed instances of incorrect implementation of analytical methods, inadequate management and preparation, and failure on the part of project personnel to communicate information essential for project execution. In these case studies, proper corrective action avoided irreparable harm to the project. RREL also carries out QA reviews of final reports. As can be seen in the case studies discussed in this paper, these reviews have been helpful in identifying conclusions that were overly generalized or unsupported by the data. It is clear from these case studies that the quality of project planning, implementation, and reporting has been substantially enhanced by the RREL QA program.

In most cases it is difficult to apply a dollar value to the enhanced quality realized through an effective QA program. However, for four case studies presented in this paper, it was possible to identify aggregate cost savings resulting from the QA program in excess of $1 million, much of which was realized simply by eliminating inappropriate or irrelevant measurements.

INTEGRATED EFFECTS OF QA PROJECT PLAN REVIEWS AND AUDITS

Case Study I

During FY'89 RREL completed the evaluation of a process for the cleanup of low-level organics in water. Review of the initial QA Project Plan and Test Plan was initiated, and field tests were started six weeks later. It is clear that the RREL QA Program had a major impact on the planning

and execution of this project. A conservative assessment revealed that the QA Program, implemented by RREL for this project, saved the Agency $300,000.

Initial review of the QA Project Plan revealed numerous, substantive problems that were ultimately resolved in a consequential meeting initiated by the RREL QA Program.

- Although VOCs were the compounds of primary interest, the intended analytical method was not sensitive enough to detect these compounds at the expected concentrations. Prior to the field test, a more sensitive method was thus selected. Without this change in methodology, it would have been impossible to measure the effect of the treatment technology.

- For many analytes, the intended method of sample preservation was incompatible with the analytical procedure that was planned. That is, many inorganic determinations would have been impossible to perform if samples were preserved as originally planned. Alternate methods of analysis and sample preservation were thus selected before field tests were initiated.

- There were no provisions for sampling the offgas resulting from the air purge, and thus, no means of distinguishing the effects of the process from simple air stripping. At the request of RREL, provisions were made to sample and analyze the overhead purge stream. This measurement turned out to be significant, in as much as 12 to 75 percent of the removal of certain compounds was by purging rather than by the process under test.

Other problems with unproven analytical methods, the collection of insufficient sample volumes, inappropriate sample collection procedures, the lack of calibration procedures for critical process measurements, and inappropriate quality control were also identified and corrected during the planning stage.

In addition, review of the QA Project Plan suggested that the analytical budget would be excessive due to a wide variety of analyses that seemed to be unrelated to project objectives, as well as a large number of QC samples of questionable value. During the planning process it was possible to eliminate a portion of the analytical costs by focusing the effort according to project objectives, and by eliminating unnecessary QC procedures without compromising data quality.

During the experimental phase, RREL performed Technical Systems Audits of both field and laboratory operations. One major problem that became clear during the field audit was a general lack of coordination between the field and laboratory staff. For example, the field technician had not been trained in the proper method for determining a critical on-site analyte, and various chemical standards had not been supplied to the field crew. In this particular instance, the auditor was able to assist in debugging the procedure for this critical on-site analyte. More importantly, by alerting management to this deficiency, more effective support of the field crew was facilitated. This audit also found that a meter for the offgas was being calibrated incorrectly, and that an incorrect monitor was being employed. These errors were corrected early enough in the field test -- as confirmed by a follow-up audit -- to avoid damage to the project.

The laboratory audit also uncovered significant problems. The QA Manager designated in the QA Project Plan actually resided in a distant city, and consequently there was no effective QA management on site during this project. As a result, most laboratory personnel were not informed of project QC requirements, and some analyses had to be repeated. Another concern was that

detection limits for a critical group of compounds had not been determined experimentally by the laboratory. Because many of the pollutants of interest were expected to be present at or near the detection limit, a reliable knowledge of actual detection limits was considered essential for the correct interpretation of the data. Once again, as a consequence of the audit, the laboratory took prompt corrective action, thereby avoiding irreparable harm to the project.

QA PROJECT PLAN REVIEWS

Case Study II

The purpose of this RREL project was to demonstrate the efficacy of an electric arc furnace for incinerating contaminated soils. Towards this end, it was necessary to characterize all influent and effluent streams, including untreated soil, treated soil, scrubber liquids and solids, and stack gases. This process presented some unusually difficult sampling problems that had not been resolved by the time the QA Project Plan had been written.

- Because treated soil from this project was in the form of molten slag cast in large blocks, non-standard sampling procedures were clearly required. However, the QA Project Plan contained no special provisions for obtaining representative samples from this medium. It was thus recommended that a suitable sampling procedure be developed and tested before the field test was carried out.

- Unlike conventional fuel-based incinerators, the gas flow in the stack from this process was quite small, consisting of a low-velocity flow in a three-inch pipe. The QA review noted that under these conditions, flow disturbances due to edge effects could be significant. According to the Test Plan, standard stack sampling procedures -- designed and validated for much larger stacks -- were to be employed. Under these conditions, it was unlikely that representative particulate samples could have been collected, or that correct flow rates could have been measured. The QA review provided an awareness of these problems along with recommendations to alleviate them.

- The intended sampling method for metals in stack gas was out of date. Had the older method been used, some metals might have been missed due to high blank levels or losses of the more volatile metals.

- There were no provisions for collecting solids that were trapped by the scrubber and removed by an internal filtering system. A complete evaluation of all effluent streams required the analysis of these samples.

- Because the incineration process was to be operated in a batch-wise, cyclic mode, starting with the intermittent charging of soil, it was likely that stack emissions would vary according to the stage of operation. It was thus important that stack sampling be coordinated with the process cycles in order that samples be representative of the complete operating cycle. However, the QA Project Plan made no provisions for this type of coordination.

The QA Project Plan also exhibited problems in the areas of analytical methods and process measurements. For example, the detection limits for the intended analytical methods were borderline for the purpose of determining the destruction removal efficiency (DRE) at the desired

level of efficiency. Thus, once the project was complete it may not have been possible to demonstrate a DRE of >99.99 percent.

In summary, the contractor was clearly unprepared to carry out a test of this technology at the time the QA Project Plan was written. Additionally, the review brought to light that much of the planned sampling and analytical effort could not be justified on the basis of project objectives. The ensuing discussion led to the elimination of over $130,000 in unnecessary sampling cost as well as $290,000 in related project costs, for a total savings of approximately $420,000 to the Agency.

Case Study III

This QA Project Plan, which was developed for an RREL solidification/stabilization project, exhibited problems that can result when a large, complex test is planned by several individuals without adequate communication and careful internal review. In particular, the QA Project Plan (together with the Test Plan) contained numerous substantive contradictions regarding the number of samples and types of tests to be performed. Under these conditions, the success of this test would have been fortuitous, to say the least. One purpose of preparing a QA Project Plan is to facilitate communication and agreement among the various experts -- engineers, chemists, and regulators -- who have an interest in the project. In this case, the QA Project Plan illustrated an obvious lack of agreement that needed to be resolved before the initiation of the tests.

The structure of the subject test consisted of several subdivisions, similar to that of the statistical factorial experiment. That is, an industrial site was subdivided according to the type of contamination found in various localized areas, each area was treated in three separate batches, each batch was divided into three forms, several samples were obtained from each form, etc. Replicate samples and analyses were intended at various levels of subdivision, although it was not clear how these various replicates were related to project objectives. Under these conditions, the type of samples as well as the number of replicates and other QC samples rapidly multiplied and became excessive, and for this reason the QA review suggested that the sampling and the associated QC be closely related to project objectives in order to eliminate unneeded samples and better focus project resources.

This QA Project Plan also contained other problems in the area of sampling and sample analysis. In some cases, it appeared that the intended quantity of sample was not sufficient for the analyses that were to be performed. In other cases, the matrix spike compounds were not appropriate for the types of pollutants expected at this particular site. In at least one case, an outdated procedure was proposed.

A major goal of the QA review process is to assure that the integrated plan is satisfactory to all project participants and consistent with project objectives. Because of this review, project participants came to realize that this goal had not been achieved, and that further planning was necessary. Since the implementation of the initial test plan would have provided for the wrong types of tests and samples and would not have satisfied project objectives, it can be stated that the QA review prevented the sampling and analytical effort from being misdirected, and this in turn saved the Agency an estimated $400,000.

Case Study IV

One of the more common shortcomings revealed by QA Project Plan reviews is the use of inappropriate analytical methods. Quite often, a standard method is planned for a non-standard application for which it was not intended. In this particular RREL project, the accurate determination of volatile organics in a low-boiling extraction solvent was critical to the success of the project. According to the QA Project Plan, Method 8240 was to be employed for determining VOCs in the extraction solvent. While this method is appropriate for determining VOCs in soil or groundwaters, it was inappropriate for VOCs in this medium, at least without some modification, due to co-elution problems.

In response to these concerns noted in the QA Project Plan review, the sampling and analytical contractor has undertaken extensive efforts to adapt Method 8240 to the extraction solvent. In particular, a pretreatment procedure was devised for removing the majority of the solvent while leaving the VOCs of interest, followed by conversion to a solvent compatible with Method 8240. Method validation data were established which demonstrated that the accuracy, precision, and detection limits for this modified method would be satisfactory for the intended use. At this time, all concerns noted in the original QA Project Plan review have been satisfied, and a field test is scheduled for early 1990. The project management and analytical team can now proceed with confidence that this analysis should yield data of known and adequate quality.

TECHNICAL SYSTEMS AUDITS

Case Study V

This field Technical Systems Audit (TSA) was carried out by the RREL QA program in support of a project involving the destruction of a compound in a commercial-scale incinerator. The only critical parameter in this case was NO_x since previous tests had established an adequate destruction removal efficiency.

This incinerator routinely monitored NO_x during its commercial operations in order to meet State permitting requirements. Because of the ongoing nature of this operation, it was possible to carry out an on-site TSA of the NO_x measurement system prior to the incineration of the compound of interest.

This TSA was carried out according to the standards presented in the QA Project Plan and Method 7E (40 CFR 60, Appendix A), which in some regards were more stringent than the State requirements. The on-site TSA revealed that the QA procedures required by these documents -- such as zero and calibration drift, sampling system bias, linearity, and leak checking -- were largely lacking. Record keeping was inadequate, and a written QA/QC program was not available. Other questionable practices, such as the use of an unheated sample line, were also observed.

Had corrective action not taken place, it is unlikely that the NO_x data would have withstood the close scrutiny of the various government agencies interested in this project, and the incineration test, conservatively estimated to cost $50,000, might have been summarily terminated. However, by carrying out this field TSA prior to the actual incineration, the aforementioned problems could be corrected ahead of time, and the tests could proceed with the confidence that the various oversite and permitting agencies would be satisfied.

Case Study VI

A common problem encountered during Technical Systems Audits (TSAs) is a lack of communication of project-specific requirements to the analyst and technicians. In this case study, a failure in this regard led to critical concerns that could only be corrected through the reanalysis of all the samples.

The purpose of this RREL project was to demonstrate the ability of a procedure for removing PCBs from soils and sediments. Unfortunately, the chemists responsible for the PCB analyses had not been informed of the specific QC requirements for this project. Not surprisingly, this critical determination was being carried out essentially without any of the required QC.

- There were no matrix spikes carried out with the PCBs. Instead, the laboratory spiked samples with pesticides, which is common practice when this determination is carried out for general survey purposes. Unfortunately, pesticides were of no interest to this project.

- An incorrect surrogate had been spiked into samples. While the surrogate that was employed may simulate the behavior of pesticides, it was not considered representative of PCBs.

- At the time of the TSA, no matrix spike/matrix spike duplicate data were available.

- Although required by the QA Project Plan and the method, no QC check sample had been included.

The data produced up to the time of the TSA was thus of unknown accuracy and precision, and of little value to the project.

The TSA also identified related concerns. In particular, extractions for all organic analyses were being carried out in a non-standard method likely to lead to sample degradation and volatilization. For the determination of volatile organic compounds (a less critical measurement), no matrix spike or matrix spike duplicate analyses were being performed, and no QC check samples were being analyzed.

Upon completion of this TSA, the laboratory agreed to promptly correct these problems and reanalyze all samples at their own expense. Because this TSA was carried out early in the analytical phase, no critical data were lost. A follow-up audit carried out one month after the initial audit confirmed that all concerns related to the critical determination had been addressed satisfactorily.

FINAL REPORT REVIEWS

Case Study VII

Perhaps the primary reason RREL carries out QA reviews of final reports is to determine whether or not conclusions are adequately supported by data. Many of the end users of these reports may rely on the summary and conclusion sections only, and it is thus important that these sections accurately reflect all findings.

The subject of this Final Report was an extraction process intended for the removal of PCBs from soils and sediments. The critical measurements included PCBs in the untreated soil, in the treated soil, and in a concentrated waste discharge stream. PCBs retained in the internal plumbing were measured at the end of the treatment by rinsing internal parts with a solvent, and a mass balance was calculated around the overall process.

According to the report, the removal efficiencies for PCBs -- the primary figure of merit for this process -- were in the range of 80 to 98 percent. However, a more careful review of the data carried out as part of the Final Report Review suggested that these control efficiencies were somewhat optimistic, at least without the addition of a cautionary discussion.

- For this particular process the sediment or soil was recycled through the extraction vessel several times in order to achieve the desire cleanup efficiency. PCB concentrations normally decrease with each cycle, but in some cases increased concentrations were observed. When calculating control efficiencies, these latter data were disregarded and only the lowest concentrations were included. Thus, the final control efficiencies were based on an unjustified, selective use of data. The Final Report Review thus recommended that the conclusions be based on all data, or that the rejection of data be justified.

- Of equal importance to the reviewer was the large fraction of PCBs that was retained by the internal plumbing of the treatment system and not discharged in the concentrated waste stream. This fact, coupled with the poor mass balance, suggested the possibility that the system had not yet reached equilibrium and that the retained PCBs would eventually find their way via recycled solvent to the treated soil effluent. Were the retained PCBs to exit with the treated soil, the control efficiencies would drop significantly.

Simply stating the control efficiencies without any discussion of the aforementioned problems leaves the reader with an overly optimistic view of the subject technology. It was thus recommended that the conclusions be made more complete to reflect all significant results.

Case Study VIII

The subject of this Final Report Review was a summary report of various hazardous waste treatment technologies. This document compared the various technologies with respect to applicability, effectiveness, and cost, and provided a brief summary of each technology. It was thus critically important that these summaries incorporate technical information and conclusions that were accurate and comparable, and that any assumptions associated with important claims or conclusions be effectively conveyed.

The most serious concern noted in this RREL QA review was that a number of conclusions presented in the summary documents were not well supported by demonstration results. Many of these questionable conclusions had been presented in the summary sections of the technical reports dealing with the individual technologies, but without adequate support from the data. It thus appeared that conclusions in the summary report had been taken from the individual reports without the supporting data being critically evaluated.

This review also noted that the summary report was deficient in providing a means for comparing the various technologies. For example, these various technologies were rated according to their

ability to achieve successful treatment. However, what constituted successful treatment was not defined and presumably varied from one technology to the next. Similarly, the various technologies were compared with respect to generalized cost without identifying the underlying assumptions. Under this situation, direct comparison of cost information was of limited usefulness.

Another concern identified in this review was that results from the site-specific tests were often over-generalized. Thus, the summary report might state that a technology was applicable to all types of soils, when in fact it had only been tested on sandy soils.

The review noted that the summary document was potentially useful, but in its current state contained significant inaccuracies and omissions.

CONCLUSION

As is illustrated by these case studies, the key to an effective QA program is early involvement. Project Plans must be reviewed before sampling and analysis are initiated, while changes can be made at relatively low cost. On-site inspections (audits) must be carried out early enough in the sampling and analytical phases to permit timely corrective action, and final reports should be reviewed before project budgets have been completely expended.

RREL has found that early interaction is best facilitated through QA awareness, and for this reason the RREL QA management has been actively developing and marketing its QA Program. A dynamic QA Program working in concert with project participants ultimately lends itself to Total Quality Management and this, in turn, avoids the costs and delays associated with repeated efforts because "the right things are done, the right way, the first time."

To Here

4

DEFINING VARIOUS LEVELS OF ASSESSING THE QUALITY OF ENVIRONMENTAL DATA

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ABSTRACT

Due to the increased importance placed upon using data of known quality to support environmental studies, almost all environmental data are reviewed at some level. This activity is often required by federal, state and other agencies to assess data being gathered in their respective environmental programs. Additionally, this activity is becoming a routine part of private sector environmental studies in order to comply with various regulatory programs. The basic topic of this presentation discusses three levels (types) of review that are commonly used in assessing environmental data. A brief outline of each data review level is presented including requirements, the intended purpose for each review type, and the information generated by each review. The overall aim is to assist data users in determining which type of review(s) will best meet their needs.

INTRODUCTION

Many regulatory programs are shifting the responsibility of environmental liability to private sector parties (potentially responsible parties or PRPs) and hence the responsibility for conducting environmental studies. Previously, data assessments were performed by government agencies and their contractors. However, this responsibility is now being transferred to the PRPs and/or their contractors.

There are many reasons for assessing the quality of data. The most important reason is being in compliance with EPA policy. The Agency-wide QA policy stipulates that every monitoring and measurement project must have a written and approved quality assurance project plan (QAPjP). An essential part of all QAPjPs includes the procedures to be used for the reduction, validation and reporting of the data. This parallels the agency's directive that all environmental data for use in studies be of adequate quality for its intended purpose.

The issue of liability raises another reason for determining the quality of environmental data. Using data of known and adequate quality to support results of environmental studies, and thus in decision making processes, will help to reduce the potential liabilities associated with these decisions. Data used in support of environmental studies are the basis upon which decisions of environmental problems are judged, therefore the use of data of known quality becomes most important.

PERFORMANCE VERIFICATION

The most basic level of data review is a performance verification review. Performance verification may be defined as a review process that evaluates the completed performance of a task according to specified protocols and requirements through review of written documentation such as raw data, logbook entries, and reports, etc. Performance verification evaluates the adequacy of sampling requirements and sample analysis according to specified protocols and methods as well as addressing completeness of the documentation.

The intended purpose of a performance verification review is to evaluate only the performance of certain sampling requirements and sample analytical procedures to the specified methods and/or other required protocols as defined in the project QAPjP. A performance verification review can be a valuable tool in aiding the assessment of data quality and more importantly to identify incomplete or non-compliant data which may compromise data quality.

A performance review requires knowledge of the sampling and analysis plan as outlined in the project QAPjP. Pertinent information such as the number of samples, matrix, sample preservation, required analyses, method(s) of analysis, frequency of field QA samples, and sample holding times are found in the QAPjP, and lay the foundation for the review. This information is reviewed and the criteria for review of the data are developed. Although many areas of data are examined, the performance verification review looks at four main areas: (1) sample preservation and holding times; (2) method performance; (3) data completeness; and (4) results verification.

Verification of the sample preservation and holding times is accomplished by review of sampling documentation (often the sample chain-of-custody forms or other sampling documentation such as logbook entries) and raw data to determine preparation and analysis date of the samples. Deviations from the required preservation and holding times are noted, as they may have a profound effect upon the quality of data.

The second area, method performance, begins with review of the specified method. The method is reviewed to determine important areas such as the scope and application of the method, applicable analytes, required instrumentation, sample preparation, detection limits, interferences, sample analysis procedure, required QA, and required documentation. The data are reviewed to determine any deviations from the method. This step is crucial to establish comparability between similar analytical results performed using the same method, and to ensure that the proper QC procedures were employed in order to estimate the quality of the data.

The third step, data completeness, is usually performed concurrently with the method performance check of the data. This step ensures that all data required to completely substantiate the analytical results are present. This may include pertinent sampling documentation, analytical data, and tabulated sample results. This step often involves communication with the laboratory (or sampling personnel, if appropriate) to ensure the completeness of the data package.

The last step, results verification, is the most painstaking part of a performance review. This involves the verification of the reported sample results using the supplied data. In the case of data results reported in handwritten format, it is often necessary to verify each data point for accuracy against the raw data. However, for computer generated results, anywhere from 10-30% of the results for each method are verified, and 100% of the results checked if discrepancies are found. This step not only includes verifying the sample results but entails review of the QC sample results, because the results of the QC sample analyses are used in determining adequate performance of the method. Obviously, the third step, data completeness, is essential to perform the results verification. Again, communication between the laboratory and/or sampling personnel is essential in the event that discrepancies or errors are determined, so that the necessary information is supplied.

The end product of the performance review is a report specifying deviations from the requirements in the QAPjP, the specified analytical method(s), data completeness, and discrepancies between the reported results and the raw data. Although the information in a performance review report is not intended to completely define the quality of the data, it will give an indication to the implementation of the requirements stated in the respective QAPjP such as data completeness, comparability (as it relates to method performance), and identification of shortcomings in the sampling and analysis precesses. This level of review by itself is generally unacceptable for use in determining the quality of data prior to use. However, performance verification reviews are used in determining contractual compliance and assuring the completeness of data deliverables. The performance verification review is a precursor to and is often an inherent part of the next level of data assessment, which does attempt to determine the specific quality of environmental data.

DATA VALIDATION

The next level of assessing data is commonly referred to as "data validation". Data validation is as "a systematic process for reviewing a body of data against a set of criteria to provide assurance that the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verification, certification, and review[1]." The purpose of data validation is to estimate the quality of the analytical results of each parameter of interest. This is an important facet in determining the overall data quality[2].

In practical terms, data validation is the review of sample and quality control analyses data and comparing the results of the quality control analyses to a set of pre-established criteria which are then used to estimate the quality of the sample results.

The basic aspects of data validation are: (1) performance verification review; (2) QC results review and criteria comparison; (3) sample results qualification; and (4) results editing and reporting. As previously discussed, performance verification is an integral part of performing a data validation study. Certainly the screening, checking, auditing and verification aspects of data validation are covered in a performance verification review. Theoretically, if the performance verification has been performed on the data, this step can be omitted during the data validation study and areas 2-4 completed; however, most data validation review guidelines incorporate the performance verification review into the process.

The QC results review and criteria comparison step is where the quality of the sample result for each parameter is estimated. The QC parameters common to most analytical procedures used in determining the quality of data results are: (1) holding times and sample preparation; (2) contamination (field and laboratory blanks); (3) surrogate recoveries; (4) matrix spike recoveries; (5) matrix spike duplicate deviations; (6) duplicate deviations (field and laboratory); (7) field replicate deviations; (8) instrument calibration performance; (9) internal standard response; and (10) primary standard recoveries (commonly called a laboratory control sample or a laboratory QC sample). This list is by no means complete, and only common elements to most types of analyses are presented. The specific QC is dependent upon which analytical method and/or sampling QC parameters are employed.

For instance, trace metals determination by the current Contract Laboratory Program (CLP) protocol requires the analysis of an interference check sample (ICS) to determine if interelement correction factors are adequately determined and applied for analysis by inductively coupled plasma (ICP) spectroscopy in the presence of high concentrations of interfering analytes.

The QC results for each specific method are reviewed and compared to the pre-established criteria. The criteria for the evaluation of the data quality is specified in the QAPjP. Criteria for qualification of data results are established in part by the data quality objectives (DQOs) determined prior to project start-up.

For CLP data, the validation review is completed using the "U.S. EPA Functional Guidelines for Review of Inorganic and Organic Data, Rev. 1988". Various state environmental programs have also generated data validation review guidelines, such as NJDEP's "Quality Assurance Data Validation of Analytical Deliverables - TAL Inorganics and TCL Organics, Rev. 1989".

For other methods/protocols where guidelines have not been clearly established, the acceptance criteria for the QC analyses are specified in the QAPjP. QC sample analysis results that lie outside the specified acceptability criteria are summarized and, depending on the nature and the severity of the problem, the quality of the associated field sample results are determined. This is considered the sample results qualification step. There are three (3) general categories into which data results are classified: (1) acceptable (meaning the datum point is considered both quantitative and qualitative, which is the result of no identified problems during the review (2) estimated (the datum point is considered qualitative, but the reported quantitative result is an estimated quantity); or, (3) rejected (the datum is considered neither qualitative or quantitative, and should not be considered for use in the project study).

This step also requires that the reasons for each qualification be summarized. This usually takes the form of a written report, detailing the qualification made to the data, the criteria with which the QC sample result was compared, and the results of the QC parameter necessitating the qualification(s).

The last step to a data validation review is editing of the final reported sample results. A variety of methods exist for performing this task. The common element to this step is the application of pre-determined and defined qualifiers to the reported sample results corresponding to the qualifications described above. Using the three general categories defined above, the established CLP data qualifiers for instance are: (1) none (no qualifiers are added to reported sample results for acceptable results); (2) "J" - (the qualifier is added to sample results deemed to be estimated values); and (3) "R" - (the qualifier indicating the reported sample result as being unusable for its intended purpose. Two common methods for this process are directly placing the qualifiers on the sample results summary forms or using separate computer spreadsheets which involve transfer of the sample results to the spreadsheets and applying the data qualifiers to the spreadsheet.

Adding the qualifiers to the reported data sheets is advantageous because it can be accomplished quickly and the chance for error in transcribing data to a computer spreadsheet is non-existent. The disadvantage is that no capability exists for statistical manipulation of the data and the analytical results may not be in a format that can be readily incorporated into a final project report. The advantage of using computer spreadsheets includes the ability to perform statistical manipulations, sorting and graphical representation of the results, and the capability and ease of formatting the results for presentation. The drawback is that additional time is required for transfer of the data to the spreadsheet and the accuracy of the data transfer must be verified. This disadvantage can easily be solved by requesting the data in computer readable format by the laboratory.

The end result of a data validation review will be a report addressing the quality of each data point, a qualified summary of the sample results and, a justification of the qualifications made to the data. The results of the review are used in determining the adequacy of the data for its intended use, and decisions for including or omitting data in the project study. Valuable information towards determining the overall quality of data through determination of the accuracy, precision, completeness, representativeness and comparability is provided from the results of a data validation review.

INTERPRETIVE REVIEWS

The final level of data assessment, an interpretive review, can be defined as the process by which the total or overall quality of data for a project is estimated in its ability to satisfy the intended use of the data. The purpose of this type of review is to attempt to determine whether the quality of data has met the quality assurance objectives for the project.

Quantitative indicators of data quality for precision, accuracy, detection limits and completeness can certainly be calculated and presented. These quantitative indicators can then be compared to the QA objectives presented in the QAPjP allowing statements concerning the results to be made. This may be confusing, because many of these parameters have been previously addressed by the performance verification and data validation reviews. To some extent this may be true; however, the data validation review is meant to determine the quality of individual measurement results for each parameter. Whereas, the interpretative review uses the information provided by the performance verification and data validation to obtain an overall picture of the data quality with respect to the stated data quality objectives.

In addition to qualitative indicators of quality, an interpretive review may include some statistical manipulation of the data such as total concentration, arithmetic and geometric means, ranges, standard deviation, relative standard deviation, statistical significance tests such as u-test, t-test, F-test, chi-quare test, the determination of confidence limits, and tests for outliers. The type of statistical analysis required varies from project to project, and again, is specified in the QAPjP.

The information generated by the interpretative review carries the assessment of data quality further yet than the previous levels and supplies more information to aid the data user to develop the overall picture of the data quality.

SUMMARY

In summary, three levels of assessing the quality of environmental data are presented. Each level produces information that is designed to assist the data user in determining whether the quality of data meets its intended purpose. The performance verification review level addresses the completeness of the data deliverables, performance of the sampling and analysis of the samples to the required frequency and methods, and verifies the accuracy of the reported results from the raw data. The data validation review addresses the specific quality of each reported results for each parameter of interest and includes the screening, checking, auditing and verification aspects of performance verification as well as the editing, certification and review aspects as included in the definition of data validation. The interpretative review is the highest level of data assessment as it relies upon the information generated by performance verification and data validation reviews and is intended to assist data users in determining the overall data quality for its intended use. The interpretive review may also provide the results of statistical and other data manipulation to assist the data user in interpretation of the data.

The data user, by understanding these different levels of data assessment will be better poised to make informed decisions on what level of review they need to meet their specific objectives.

ACKNOWLEDGEMENTS

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REFERENCES

1. "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans", QAMS-005-80, United States Environmental Protection Agency, EPA Document 600/4-83-004, 1983.

2. "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans", QAMS-005-80, United States Environmental Protection Agency, EPA Document 600/4-83-004, 1983, pp. 27-28.

5 CONTINUOUS QUALITY IMPROVEMENT IN THE ANALYTICAL LABORATORY

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ABSTRACT

The legal requirement for "compliance" dictates most laboratory quality assurance (QA) programs. An external authority, usually the U.S. Environmental Protection Agency, sets minimum standards, and the laboratory designs a QA program to meet those standards. This paper describes an approach to assuring analytical quality that considers compliance with minimum standards not as a goal but as a starting point. Called quality improvement (QI), this approach is actually a continuous process. It begins with the resolve to meet existing standards and moves on to embrace continuous change as a positive force in the organization. Through this process, the laboratory can anticipate higher standards rather than struggle to meet them after they are promulgated. To implement the QI process, three ingredients are critical: management commitment, employee involvement, and a system for measuring performance and progress. By describing one laboratory company's experience in making continuous QI part of its culture, this paper examines these three areas.

INTRODUCTION

How do we define "quality" in an environmental laboratory? With the 1979 publication of its "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," USEPA set the stage for the use of the terms Quality Control (QC) and Quality Assurance (QA) as the definitions of record. QC typically refers to the specific techniques and activities applied at the bench to verify that analytical results are precise, accurate, and consistent. QA refers more broadly to an overall management program aimed at assuring data defensibility on a continuing basis. Both terms suggest rigidity: labs that follow accepted QC techniques under the guidelines of an organizationwide QA program are, by definition, meeting quality objectives. Nothing more is needed.

The term Quality Improvement (QI) recognizes that, where quality is concerned, more is always needed. While this term

is quite new to the environmental laboratory community, the manufacturing industry has been practicing QI for a considerably longer time. The best American businesses realize that to thrive in a competitive market, they must produce a high-quality product and then make it better. Environmental labs can apply the same principle to their product, analytical data: adopting the concept of QI, the analytical team learns to do its work well, then better, and then better still. In the process, the quality of the product and of overall laboratory operations improve far beyond minimum compliance standards, much to the satisfaction of laboratory clients--and regulators.

Where the goal of QC/QA is to make laboratory operations sufficiently rigid to ensure data defensibility, QI's goal is to improve every operation--continuously. Expanding the definition of quality from QC/QA to include QI involves more than just adopting new techniques, however. At B C Analytical (BCA), we have spent the past two years on just such an expansion, developing and incorporating the QI concept throughout our three California laboratories. We found three ingredients to be critical in implementing a QI process: a commitment from the management, the involvement of every employee, and the identification--and measurement--of areas to be improved.

MANAGEMENT COMMITMENT

Like many other environmental laboratories, B C Analytical (then Brown and Caldwell Laboratories) was undergoing rapid growth in size and revenue in the mid-1980s. In that seller's market, the company's management recognized that short-term production demands were preventing a rational approach to long-term planning. We hired a management consulting company to assist with the planning effort. The first step was a client survey.

Through some 40 interviews with clients, BCA managers not only identified some possible directions for long-range planning, we learned of areas in the company that could benefit from immediate improvement. One of these areas surprised us as it concerned the quality of our product. We had assumed our quality spoke for itself: we had a quality assurance manager dedicated to overseeing our QA program since 1985, and we routinely complied with regulations, doing QC techniques (spikes, duplicates, blanks, and laboratory control standards) just as the methods required. Yet according to our clients, our reputation for quality was good but not outstanding.

In 1988, BCA chose to move beyond the "minimum compliance" approach and began a deliberate shift to continuous quality improvement. Because a QI process represents a fundamental shift in managing laboratory quality, it must be fully supported by top management. Fortunately, members of the management team had been doing some reading in modern industrial practices and were becoming familiar with terms like Total Quality Management, Quality Improvement, and World Class Manufacturing. Like the other quality initiatives that have preceded it--Shewhart charts, statistically based control limits, and so forth--QI derives from industrial experience.

BCA's management therefore enlisted a management consultant with industrial experience to help the company make positive changes in a variety of areas: analytical operations, human resources, marketing, and profitability. Management meetings quickly identified the quality improvement process as the engine to drive these changes. We realized that QI would give BCA a three-fold advantage in our competitive arena. By adopting this process, we could correct specific deficiencies perceived by clients, stay ahead of regulatory compliance, and distinguish ourselves in the marketplace in a readily identifiable way.

The decision to adopt the QI process and then hiring a consultant to help set that process in motion was not the extent of management's commitment. Nor could it be. To make any program work, management must back up its verbal commitment with an allocation of resources. In BCA's case, these resources included assigning me in 1988 to manage BCA's conversion from QC/QA to QI as part of my job as QA director and also providing time during business hours for educating and training staff in the QI process. BCA's commitment went even further--to involving employees in the actual design and implementation of that process.

EMPLOYEE INVOLVEMENT

If a company's culture encourages a view that only some employees, such as a Quality Control Department, are responsible for quality, QI will not be effective. BCA's management realized we could not only improve laboratory quality but also enhance the feeling of involvement in the company's future by having the employees themselves craft and operate the improvement program.

Management had reason to believe our employees could have a positive influence on turning the concept of QI into an actual and effective process. When the company conducted its

client survey in 1987, it also conducted one for staff. Employee suggestions for change resulted in a training program on problem-solving techniques and the formation of a task force to address ways to improve turnaround time. Although this was BCA's first experience with a focused task force, employee standing committees had long been a part of laboratory operations. Safety committees in each lab, for example, combined their efforts to develop the company's comprehensive Safety Manual.

Thus, management found the decision to pursue QI through employee involvement a logical one. However, having made that decision, we then faced another one: whether to adopt the principles of a single expert or to develop a custom program. Both sides have merit. If a company follows one of the so-called quality "gurus," it will find a mature philosophy with a proven track record. But in this "expert" approach, any mismatch with the existing company culture may cause the program to falter for lack of employee acceptance. With a customized or home-grown system, a company is assured of a good cultural fit with existing staff, but the techniques applied have no track record and may not be effective. Wanting our employees to feel free to be innovative, BCA decided on a home-grown approach.

Volunteers from all lab disciplines responded to our call for participation. They formed a 21-member Steering Committee whose purpose was twofold: to identify performance areas that contribute to quality in the laboratory and--based on the belief that no area could be expected to improve if not measured--to determine procedures for measuring that performance.

In our preliminary design of the QI process, management had come up with suggestions of several areas for measurement and improvement. With help from our management consultant, the Steering Committee undertook a comprehensive review of those suggestions, breaking into smaller subcommittees to examine different aspects of the measurement program.

MEASUREMENT SYSTEM

After three months of work, the Steering Committee had endorsed some of the suggested performance areas, deleted others, and modified most. In settling on a final structure they selected seven indicators of laboratory performance, which are directly related to quality, for regular measurement and reporting: turnaround time, amended work products, quarterly internal audits, performance on external

check standards, QC frequency, corrective action, and housekeeping/safety. The areas are defined as follows:

Turnaround time. An indication of our responsiveness to clients' schedules; measures the time spent handling a sample between log-in and final report of analytical results.

Amended work products. A review of the quality of our product; measures the number of reports and invoices we have to correct after clients have received and reviewed them.

Quarterly internal audits. A self-evaluation of our quality assurance program; measures performance against a lengthy checklist based on criteria expressed by external auditors.

External check standards. A test of the accuracy of our data; measures results of analyses on check samples provided by clients, agencies, or other outside organizations.

QC frequency. A display of how often we comply with specific quality control requirements; measures the actual rate of QC activity against the "ideal" rate.

Corrective action. A verification that we have acted on QC sample results that appear outside established control limits; measures how well we solve and document our response to an identified problem.

Housekeeping/safety. Evidence of our commitment to quality in the workplace; measures each laboratory area against company and regulatory standards for the well-being and safety of employees and client samples.

Using these indices, the committee developed a numerical system for measuring and scoring performance on a monthly basis. The scores are applied to an overall performance matrix (Table 1) so improvement can be tracked on an ongoing basis both by individual lab and for the company as a whole.

The measurement system was initiated in the laboratories in September 1988. Through a simple newsletter and informal discussions, Steering Committee members had kept co-workers regularly apprised of their progress. In addition, they conducted in-depth training sessions to familiarize each employee with the system and the personal involvement it entailed. Data for September's indices were collected and

given to staff as a baseline against which future improvements would be measured.

As expected with any new program, some fine-tuning was needed a few months after the measurement system went into effect. Such fine-tuning is a given in the continuous QI process. The Corrective Action index is a case in point. Laboratory experience first showed us that the index as designed did not accurately measure performance. Initially conceived simply as a manual check of notebooks and other documentation for obliterations, missing dates/analyst initials, and the like, this index was redefined to be a truer measure of "corrective" action: the identification of QC outliers was added to the manual check, which also verified that the analyst had documented any action taken.

A few months after this revision, changing regulatory requirements and increasing client demands for a high quality product prompted us to revise it again. Needing to define what constituted documentation of corrective action, we generated a Standard Operating Procedure (SOP) for this subject, held lab-wide training sessions, and changed the measurement formula for the index to reflect the new requirements. Figure 1 shows our performance in this index; just after each revision, performance drops and then rises as employees master the techniques involved. Our overall progress demonstrates not only an improvement in quality, but an ability to respond to changing requirements.

PROGRESS

Almost every performance index has improved since baseline data were established in the fall of 1988. Monthly reports continue to be provided to management and employees showing scores for that month's performance in each index. An examination of the QC Frequency index scores shows the progress that can be achieved when employees know and understand the standards under which they should be operating (Figure 2). Most of the indices have worked as well as this one. Turnaround time is improving, QC frequency is up dramatically, and corrective action is now very high--in spite of tightened standards during the past two years. Table 2 shows the progress BCA has made in each of the seven indices since we began measuring them two years ago.

Management remains committed to the process, as evidenced in its continued support of employee involvement activities. Employee groups routinely address and solve laboratory related issues. One task force was formed after USEPA Region 9 issued data validation requirements for data packages that

do not fall under its Contract Laboratory Program. Many laboratories, including ours, found the requirements difficult to interpret and challenging to meet. This task force developed our response to the Region's data validation requirements. We now have in place an SOP for the packages and a well-defined system for producing them. They are still difficult and expensive, but we can do them routinely with a high expectation of passing the validation review.

Another task force is currently working on the measurement and improvement of service quality. Comparing ourselves to the best of service companies (hotels, car rental agencies, and the like), we expect to identify and measure improvements in the purely service aspects of our work.

For ongoing improvement in areas which need continuous attention, standing committees are used. Of particular value are the quality improvement committees in each laboratory. Consisting of staff from every area--including sample receiving and client services--these committees select their own improvement agenda. Chaired by the lab's QA coordinator, the committee meets weekly to assess progress and chart improvements.

Supported by laboratory management, the QA committees have been instrumental in many quality successes throughout the company. Responding to an outside audit program that found fault with our records relating to receipt and preparation of standard materials, our southern California improvement committee developed a comprehensive, consistent system of standards log books for use companywide. The northern California committee took on and completed the challenging task of defining a two-tier corrective action system which is now in place. The committees worked together to implement a program of custom-printed serially-numbered bench books now in use. Ordered in a single series, every notebook in the company is uniquely identified as to purpose and location.

SUMMARY

By devising procedures for measuring performance and involving employees directly in the concept and implementation of the process those procedures support, laboratories can see positive change in the quality of their product. As their quality improves, so does their standing in the industry. Instead of merely responding to requirements devised by outside agencies, quality-conscious laboratories can help those agencies shape programs that meet today's environmental demands.

Through the QI process, for example, BCA has improved relationships with regulators. In California, the Regional Water Quality Control Boards have enforcement authority over a wide variety of water, wastewater, and hazardous waste disposal activities. Once viewed as adversaries, we now have a positive relationship with the boards. One of the boards has pointed out our superior quality program from among a group of State-certified laboratories.

We have also improved relationships with clients. All three of our laboratories have undergone the rigorous audits by Mitre Corporation on behalf of the U.S. Air Force. While there were several corrections requested--and made--our improvement process helped us make a generally favorable impression. Although audited for current performance on a single contract, our continued good standing with the program has brought BCA two more Air Force projects.

Our measurement system has also demonstrated that high quality and financial health are compatible. That may not seem surprising, but one often hears that higher quality can be achieved only at the expense of lost earnings or higher prices. While we have not proved Phillip Crosby's postulate that "quality is free," we have found that resources allocated to the QI process provide a favorable return on the investment. As quality improves, so too can a laboratory company's size and revenues. Since BCA initiated the QI process in 1988, we have added one new lab in southern California, relocated into another, larger facility there, and doubled our operations in northern California. During the summer of 1989, we accomplished the physical move from one lab to another with no appreciable drop in our performance scores, because lab staff were thoroughly practiced in the skills necessary to maintain quality work.

Almost two years after the QI process began, employees are seeing positive results from their involvement, which reinforces management's commitment. With management's support, a new task force of employee volunteers is now reviewing the entire performance measurement system in order to hear employee concerns and propose further improvements. This review is a good example of what continuous QI entails: every aspect of laboratory operations is subject to change and improvement. Just as a conscientious environmental lab can never consider the quality level of any work product to be "good enough," neither can it consider any improvement process to be "good enough." In the continuous quality improvement process, change is indeed a constant.

Table 1. Performance Matrix

Score	Turnaround Time (%)	Quarterly Audit (% yes)	External Check Stnds (% in range)	QC Frequency (% of Assigned	Correc Action (Fraction Complete)	Amended Work Prod (parts / 1,000)	Housekeep/ Safety (1-5)
10	95—99	98+	98+	98+	.95+	0—2	4.7—5.0
9	90—94	96—97	96—97	96—97	.90—.94	3—7	4.3—4.6
8	85—89	94—95	94—95	94—95	.85—.89	8—12	3.9—4.2
7	80—84	92—93	92—93	92—93	.80—.84	13—17	3.5—3.8
6	75—79	90—91	90—91	90—91	.75—.79	18—22	3.1—3.4
5	67—74	88—89	88—89	88—89	.70—.74	23—27	2.7—3.0
4	59—66	86—87	86—87	86—87	.65—.69	28—32	2.3—2.6
3	51—58	84—85	84—85	84—85	.60—.64	33—37	1.9—2.2
2	41—50	82—83	82—83	82—83	.55—.59	38—42	1.5—1.8
1	40	80—81	80—81	80—81	.50—.54	43+	1.0—1.4

Table 2. Performance Results, first 18 months

Index	Sept `88	Feb `90
Turnaround time	42%	77%
QA Audit	92%	95%
External Check Stnds	83%	91%
QC Frequency	72%	90%
Corrective Action	.25	.78
Amend Work Product	23	28
Housekeeping/Safety	3.5	4.3

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Figure 1. Corrective Action

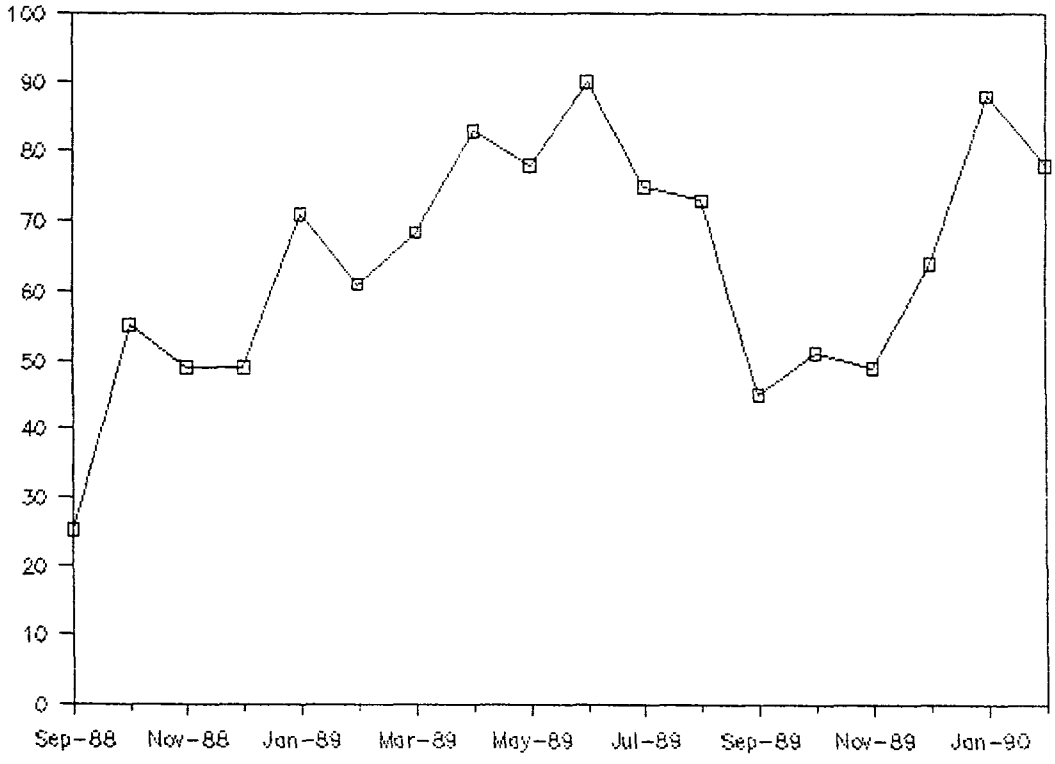
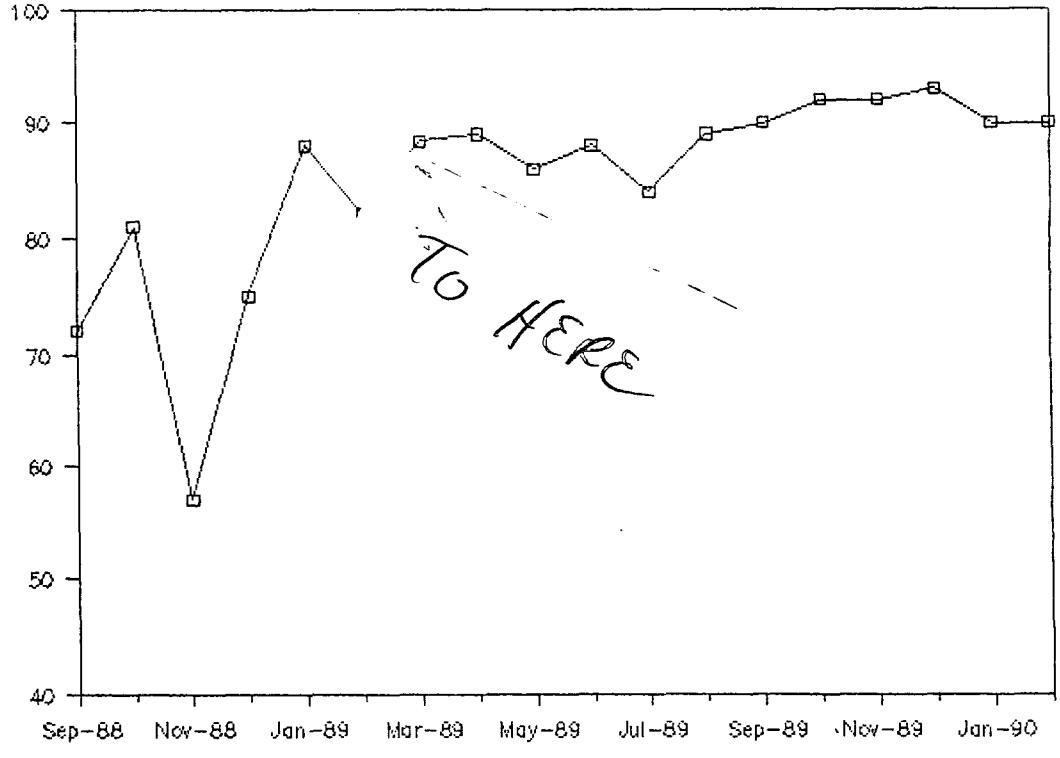


Figure 2. Q C Frequency



6

A LANDBAN DATABASE APPLICATION

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ABSTRACT

With the advent of the Land Disposal Restrictions and subsequent First and Second Thirds regulations, it became apparent to CWM that a database management system should be developed to manage the volume and complexity of the information. The development of the application identified the variability of the standards, a number of inconsistencies and that the use of this information is at best complicated and confusing. Furthermore, it became evident that incorporation of additional data (e.g., SW - 846 Method Numbers, PQLs and CAS Numbers) into the database application was necessary to provide more precise information and clarify the use. Since its distribution within the corporation, it has proven to be a valuable tool.

INTRODUCTION

The Land Disposal Restriction regulations (Landban) contain an enormous amount of data in an extensive tabular format from multiple data sources. Moreover, much of the data in the Landban list have been added or changed as each of the Landban regulations have gone into effect.

In its present form, the Landban list is very time consuming to manually search through, increasing the possibility of human error when identifying which Method of Treatment or Treatment Standard is associated with a Waste Code. This makes interpretation difficult because of the manner in which data is tabulated.

The CWM people responsible for tracking Landban information found a need for a flexible way to easily access the entire Landban listing. As a solution, the Riverdale Technical Center created a relational database which could query all Waste Codes associated with known compounds and display these in a tabular format.

The original Landban Application was written in Lotus Symphony™. However, this version was restrictive for two reasons: data was not easily retrieved, and 20 or 30 different versions of the same basic design had to be written in order to accommodate each of our lab's specific requirements.

From the amount and type of data involved, it was decided that the Landban list was an excellent candidate for a relational database. Microrim's R:base for DOS™ was selected for the next prototype because of programmer familiarity and ease of use.

The first release of CWMs Landban software (version 1.0) was in September 1989 and contained EPA Treatment Standards and Methods of Treatment for solvent and dioxins, the California list, and First and Second Thirds (see Figure 1). It was accessible by Waste Code or compound. This version was simple to use, but not very user-friendly because the query screen did not permit the user to scroll through the list and some numbers were difficult to read (see Figure 2).

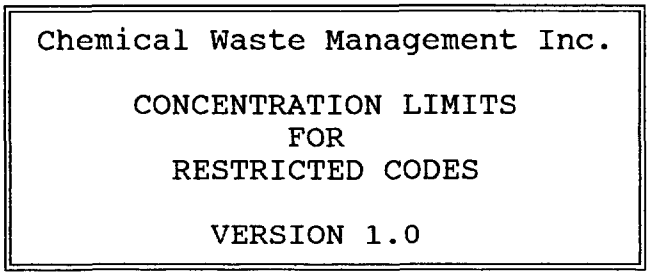

Figure 1: Initial Screen for Landban Application (version 1.0)

Version 2.0 (shipped in January 1990) contained the proposed Third Thirds requirements, SW - 846 Method Numbers, an incomplete list of CWM Practical Quantification Limits (PQLs), EPA PQLs, and CAS Numbers, in addition to the same contents as version 1.0. This version was easier to use than version 1.0 because the user could scroll up and down through query screens, and more readily see which record was displayed and the numbers highlight with different colors when the cursor rests on them (see Figure 3).

Chemical Waste Management Inc.
Hazardous Waste Codes

WASTE CODE	WW/ NWW	COMPOUND	TRMT. STANDARD	CCW/ CCWE	REG. SOURCE
K086	NWW	1,1,1-TRICHLOROETHANE SOL WASHES	0.044	CCW	1ST 3RD
K086	NWW	1,2-DICHLOROBENZENE SOL WASHES	0.49	CCW	1ST 3RD
K086	NWW	ACETONE SOL WASHES	0.37	CCW	1ST 3RD
K086	NWW	BIS(2-ETHYLHEXYL) PHTHALATE SOL WASHES	0.49	CCW	1ST 3RD
K086	NWW	CHROMIUM TOTAL SOL WASHES	0.094	CCWE	1ST 3RD
K086	NWW	CYCLOHEXANONE SOL WASHES	0.49	CCW	1ST 3RD
K086	NWW	ETHYL ACETATE SOL WASHES	0.37	CCW	1ST 3RD
K086	NWW	ETHYL BENZENE SOL WASHES	0.031	CCW	1ST 3RD
K086	NWW	LEAD SOL WASHES	0.37	CCWE	1ST 3RD
K086	NWW	METHANOL SOL WASHES	0.37	CCW	1ST 3RD
K086	NWW	METHYL ETHYL KETONE SOL WASHES	0.37	CCW	1ST 3RD
K086	NWW	METHYL ISOBUTYL KETONE SOL WASHES	0.37	CCW	1ST 3RD
K086	NWW	METHYLENE CHLORIDE SOL WASHES	0.037	CCW	1ST 3RD
K086	NWW	n-BUTYL ALCOHOL SOL WAHSES	0.37	CCW	1ST 3RD
K086	NWW	NAPHTHALENE SOL WASHES	0.49	CCW	1ST 3RD
K086	NWW	NITROBENZENE SOL WASHES	0.49	CCW	1ST 3RD

More output follows, [ESC] to quit, any key to continue

Figure 2: Landban Screen (version 1.0)

Although users found version 2.0 easier to use than version 1.0, an important need of theirs was the ability to query multiple Waste Codes and report the lowest "unique" Treatment Standards (see Figure 4). Version 3.0 (June 1990) was designed to accommodate this feedback and contains the final regulations for the Third Third Land Disposal Restrictions.

Next Previous Quit

Chemical Waste Management
Hazardous Waste Codes

```
Waste Code : F001          Compound: 1,1,1-TRICHLOROETHANE
Waste Water: WW         Trmt. Stand: 1.05            CCW/CCWE: CCWE
REG. SOURCE: S&D            EPA PQL:                  CWM PQL:
        CAS:                 SW-846:              CWM METHOD#:

Waste Code : F001          Compound: 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE
Waste Water: WW         Trmt. Stand: 1.05            CCW/CCWE: CCWE
REG. SOURCE: S&D            EPA PQL:                  CWM PQL:
        CAS:                 SW-846:              CWM METHOD#:

Waste Code : F001          Compound: 1,2-DICHLOROBENZENE
Waste Water: WW         Trmt. Stand: 0.65            CCW/CCWE: CCWE
REG. SOURCE: S&D            EPA PQL:                  CWM PQL:
        CAS:                 SW-846:              CWM METHOD#:
```

Figure 3: Landban Screen (version 2.0)

With version 3.0, the user can determine whether or not sample results are greater than the list of Treatment Standards for the Waste Codes associated with that waste stream. This ability to query lowest "unique" Treatment Standards will increase productivity tremendously. For example, when a sample is received at CWMs Riverdale Technical Center, the user only has to enter all Waste Codes and forms into the Landban Application to produce a report showing the "unique" lowest Treatment Standard for each applicable compound.

Next Previous Quit

Chemical Waste Management Landban Application

COMPOUND	Treatment Standard	WW/ NWW	CCW/ CCWE	EPA PQL
1,1,1-TRICHLOROETHANE SOL WASHES	0.044	NWW	CCW	0.005
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	0.96	NWW	CCWE	
1,1,2-TRICHLOROETHANE	6.2	NWW	CCW	0.005
1,2-DICHLOROBENZENE	0.125	NWW	CCWE	0.66
ACETONE	0.05	WW	CCWE	0.1
ACETOPHENONE	9.6	NWW	CCW	0.01
BIS-(2-ETHYLHEXYL) PHTHALATE SOL WASHES	0.49	NWW	CCW	0.66
BUTYL BENZYL PHTHALATE	28.	NWW	CCW	
CARBON DISULFIDE	1.05	WW	CCWE	0.1
CARBON TETRACHLORIDE	0.05	WW	CCWE	0.005
CHLOROBENZENE	0.05	NWW	CCWE	0.005
CHROMIUM TOTAL	0.094	NWW	CCWE	

[ESC] Done [F2] Clear field [Shift-F2] Clear to end [Shift-F10] More
Form: T2_SUM2 Table: T2_SUM2 Field: cc_limit Page: 1

Figure 4: Landban Screen (version 3.0); Multiple Waste Code Summary for F001 WW, F002 NWW, and K086 NWW

All three versions are capable of querying specific compounds to determine which Waste Codes are applicable, as well as which Treatment Standards to use. Moreover, the software is flexible enough to permit single Waste Codes to be queried to determine which compounds and Treatment Standards apply to them, or to query for specific compound and Waste Code combinations. This method of entering compounds to retrieve Waste Codes enables all results for a given treatment which are greater than the Treatment Standard to be marked for further study.

Some typical laboratory examples which show the diversity of the software follow:

• A sample is received at the Riverdale Technical Center with an F006 Waste Code. The user enters the Waste Code into the Landban Application and whether the sample is Wastewater or Nonwastewater. The application will print to screen and/or printer all Treatment Standards associated with the F006 Waste Code for total and amenable cyanides.

• Another sample is received containing incinerator ash. Associated with this sample are Waste Codes: F006, F007, K020, K022, P021, P089, U028, and U223. In order to identify all the Treatment Standards for all possible compounds associated with this sample, each Waste Code would be entered into the Landban Application and the lists printed.

• Lastly, an Incinerator scrubber filtercake sample is received. Like incinerator ash, the filtercake sample will contain multiple Waste Codes. These Waste Codes would be entered into the Application to produce a list of Treatment Standards. It's very important, then, to know all Waste Codes associated with the filtercake in order that all Treatment Standards for all associated Waste Codes can be met. Otherwise, it would not be reasonable to identify all the correct Treatment Standards or treatment methods.

It is important to note that not only is the Lanban Application valuable for the Riverdale Technical Center's laboratories, but it is an excellent operational tool for CWM's sites. For example, one site will receive multiple shipments of waste streams for land disposal, which have already been treated and contain certification sheets.

In this instance, the Landban Application is an excellent means of varifying whether or not the Treatment Standards for the Waste Codes already listed on the certification sheets meet what is listed in the Landban Application. If they are correct, the final stabilization process can continue. If they are not correct, the waste streams will be sent back to the generator to again receive initial stabilization.

Another typical case for use of the Application is when untreated wastes are received with Waste Codes. The user enters these Codes to get a list of Treatment Standards for this particular waste stream. As an example, we can receive blending fuels at one of our incinerators with 30 or 40 Waste Codes associated with it. This blend, once incinerated, should yield another predetermined waste stream in the form of incinerator ash. Here, the Application helps us identify whether or not the resultant ash meets predetermined Treatment Standards.

A final example involves metal wastes. The Landban Application is used in the same manner as that of blending fuels, although it's less extensive. Typically, there are only one or two Waste Codes associated with metal waste. And once this load undergoes stabilization, the stabilized material is then checked against the predetermined Treatment Standards identified before stabilization.

Although it is relatively easy to look up one or two Waste Codes or compounds in the current paper-copy Landban list, it is easy to see that this process becomes increasingly more tedious for samples with 10 or more Waste Codes or compounds. To manually search the paper-copy list for 30 or 40 Waste Codes, such as in the case of untreated wastes, would take an exorbitant amount of time compared with using our Application. The time required to manually locate and identify this information decreases productivity significantly. The Landban Application makes this task simple and easy to perform.

It's interesting to note that the Landban software was developed as the Land Disposal Restrictions Act has been implemented. This demonstrates CWMs commitment to apply the most current technology to keep abreast of all Treatment Standards for hazardous material. Computerizing the Landban list helped us clarify its dimensions and eliminate human error when querying Waste Codes or compounds.

Future versions of the Landban software will be incorporated into CWMs LIMS (Laboratory Information Management System) for automatic comparisons between compounds and Treatment Standards. There will also be maintenance updates as new or pertinent information to land disposal becomes available.

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From Production to Regulation: Quality Assurance and the Establishment of Defensible Environmental Chemistry Data

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Many industrial and governmental production facilities have long established analytical chemistry departments. Historically, their laboratories have served solely as quality control support groups for production operations. Within the past ten years, many of these laboratories have been tasked, by cost conscious managements, to initiate programs for environmental trace analysis in support of environmental monitoring requirements (e.g., NPDES, NESHAPS, etc.) or on-site remedial activities (i.e., RCRA or CERCLA).

During numerous audits of production facilities, we have observed that there is a general failure by these laboratories to successfully adapt to a level of quality assurance (QA) required to produce defensible data. The QA programs, developed by these laboratories, appear to be holdovers of their production missions. They do not reflect the data quality objectives and priorities

required to successfully operate in the strict regulatory and potentially litigious social environment in which they must perform.

Within the production setting, the data quality objectives and priorities are defined by: 1) the need for rapid turnaround; 2) employment of industry-based analytical methods; 3) direct and informal data reporting; and, 4) statistically-based quality control practices (i.e., accuracy and precision determinations). Little emphasis is placed on formalizing QA procedures and programs, or on generating the documentation that can assure verification and traceability of data which form the chief components of producing, what is now recognized as, analytically defensible data (e.g., chain-of-custody, corrective actions, sample tracking, reagent preparation, etc.). We have also seen that, when faced with the task of producing environmentally sensitive data, these production-oriented laboratories are generally unaware of the regulatory requirements for specific analytical methodologies and are usually uninformed about the importance of formal documentation needed to help defend their data against potential challenges.

Our audits have shown that these laboratories have the talent and capital resources available to meet the challenge of producing defensible data. What is needed is a change in mission and QA

orientation. This conversion not only requires change by laboratory staff and management, but also involves corporate support and, in many cases, an organizational restructuring to assure the independence of the QA function.

Our paper will focus on the specific problems and challenges in establishing a QA program at production facilities, and offer efficient and effective approaches to implementing workable solutions to these problems.

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DATA QUALITY OBJECTIVES FOR TC/MS IN THE PREREMEDIAL FASP PROGRAM

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Abstract:

Data quality objectives (DQOs) are qualitative and quantitative statements specified to ensure that data of known and appropriate quality are obtained. The DQO requirements for a specific project are based on the end use of the data generated. To ensure that the data generated during preremedial activities are adequate, a clear definition of the objectives and the method by which decisions are made must be established early in the project planning process. All data generated in the preremedial program are ultimately applied to the Hazard Ranking System (HRS) model for placement of the site on the National Priorities List (NPL). In Region 2, the Field Investigation Team (FIT), in cooperation with the US Environmental Protection Agency, has developed a Field Analytical Screening Project (FASP) for the production of high-quality data in a minimum amount of time in support of the preremedial program.

An objective of the Region 2 FASP program was to use transportable instruments as opposed to mobile laboratories. Specific DQOs needed to be established early in this project to ensure the appropriate selection of instruments for the application of FASP to the preremedial program. The instrument chosen for the determination of organic contamination in soil, sediments, or other solids was the thermal extractor/gas chromatograph/mass spectrometer (TC/MS). The TC/MS provides mass spectral identification of target contaminants on site within a hour of sample receipt with no sample preparation or generation of waste. The DQOs established for the FASP program were met by the TC/MS.

Presented is the DQO process for the selection of the TC/MS and the application of TC/MS to the preremedial program.

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ABSTRACT

DEVELOPING DATA QUALITY OBJECTIVES AT A CONTAMINATED SOIL SUPERFUND SITE

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The Data Quality Objectives (DQO) process is intended to help structure planner's thinking beginning with the perception that there may be a problem which requires environmental data to answer through the specification of explicit qualitative and quantitative data performance requirements. For Superfund sites, the planners, who are the primary data users, are most frequently led by the remedial program manager (RPM), who is the site decision-maker, during scoping (planning) for the Remedial Investigation/ Feasibility Study (RI/FS). These individuals frequently must balance difficult scientific, engineering, social, political and economic issues during the RI/FS. In their endeavor to walk this fine line, RPMs and their support staff often ask:

1) How many samples need to be collected?
2) Where should those samples be collected?
3) How "good" do the data need to be?

The Quality Assurance Management Staff (QAMS), as part of its Agency quality assurance responsibilities, developed the DQO process and is facilitating the Agency's implementation of the process. Many planners have recognized the inherent common-sense logic found in the DQO process and embrace the concept. In moving from concept to application planners sometimes have difficulty. Understanding the problem is crucial and is the first step in the DQO process. This information is used primarily to focus the data users on which selected decision or major question environmental data will be used to answer. Further focusing is accomplished when the planners consider the information needed to make the decision, such as site characteristics, social and political factors, and spatial and temporal constraints. This focused decision must be clarified and quantified by specifying how the data will be summarized, such as contaminant concentration averages which pose an unacceptable exposure to individuals working in a defined area at the site. In this case the exposure concentration becomes the result upon which the decision will be made. To control the error in the decision (now in reality the decision result) to an acceptable level, the RPM needs to quantitatively specify the uncertainty acceptable in the result. Collectively the outputs from the above steps form the constraints on data performance or the DQOs used to bound the survey design. Usually a statistician assists planners in developing survey designs that meet the specified DQOs and optimizes the design to be efficient for this set of constraints.

Considering the complex array of issues found at most Superfund sites, QAMS has been collaborating with two regions in their application of the DQO process. This cooperative interaction

was viewed as an effective way to assure the practicality and feasibility of the DQO process to RI/FS planners and for QAMS to understand planning obstacles the regional staff encounters in DQO development. A case study will be presented that documents DQO development and their application in the RI/FS data collection design.

While this case study was accomplished at a Superfund site, there are commonalities with the RCRA Facility Investigations program. An important benefit of the DQO process is its flexibility, as its steps are those a planner would use to answer any question requiring data. This flexibility coupled with the program commonalities make this case study relevant to those with interest in SARA and RCRA.

CERCLA/SARA/RCRA

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USING PROCESS FLOW MODELS IN MANAGEMENT SYSTEMS REVIEWS

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ABSTRACT

The Management Systems Review (MSR) is an important component of EPA's quality assurance program. MSRs enable managers to assess the effectiveness of environmental data operations and the quality assurance/quality control activities designed to ensure that the results are of the expected quality. The effectiveness of the MSR is increased by the use of a comprehensive flow model of the principal steps and critical decision points in the process being studied. The flow model provides management with a powerful tool to understand complex environmental data operations, particularly the critical sequencing of key steps and how environmental data are used at important decision points in the process. A recent review of the Superfund remedial investigation/feasibility study (RI/FS) has shown that the MSR is an excellent tool for providing a systematic definition of major environmental data operations and for enabling a thorough analysis of these operations. The MSR utilized information gathered from interviews of Regional staff and management and from case studies of recently completed RI/FSs. A comprehensive process flow model was developed from this information and showed how environmental data play an important role in most RI/FS decisions and why thorough and structured scoping is critical to the effectiveness of the RI/FS. Using the flow model and the information compiled from Regional visits, the MSR identified several opportunities for changes that may increase efficiency in data collection and the reliability of RI/FS decisions. These changes provide for more effective scoping activities, a streamlined feasibility study, and increased use of treatability studies during the RI. The experience from this MSR indicates that the process flow model technique significantly enhances the MSR process and may be applied effectively to other environmental data operations, including the RCRA program.

INTRODUCTION

The Environmental Protection Agency (EPA) spends annually about $500 million in the collection of environmental data for scientific research and regulatory decision-making. In addition, the regulated community may spend as much as an order of magnitude more each year to respond to Agency-defined environmental monitoring requirements. While the scope of environmental data operations for both the EPA and the regulated community is very broad, there are several important common concerns. Both want to make decisions using the right data; that is, data which are of the correct type and valid for their intended use. Rework to collect new data is cost-prohibitive to all parties. In like manner, neither EPA nor the regulated community can afford to collect more or "better" data than are really needed. Recognizing this, EPA has initiated an innovative application of Total Quality Management (TQM) principles to environmental data operations. Applying TQM to the non-routine collection of environmental data upon which the Agency bases important regulatory, enforcement, and research decisions is significantly different

from more traditional applications of TQM in industry and other Federal Government operations. These traditional applications have included manufacturing and administrative operations.

In the case of EPA, every environmental data collection operation has a customer, whether the customer is outside the Agency, like a regulated industry, or inside the Agency, like a Region or Program Office. The success of an environmental data operation is determined largely by how well the needs of the customer have been satisfied; that is, can the data produced be used with confidence for their intended purpose. The use of measures of performance, developed through interactions between the data producer (or supplier) and the customer (or data user), provides the basis for defining what is needed to satisfy the customer.

During the past five years, the application of Total Quality Management principles to the Agency's environmental data operations has produced new and effective tools to assist senior managers in planning, implementing, and evaluating the results of such operations. One of these important tools is the **Management Systems Review (MSR)** process[1,2], which uses **Process Flow Models** as an integral element. MSRs enable senior management to determine whether an organization's environmental data operation is performing as intended and designed. The MSR process allows managers to measure the effectiveness of the framework and infrastructure of quality assurance and quality control (QA/QC) activities necessary to support a successful environmental data operation. From this analysis, Managers can identify appropriate adjustments to improve the operation.

THE MANAGEMENT SYSTEMS REVIEW

Over a decade ago, EPA recognized the need to ensure that the data being used for important decisions were of adequate and expected quality for their intended use. In EPA Order 5360.1[3], the EPA Administrator directed EPA organizations participating in any aspect of environmental data operations to develop, implement, and review periodically, a process for determining the quality of data produced by their operations. Quality assurance programs were established throughout the Agency to provide a framework and infrastructure for this function. As EPA's reliance on environmental data for enforcement, regulatory, and research decisions continued to grow, so did the importance of the QA/QC programs applied to environmental data operations. In order to provide a tool for managers to assess the effectiveness of the QA/QC program framework, the MSR was developed.

The MSR is designed to evaluate systematically how QA and environmental data operations are planned, implemented, and reviewed. The MSR is not an audit, even though its function may appear to be similar. Audits measure conformance of systems to specifications of technical performance and quality. MSRs examine processes to define how they work, even when, in some cases, performance measures do not exist. MSRs enable management to identify where an operation is working satisfactorily, and to consider where modifications to improve process effectiveness may be appropriate.

PROCESS FLOW MODELS IN MSRs

The use of a process flow model is particularly helpful in enabling management to gain additional insights on the relationship of all activities in an operation. In addition, managers can experiment

with potential process modifications and observe their impacts. The contribution of the process flow model to the Superfund MSR is discussed later in a specific case study.

Traditionally, process flow models have been used in the engineering design of complex systems to help engineers understand the intricacies of the process, observe how inputs and outputs from each step were interrelated, and assure that the sequence of the steps provided the desired output from the process. Likewise, the application of the process flow model technique to environmental data operations provides added information and clearer understanding of the activities under review. For example, the model presents the data operation as a series of interlinked activity and decision steps which describe the sequence of logic flow and use of data throughout the process.

Components of Process Flow Models

In this application, the process flow model is composed of all of the steps needed to describe fully an environmental data operation and the QA/QC activities applied. The model covers the entire scope of the data operation, including planning (or scoping), implementation, and evaluation of the results, and shows the logical sequence in which actions or decisions must occur in order to produce a desired result or product. A typical flow model step is given by Figure 1. For each step in the process, the input and output is identified in terms of specific environmental data used. If a decision is involved in the step, the decision paths emerging from the decision are shown. The steps are linked together in the appropriate sequence to show the flow of decisions and data throughout the process.

For each step in the flow model, there is a detailed Data Sheet that contains the following information:

- the purpose of the step,
- the goal or objective of the step,
- a description of the activity performed in the step and how environmental data are used,
- the criteria for performing the activity in the step, and
- any implications of the step relative to preceding or succeeding steps.

An example Data Sheet is given in Figure 2. The Data Sheets provide the necessary "data base" on each step in order to present the user of the flow model with a clear picture of what the step involves and how it relates to other steps in the process. The Data Sheets are not essential to getting benefits from the flow model. The sequencing of steps and decisions can provide very powerful information on the effectiveness of the process. However, there are often subtleties in processes which may not be clear until critical relationships among steps are fully identified. The Data Sheets provide a record of each step that captures the necessary detail to allow a fuller utilization of the flow model technique.

Use of the Flow Models in Reviews

As noted earlier, the principal benefit of the flow model is to make complex processes easier to understand. Environmental data operations associated with major Agency programs, such as the Superfund Remedial Investigation/Feasibility Study (RI/FS), involve many complicated and diverse steps that produce and use environmental data throughout the process. Frequently, such operations have many users (or customers) of the data generated, and satisfying the data needs of such a large array of customers becomes increasingly difficult. The process flow model provides a framework in which the data needs for each step in the process may be identified and their sequence examined. This information is very helpful to the planners of the data operations in assuring that data needs are met within the available resources. In addition, a flow model of a complex process can be an effective training tool in helping newcomers to understand all of the important activities and the order in which they should occur.

Perhaps the greatest value of the flow model is the opportunity it allows for optimizing the process. By ordering the steps in their proper sequence in a flow model, it is possible to visualize the interrelationships among various steps, which otherwise may not be obvious. For example, one may find that a particular step produces data that are not used until much later in the process. Such a finding could allow the step using the data to occur earlier and possibly save time and resources. Similarly, it may be possible to identify more effective sequencing of the steps, which again could yield time and cost savings or provide significant technical improvements to the process.

CASE STUDY: THE SUPERFUND RI/FS MSR

The value of process flow models to MSRs can be shown best through example. The Office of Emergency and Remedial Response (OERR) invited the Quality Assurance Management Staff (QAMS) to perform a review of the Superfund RI/FS[4] in order to provide an independent assessment of this important process. The collection and analysis of environmental data are the most significant cost and time components of the RI/FS. These data are also key to the efficacy and reliability of important RI/FS decisions, such as determining if an unacceptable risk is posed by a site and selecting an appropriate remedy.

As part of its ongoing efforts to reduce costs and improve the effectiveness of Superfund activities, OERR requested that QAMS conduct a comprehensive review of the RI/FS process, focusing on the role of environmental data. The review had the following objectives:

- identify the RI/FS decisions that rely on environmental data;
- determine how data needs are defined and how their collection is planned and executed; and
- examine the impacts of the planning, collection, and use of RI data on the scheduling and quality of RI/FS outputs, including remedy selection.

The review was conducted by QAMS with the assistance of the OERR Hazardous Site Control Division and the Office of Program Management, and included participation by Regional QA Managers.

From the outset of the MSR, the process flow model was an integral element of the study. During the planning of the MSR, documents such as QA program plans and RI/FS guidance provided a

general blueprint of the data collection and QA operations, and gave a picture of how the RI/FS is supposed to operate. This information was used to define the first-order process flow model of the major RI/FS activities, and to assemble these activities or steps into logical groups for data gathering and analysis. The flow model became a template for obtaining and organizing information during subsequent interviews with Regional personnel.

Data gathering for the MSR involved interviews of more than 25 Remedial Project Managers (RPMs) and their management in three Regions. The interviews traced the logic and decision flow of the RI/FS, with emphasis on:

- the types of environmental data collected and how data needs were determined;
- the participants in RI/FS scoping and their roles;
- the way in which remedial alternatives were identified, evaluated, and selected;
- how the RPM decides that sufficient RI data have been collected; and
- factors that facilitated or impeded timely, effective remedial investigations.

Just as the review of Superfund planning documents and guidance helped to formulate a framework for the flow model and to describe how the RI/FS process was supposed to operate, the interviews showed how the RI/FS was performed in practice. There was significant variability among RI/FSs within a Region and across Regions. However, the planning and site investigation activities were sufficiently similar to identify a typical or representative RI/FS in the process flow model. The outcome was then used as a basis for analyzing the process.

In order to validate the process captured in the flow model and to add to the understanding of how environmental data were being used, case studies were obtained for eight sites. These sites were identified by the Regions as fairly typical sites and had Records of Decision (RODs) completed in 1987 or 1988 to ensure that they reflected recent procedures. The case study documentation generally included, for each site: the work plan, sampling and analysis plan, quality assurance project plan, Remedial Investigation (RI) report, Feasibility Study (FS) report, and ROD. This information was critical to understanding what data were typically collected and how the data were used in making site-related decisions, and was very helpful in validating the process flow model of the RI/FS.

When the data from the interviews and case studies had been integrated into the process flow model, the model and the data were analyzed with respect to the study objectives. It was found that many of the steps in the RI/FS process depend to some degree on environmental data. The flow model simplified the identification of the major decisions that rely on data. These are:

- assessment of risk and determining if the no-action alternative is appropriate for the site;

- identification and screening of remedial process options; and

- screening, evaluation, and selection of remedial alternatives.

Having confirmed the specific and critical role of environmental data in the RI/FS (the first objective of the MSR), the flow diagram was used to document the process typically used by the Regions for defining data needs. Next, the process used for planning and executing field sampling activities (the second MSR objective) was identified and documented in the flow model.

Further analysis indicated several opportunities for process changes related to the third objective of the MSR; i.e., how the collection and use of environmental data impacts the scheduling and quality of RI/FS outputs. These included:

1) Know when to stop sampling;

2) Reduce the number of unplanned sampling episodes;
3) Reduce false starts and rework through structured planning;

4) Begin feasibility study during scoping;

5) Reduce the number of alternatives considered and evaluated during the feasibility study; and

6) Conduct treatability studies during remedial investigation field work.

Superfund has already begun to implement many of these improvements and several others are to be tested in a Regional pilot. While some of the improvements were already known to management, the process flow model demonstrated the feasibility of additional changes. These changes show significant promise for improving the effectiveness of the RI/FS process.

APPLICATION TO OTHER PROGRAMS -- RCRA

The applicability of the process flow model technique to other environmental data collection programs is very encouraging. For example, the flow model technique may be used effectively in reviews of several RCRA programs. QAMS is working with the Office of Solid Waste (OSW) to identify the environmental data operations associated with hazardous waste treatment, storage, and disposal (TSD) facility permitting and operation. This study will evaluate the role of environmental data in decision making for these operations.

Generalized process flow models for the permit process and for facility operations will identify the key components of each process and facilitate the identification of environmental data-related decisions. Examples of data-related or dependent elements for these processes include:

- preparation and review of waste analysis plans,

- preparation and review of sampling and analysis plans,
- review of results from hazardous waste incineration trial burns,

- implementation of approved waste analysis plans,

- implementation and approval of ground water monitoring programs and associated sampling and analysis plans, and

- RCRA facility assessments and RCRA facility investigations.

When the environmental data operations supporting this program have been identified, QAMS and OSW will work cooperatively to select an important operation for detailed study. A comprehensive process flow model will be developed for that operation using the techniques described earlier, and will be utilized to examine and evaluate the key steps in the operation, how the steps interrelate, and how environmental data are used in making important decisions. As was the case in Superfund, the process flow model will allow OSW management to optimize the process, perhaps to reorder certain steps and improve the efficiency of a permitting operation, or perhaps to acknowledge where the operation is performing exceptionally well. In either case, management will have a powerful tool at its disposal for future evaluations of RCRA activities.

SUMMARY

The process flow model technique is a powerful adjunct to the Management Systems Review process. Such models may aid management's understanding of complex environmental data operations and provide a means of optimizing the process to increase effectiveness and efficiency. The value and benefits of using process flow models have been successfully demonstrated in the Superfund RI/FS MSR. Possible reviews of several important RCRA programs may also be augmented by use of process flow models.

References

1) Johnson, G.L.,"Management Systems Reviews- Measuring Quality Process and Structure in Quality Assurance Programs," Symposium on Measurement of Toxic and Related Air Pollutants, US EPA and Air & Waste Management Association (May 1989).

2) Interim Policy and Guidance for Quality Assurance Management Systems Reviews of Research Operations. U.S. Environmental Protection Agency (1987).

3) EPA Order 5360.1, Policy and Program Requirements to Implement the Mandatory Quality Assurance Program, U.S. Environmental Protection Agency (April 3, 1984).

4) Johnson, G.L. and L.H. Wynn, "A Management Systems Review of the Superfund RI/FS Process: Opportunities for Streamlining," JOURNAL of the Air and Waste Management Association **40**(5) (May 1990).

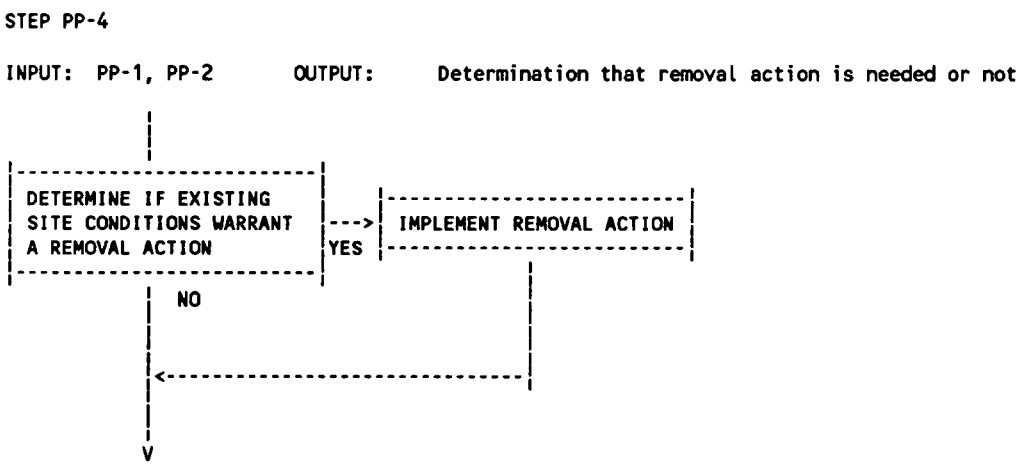
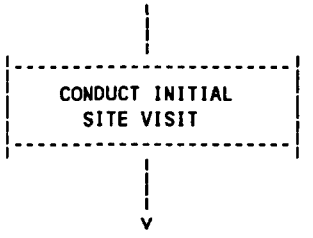


Figure 1. Sample Step from Process Flow Diagram

STEP PP-2

INPUT: PA/SI Results

OUTPUT: Assessment of current surface conditions and potential receptors.



PURPOSE: To obtain first-hand observations of current site conditions.

GOAL/OBJECTIVE: Acquire current information about the site through visual inspection and/or limited field measurements.

ACTIVITY PERFORMED/DATA USE:

Historical data are used to guide the visual inspection of the site, which may include observations on the presence and appearance of surface water, and obvious evidence of impacts from contamination such as stressed vegetation and soil discoloration. Very limited sampling with portable equipment may be conducted.

CRITERIA/ISSUES:

Information that may be collected include:

- Have site surface conditions changed from the historical data? What are the implications of the change?
- Visual evidence of contamination.
- Apparent stability of site (e.g., weakened beams, leaking tanks).
- Proximity of population or sensitive ecosystems to the site.

IMPLICATIONS:

- Visual inspection may identify areas of concern which may require removal action or short-term mitigation.
- Provides the RPM with a subjective view of the site which helps to define the magnitude of the effort required for the RI/FS (i.e., where to sample, what site preparations are needed, etc.).

Figure 2. Sample Process Flow Model Data Sheet

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THE IDENTIFICATION, PREPARATION, AND USE OF SITE COMPARISON SAMPLES AT SUPERFUND SITES

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ABSTRACT

A Site Comparison Sample (SCS) is a site specific reference material which is representative of the type of problems encountered when analyzing or treating materials from a hazardous waste site. SCS's 1) contain key contaminants in the matrix of the site; 2) are available in sufficient numbers to satisfy numerous site management and QA/QC purposes; 3) exhibit the lowest possible coefficient of variation (cv); and 4) are managed by an organization capable of being a depository of analytical results, and providing a common management point for quality assurance purposes. SCS materials differ from Standard Reference Materials (SRM's) by virtue of being site-specific, and not produced under a protocol requiring the pre-release of rigorous method-specific, statistically validated characterization data.

Site comparison samples fulfill several needs. First, sites typically require from 8 to 12 years from discovery to remediation. Managers, analytical needs, laboratories, and methods are all likely to change. The SCS provides a tool for

relating past to future work. Second, the needs at a site change. In the early years, studies to understand the fate and transport of contaminants predominate. This is the time when the maximum investment in field data acquisition is made. Data needs are different from those in later phases of management, such as design and post-remediation compliance monitoring. An SCS developed early in the life of a site facilitates activities in all subsequent phases. Third, treatability studies are now recognized as an important element of response at Superfund sites; the SCS methods were first developed to service the needs of treatability studies. Fourth, SCS materials provide a source of material for a site-specific performance evaluation program. This has been shown to be useful at large, complex sites where many laboratories are likely to be involved. Finally, in an attempt to accelerate the remediation process and to reduce costs, more use is being made of field screening techniques. The SCS material is a convenient source of material to both calibrate field screening methods (such as XRF), and to correlate the field methods to standard analytical techniques.

SCS material can derive from any matrix. Soil, sediment, and sludge are the most interesting matrices, however. Site specific decisions on whether one or more SCS materials are required are based on the nature of the contaminants, the variability of the matrices, the presence of interferring compounds (from a treatability perspective), and the prevalence of these factors in combination. Attempts are made to minimize the number of separate SCS materials for a site.

Two case studies from Superfund sites illustrate the identification, preparation and use of SCS materials. Field techniques for obtaining sufficient material is described. The process of transforming bulk materials in to numerous standard containers in a manner that ensures the lowest possible cv is reviewed. The allocation of SCS materials to treatability, performance evaluation, and field screening calibration standards is discussed. Finally, the statistical techniques used to manage life cycle data which derives from the SCS material is presented.

The overall conclusion is that Site Comparison Samples are a powerful tool for the total quality management of a Superfund site.

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EVALUATION OF QA/QC DATA FOR ORGANIC ANALYSES OF TREATMENT RESIDUALS FROM THE INCINERATION OF HAZARDOUS WASTE

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ABSTRACT

For the Land Disposal Restriction Program, EPA's Office of Solid Waste collected data for over 14 incineration studies of hazardous waste. For the organic analyses completed for these studies, the QA/QC requirements included the analyses of matrix spikes, matrix spike duplicates, and surrogates. The recovery values of the spikes and surrogates can be used to assess the effect of the sample matrix, in this case incineration ash and scrubber water, on the data. Because of limited data available for hazardous waste samples and their treatment residuals, precision and accuracy ranges as a condition of accepting the analysis of the treatment residuals were not specified (especially for surrogates). An evaluation of the QA/QC data collected for the incineration studies completed by EPA for the program or submitted as part of the Administrative Record for this program should provide insight into the effect the ash and scrubber water matrix has on the recovery of spikes and surrogates. In addition, the data can be used as a basis for determining the quantitative precision and accuracy values for these matrices that may be used to set quantitative data quality objectives for future incineration studies to establish acceptable criteria for precision and accuracy for surrogate and spikes.

The results will be assessed to determine the accuracy ranges obtained for the existing data and will compare these values to the existing accuracy ranges established for water and soil matrices.

Guidelines have been established for the acceptability of QA/QC data generated for water and soil matrices. These data are published in EPA's SW-846 Test Methods for Evaluating Solid Waste. In addition, guidance is presented to calculate the acceptable quality control limits for each matrix that a laboratory evaluates. However, no data are published for recommended QC windows for other matrices. Information on the precision and accuracy values obtained by laboratories will be useful for individual laboratories to evaluate the values they are achieving and will provide some guidance to individuals involved in setting quantitative data quality indicators for precision and accuracy for incinerator ash and scrubber water matrices.

INTRODUCTION

For the Land Disposal Restrictions Program, a generic quality assurance document entitled "Generic Quality Assurance Program Plan for the Land Disposal Restrictions Program (BDAT)," (EPA/530-SW-87-011) was published in 1987. This document provided guidance for all of the treatment tests conducted by EPA for the Land Disposal Restrictions Program. At the time the document was published, insufficient data were available for matrix spike recoveries and for surrogate recoveries to establish specific criteria for data acceptability for treatment residuals that could be generated from the various treatment technologies that could be used for a variety of wastes matrices containing hazardous constituents. It was determined that the best approach would be to evaluate the analytical data obtained for each treatment test individually and to accuracy correct the data used to calculate treatment standards for the Land Disposal Restrictions Rules, in order to take into account those matrix affects that could impact the accuracy of the data.

Between 1987 and 1989, EPA-OSW's Treatment Technology Section conducted 14 incineration tests for various listed hazardous wastes. The matrix spike recoveries and the surrogate recoveries for the ash and scrubber water residuals for most of the tests fall in the acceptable ranges established for the soil and groundwater, respectively. The data from these incineration tests provides information which can be used to develop a quantitative data quality indicators for accuracy for incinerator residuals.

SAMPLE COLLECTION

Ash and scrubber water samples were collected from the following listed wastes:

K001-creosote:	listed hazardous wastes from wood preserving processes that use creosote.
K001-PCP:	listed hazardous wastes from wood preserving processes that use pentachlorophenol (PCP).
K011/K013/K014:	listed hazardous wastes from the production of acrylonitrile.
K024:	listed hazardous wastes from production of phthalic anhydride.
K037:	listed hazardous wastes from the production of disulfoton.
K048-K052:	listed hazardous wastes from the petroleum refinery industry.
K087:	listed hazardous wastes from coking operations.

K101:	listed hazardous wastes from distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.
K102:	listed hazardous wastes from use of activated carbon in the production of veterinary pharmaceuticals from arsenic or or organo-arsenic compounds.
F024:	listed hazardous wastes from the production of chlorinated aliphatic hydrocarbons, having carbon content from one to five, utilizing free radical catalyzed process.
K015:	listed hazardous wastes from the production of benzl chloride.
Pesticides I:	incineration of isosafrole, bis(2-ethyl hexyl) phthalate, dinoseb, ethyl acetate, 1,4-naphthoquinone, phenol, 1,1,1-trichloroethane, toluene, xylene, methyl ethyl ketone, and methylene chloride.
Pesticides II:	incineration of D014, D016, heptachlor wastes, hexachlorobenzene, methoxychlor, 2,4,-D, pronamide, and clean fill dirt.

All samples of the two treatment residual--ash and scrubber water--were collected as grab samples. The number of samples collected for each test were determined on a site-by-site basis, however, at a minimum two samples and at a maximum eight samples were collected form each site. For most tests, only the specific waste of interest was incineraed. However, for K019 and K048-K052 additional hazardous feeds were also incinerated. For these cases, the waste of interest constituted a significant portion of the feed materials, therefore, the treatment residuals are believed to be representative of the waste treated.

ANALYTICAL METHODS

All samples were analyzed using methods published in EPA's "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, Third Edition. Volatile organics were analyzed using Method 8240. Semivolatile organics were analyzed using Method 8270. Samples were spiked with the surrogates recommended in the methods. Matrix spikes and matrix spike duplicates were spiked with most of the constituents recommended by EPA's Contract Laboratory Program (CLP). The results for the surrogate recoveries and matrix spike recoveries of these constituents are discussed below. In addition, samples were spiked, if possible, with constituents that were suspected or known to be present in the waste feed. Since the constituents vary for the 14 tests the results can not be compared across all of the incineration

tests nor are the recommended recovery values available for these constituents from the CLP program, therefore, they were not evaluated at this time.

RESULTS

Matrix spikes are used to provide a measure of accuracy for the method used in the given matrix. Matrix spikes were completed for the incineration tests for both residuals generated from the treatment test--the incinerator ash and the scrubber water.

For the five constituents used to spike virtually all of the samples for the incineration studies for volatile organics (Table 1), the results suggest that these quality control limits recommended for soil in SW-846 may be appropriate as a "first-cut" guidance limit for incinerator ashes. For the 13 incinerator studies which generated ash, only three of the tests had any spike recoveries outside the limit and only one study had more than two of the five constituents outside the limits. For the acid fraction of the semivolatile organic constituent (Table 2), the extraction efficies are usually expected to be low, therefore, the control limits may be biased on the low side for incinerator ash. For the 12 incineration tests for which matrix spikes were completed for semivolatiles, six of the tests had spikes outside the limits, however, if the upper limit of the acceptable range was increased to 125 then only four tests would have any constituents outside of the range and only one test would have more than one constituent that did not meet the criteria. For the base-neutral semivolatiles (Table 3), nine of the tests had between one and four constituents outside of the recommended limits with most of the tests having 2,4-dinitrotoluene being the constituent that was outside the limits most frequently. However, if the limits for this constituent were increased to 28-125 from 28-89 percent, then this constituent would be outside the limits only once for all of the tests.

For the five constituents spiked into most of the scrubber water samples for the incinerator studies, the results suggest that the quality control limits recommended for water may be appropriate as a "first-cut" guidance limit for both volatile and semivolatile organics for scrubber waters generated from incineration of hazardous waste. For the volatile organics (Table 4), four of the 14 studies had no constituents outside of the limits, eight of the studies had only one constituent outside of the limits, and only two of the studies had two constituents outside of the limits. Therefore, at a minimum, three of the five constituents did meet the criteria for volatile organics for all of the studies. For the acid fraction of the semivolatiles (Table 5), all 13 of the studies for which matrix spikes were completed had at least one of the five constituents outside of the range. However, only three of the studies had more than two of the

constituents outside of the recommended range. As for the ash (or soil) matrix, the recommended quality control limits are biased on the low side for four of the constituents; if the upper boundary was increased to 125 percent for all of the constituents, then only seven of the tests would have one of the spike constituents outside of the recommended limits. For the base-neutral constituents (Table 6), 11 of the 13 studies had at least one constituent outside of the recommended range, however only four studies had two constituents and only one study had three constituents outside the recommended range. Therefore, most of the constituents for all of the tests did fall within the recommended quality control limits established for water samples.

Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. They are used to provide a measure of the extraction efficiency.

For the surrogates spiked into the ash samples for volatile and semivolatile organics, the results indicate that the recommended quality control limits for surrogates for a soil matrix are appropriate as a "first-cut" guidance limit for both volatile and semivolatile organics. Although eight of the tests had at least one surrogate outside the recommended limits for volatiles (Table 7), not all of the samples for the test were outside the limit for all of the constituents. For the semivolatile organics (Table 8), the incinerator ash sample for only five of the 14 tests had between one to three surrogates outside the recommended range for soil. Therefore, the data indicate that the recommended quality control limits for soil are appropriate for setting initial quantitative limits for ash samples.

For the surrogate spiked into the scrubber water samples for volatile organics (Table 9), the results indicate that the recommended quality control limits for a water matrix are appropriate as a "first-cut" guidance limit. Only five of the 14 tests had one to two surrogate outside of the limits and with the exception of one test only a few of the total number of samples analyzed were outside of the range. For the semivolatiles (Table 10), 11 of the 14 tests had between one and five of the surrogates outside of the recommended ranges for the six surrogates used. Once again only a small number of the total samples analyzed had surrogates outside of the recommended quality control range. Therefore, the data indicate that the recommended limits for water samples are appropriate as a "first-cut" for establishing recommended quality control limits for scrubber water. However, it may be appropriate to increase the high end of the recommended ranges for nitrobenzene-d5, 2-fluorobiphenyl, phenol-d5, and 2-fluorophenol to a level of 125 percent this would reduce the number of samples that

had surrogates that exceeded the recommended limit and would still be lower than the upper end of the acceptable range for terphenyl-d14.

CONCLUSIONS

Based on the 14 incinerator studies evaluated, the data are insufficient to establish recommended quality control limits for treatment residuals from incineration. In general, the recommended quality control limits established for soil can be used to evaluate both matrix spike and surrogate recoveries for the ash and the limits established for water can be used to evaluate the scrubber water. However, the quality control data for each incinerator test should be evaluated on a case-by-case basis. The data are not sufficient to determine the full impact of the waste feed and the operating conditions of the incinerator on the ash and scrubber water and how they may impact the matrix affects that contribute to poor spikes and surrogate recoveries. Therefore, the data from each incinerator test of hazardous waste should be evaluated on a case-by-case basis to establish the data quality indictor for acceptable accuracy. The evalution should take into account the purpose of the test, the waste feed, and the operating conditions of the incinerator.

REFERENCES

U.S. EPA. 1986. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846 (3rd edition), Washington, D.C., November 1986.

U.S. EPA. 1987. US. Environmental Protection Agency. Office of Solid Waste. OSW's Generic Quality Assurance Project Plan for Land Disposal Restrictions Program (BDAT), March 1987.

U.S. EPA. 1987. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Technology Performance and Operation for Incineration of K001-Pentachlorophenol (PCP) Waste at the U.S. Environmental Protection Agency Combustion Research Facility. November 12, 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1987. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Performance and Operation for Incineration of K001-Creosote WAste at the U.S. Environmental Protection Agency Combustion Research Facility. November 23, 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1987. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Performance and Operation for Incineration of K011/K013/K014 Sludge at the John Zink Test Facility. November 2, 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Non-confidential Version of the Onsite Engineering Report of Treatment Technology Performance and Operation for Rollins Environmental Services (TX) Inc., Deer Park, Texas. March 11, 1988. Washington, D.C.: U. S. Environmental Protection Agency.

U.S. EPA. 1987. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Technology Performance and Operation: Incineration of K024 Waste at the U.S. Environmental Protection Agency Combustion Research Facility. 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1987. Onsite Engineering Report of Treatment Technology Performance and Operation for Incineration of K037 Waste at the Combustion Research Facility. November 16, 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Technology Performance and Operation for Amoco Oil Company, Whiting, Indiana. February 29, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. Onsite Engineering Report of Treatment Technology Performance and Operation for Amoco Oil Company, Whiting, Indiana. July 15, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Technology Performance and Operation for Incineration of K087 Waste at the Combustion Research Facility, Jefferson, Arkansas. February 22, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Onsite Engineering Report for John Zink Company for K101. April 25, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Onsite Engineering Report for John Zink Company for K102. April 25, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1988. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Technology Performance and Operation for Incineration for ENSCO, El Dorado, Arkansas. December, 1988. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1987. U.S. Environmental Protection Agency. Onsite Engineering Report of Treatment Performance and Operation for Incineration of K015 Waste at the John Zink Company Test Facility. December 4, 1987. Washington, D.C.: U.S. Environmental Protection Agency.

U.S. EPA. 1989. U.S. Environmental Protection Agency. Onsite Engineering Report for the Third Thirds Incineration Treatment Test. 1989. Washington, D.C.: U.S. Environmental Agency.

Table 1. Matrix Spike Recoveries for Volatile Organics for Incinerator Ash

	1,1-Dichlorcethene		Trichloroethene		Benzene		Toluene		Chlorobenzene			
Recommended QC limits based on soil matrix	59-172		62-137		66-142		59-139		60-133		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	86-95	2	67-77	2	78-88	2	99-110	2	102-112	0	0
K001-PCP	-	-	2	84-88	2	88-88	2	108-108	2	120-124	0	0
K011/K013,K014	2	99-104	2	104-105	2	114-146	2	113-117	2	107-107	0	0
K019	2	78-85	2	107-112	2	85-90	-	-	2	99-100	0	0
K024	2	136-140	2	104-108	2	104-104	2	107-122	2	112-112	0	0
K037	2	56-66	2	84-84	2	104-104	2	84-124	2	108-108	0	0
K048-K052	1	88	1	76	1	80	1	46	1	96	1	1
K087	2	114-114[1]	2	114-114	2	98-100	2	104-106	2	106-106	0	0
K101	2	96-100[1]	2	116-126[2]	2	102-106	2	106-116	2	104-110	0	0
K102	2	126-130[1]	2	112-116[2]	2	104-108	2	112-114	2	106-110	0	0
F024	2	80-122	2	178-216	2	126-130	2	170-222	2	90-108	2	4
K015	-	-	-	-	-	-	-	-	-	-	-	-
Pesticides I	2	73-75	2	103-109	2	97-103	2	103-109	2	109-115	0	0
Pesticides II	2	32-35	2	210-294	2	117-156	2	153-243	2	56-92	5	8
Number of tests with spike outside limit	1		2		1		3		1			

[1] Results for 1,1-Dichloroethane
[2] Results for Trichloroethane

Table 2. Matrix Spike Recoveries for Acid Fraction of the Semivolatile Organics for Incinerator Ash

	2-Chlorophenol		4-Chloro-3-methyl phenol		4-Nitrophenol		Pentachlorophenol		Phenol			
Recommended QC limits based on soil matrix	25-102		26-103		11-114		17-109		26-90		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	53-59	2	35-63	2	1.2-2.6	2	0-0	2	65-72	2	2
K001-PCP	2	100-105	2	90-95	2	90-100	2	95-105	2	80-85	0	0
K011/K013/K014	-	-	-	-	-	-	-	-	-	-	-	-
K019	2	98-100	2	110-120	2	97-110	2	88-88	2	90-97	2	3
K024	2	107-109	2	86-88	2	114-120	2	91-98	2	94-96	3	5
K037	2	75-75	2	88-88	2	86-100	2	33-48	2	67-70	0	0
K048-K052	2	70-70	2	56-57	2	31-32	2	34-34	2	65-65	0	0
K087	2	78-83	2	87-92	2	35-37	2	7-11	2	77-80	1	2
K101	2	39-41	2	44-47	2	32-33	2	25-30	2	40-41	0	0
K102	2	58-62	2	64-66	2	21-22	2	35-38	2	61-65	0	0
F024	2	78-102	2	98-135	2	50-90	2	27-64	2	101-122	2	3
K015	-	-	-	-	-	-	-	-	-	-	-	-
Pesticides I	2	42-53	2	78-90	2	64-77	2	68-77	2	60-70	0	0
Pesticides II	2	42-49	2	84-88	2	48-91	2	0-74	-	-	1	1
Number of tests with spike outside limit	1		2		2		3		3			

Table 3. Matrix Spike Recoveries for Base/Neutral Fraction of the Semivolatile Organics for Incinerator Ash

	1,4-Dichlorobenzene		N-Nitroso-di-n-propylamine		1,2,4-Trichloro-benzene		Acenaphthene		2,4-Dinitrotoluene		Pyrene			
Recommended QC limits based on soil matrix	28-104		41-126		38-107		31-137		28-89		35-142		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	46-48	2	62-67	2	30-30	2	0-3.4	2	0-0	2	0-0	4	8
K001-PCP	2	94-94	2	81-82	2	95-100	2	120-120	2	120-120	2	96-100	1	2
K011/K013/K014	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K019	2	90-99	2	120-130	2	75-80	2	110-110	2	107-110	2	92-120	2	3
K024	2	89-90	2	26-40	2	90-90	2	96-96	2	118-118	2	82-94	2	4
K037	2	74-74	2	56-62	2	85-88	2	100-103	2	109-112	2	26-47	2	3
K048-K052	2	75-76	2	70-70	2	86-90	2	63-66	2	52-54	2	53-58	0	0
K087	2	79-89	2	82-84	2	84-89	2	91-93	2	109-121	2	34-39	2	3
K101	2	38-40	2	45-46	2	39-41	2	39-41	2	47-48	2	45-46	0	0
K102	2	70-75	2	61-64	2	75-76	2	73-74	2	58-58	2	79-85	0	0
F024	2	72-90	2	110-118	2	60-90	2	30-38	2	38-100	2	6-82	3	3
K015	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pesticides I	2	17-29	2	46-53	2	24-36	2	54-60	2	63-71	2	66-73	2	3
Pesticides II	2	23-26	2	50-58	2	25-30	2	24-51	2	56-73	2	0-49	4	6
Number of tests with spike outside limit		2		2		3		3		7				

Table 4. Matrix Spike Recoveries for Volatile Organics for Scrubber Water

	1,1-Dichloroethene		Trichloroethene		Benzene		Toluene		Chlorobenzene			
Recommended QC limits based on water matrix	61-145		71-120		76-127		76-125		75-130		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	97-100	2	64-69	2	85-90	2	99-103	2	90-95	1	2
K001-PCP	2	92-112	2	84-84	2	92-120	2	120-120	2	104-122	0	0
K011/K013/K014	2	56-71	2	91-93	2	103-109	2	88-97	2	96-102	1	1
K019	2	44-48	2	84-100	2	68-84	-	-	2	92-116	2	3
K024	2	164-180	2	80-84	2	112-112	2	116-116	2	116-120	1	2
K037	2	39-50	2	80-80	2	85-87	2	116-122	2	128-132	1	2
K048-K052	2	154-156	2	112-116	2	111-117	2	110-119	2	116-118	1	2
K087	-	-	2	112-114	2	106-108	2	124-124	2	106-112	0	0
K101	2	60-62[1]	2	98-102[2]	2	80-82	2	90-92	2	100-102	1	1
K102	2	74-78[1]	2	110-114[2]	2	90-92	2	102-104	2	110-114	0	0
F024	2	80-80	2	106-108	2	86-90	2	114-114	2	110-112	0	0
K015	2	48-48	2	96-96	2	92-92	2	100-104	2	112-112	1	2
Pesticides I	2	57-69	2	88-115	2	70-88	2	81-106	2	87-115	2	2
Pesticides II	2	73-76	2	114-123	2	96-103	2	113-122	2	121-130	1	1
Number of tests with spike outside limit		8		2		2		0		0		

[1]Results for 1,1-Dichloroethane
[2]Results for Trichloroethane

Table 5. Matrix Spike Recoveries for Acid Fraction of the Semivolatile Organics for Scrubber Water

	2-Chlorophenol		4-Chloro-3 methyl phenol		4-Nitrophenol		Pentachlorophenol		Phenol			
Recommended QC limits based on water matrix	27-123		23-97		10-80		9-103		12-89		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	61-65	2	73-80	2	0-0	2	80-85	2	61-65	1	2
K001-PCP	2	20-28	2	22-29	2	0.8-1.5	2	1.7-3	2	22-30	4	6
K011/K013/K014	-	-	-	-	-	-	-	-	-	-	-	-
K019	2	78-81	2	35-87	2	43-82	2	45-56	2	70-74	1	1
K024	2	46-46	2	47-49	2	77-90	2	60-64	2	34-36	1	1
K037	2	90-95	2	35-95	2	120-140	2	90-95	2	85-95	2	3
K048-K052	2	96-115	2	31-133	2	62-76	2	51-59	2	59-108	2	2
K087	2	106-108	2	103-107	2	117-118	2	85-107	2	93-96	4	7
K101	2	59-62	2	69-73	2	0-0	2	51-53	2	58-60	1	1
K102	2	85-92	2	104-109	2	113-127	2	56-62	2	100-107	3	6
F024	2	46-59	2	136-144	2	24-46	2	6-15	2	73-86	2	3
K015	2	70-75	2	90-95	2	100-120	2	75-80	2	55-60	1	2
Pesticides I	2	51-74	2	31-93	2	98-110	2	103-111	2	40-72	2	3
Pesticides II	2	59-63	2	72-96	2	0-0	2	77-91	2	62-80	1	2
Number of tests with spike outside limit		0		5		11		4		4		

Table 6 Matrix Spike Recoveries for Base/Neutral Fraction of the Semivolatile Organics for Scrubber Water

	1,4-Dichlorobenzene		N-Nitroso-di-n-propylamine		1,2,4-Trichloro benzene		Acenaphthene		2,4-Dinitrotolene		Pyrene			
Recommended QC limits based on soil matrix	36-97		41-116		39-98		46-118		24-96		26-127		Number of constituents outside recommended range	Number of spikes outside recommended range
Incinerator test	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries	# of spikes	Range of recoveries		
K001-Creosote	2	51-61	2	56-70	2	54-72	2	66-81	2	17-21	2	60-62	1	2
K001-PCP	2	85-87	2	66-70	2	110-120	2	110-110	2	79-84	2	110-112	1	2
K011/K013,K014	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K019	2	102-102	2	92-100	2	68-70	2	60-68	2	84-86	2	86-86	1	2
K024	2	68-68	2	42-44	2	72-72	2	96-98	2	114-120	2	98-100	1	2
K037	2	79-94	2	81-88	2	94-100	2	130-140	2	120-130	2	110-110	3	5
K048-K052	2	64-78	2	70-93	2	66-83	2	57-92	2	56-111	2	62-121	1	1
K087	2	78-87	2	98-104	2	77-85	2	94-104	2	124-125	2	136-143	2	4
K101	2	33-33	2	59-60	2	40-41	2	55-58	2	42-53	2	62-63	1	2
K102	2	48-49	2	91-92	2	52-54	2	82-85	2	92-94	2	98-102	0	0
K024	2	58-64	2	116-132	2	62-64	2	78-80	2	114-114	2	82-88	2	3
K015	2	37-40	2	65-75	2	35-37	2	76-80	2	25-25	2	52-62	0	0
Pesticides I	2	30-36	2	56-72	2	32-38	2	50-55	2	71-77	2	47-49	2	3
Pesticides II	2	31-34	2	67-70	2	35-35	2	53-64	2	37-38	2	66-74	2	4
Number of tests with spike outside limit		3		1		5		1		6		1		

Table 7. Surrogate Recoveries for Volatile Organics for Incinerator Ash

	Toluene-d8		Bromofluoro-benzene		1,2-Dichloro-ethane d4			
Recommended QC limits based on soil matrix	81-117		74-121		70-121		Number of constituents outside recommended range	Number of samples outside recommended range
Incinerator test	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries		
K001-Creosote	7	77-114	7	106-112	7	98-106	1	1
K001-PCP	3	111-115	3	102-113	3	81-116	0	0
K011/K013/K014	7	79-88	7	103-121	7	85-88	0	0
K019	6	94-106	6	74-76	6	104-112	0	0
K024	4	94-99	4	93-111	4	98-103	0	0
K037	6	110-125	6	101-127	6	46-96	3	7
K048-K052	6	88-130	6	68-72	6	84-96	2	8
K087	5	101-194	5	49-102	5	59-98	1	4
K101	3	106-115	3	76-88	3	98-96	1	1
K102	4	102-122	4	49-101	4	89-96	2	2
F024	6	145-202	6	61-83	6	44-64	2	12
K015	-	-	-	-	-	-	-	-
Pesticides I	4	99-101	4	93-94	4	91-93	0	0
Pesticides II	4	103-179	4	48-97	4	48-80	3	7
Number of tests with surrogate outside limit		8		4		3		

Table 8. Surrogate Recoveries for Semivolatile Organics for Incinerator Ash

	Nitrobenzene-d5		2-Fluorobiphenyl		Terphenyl-d14		Phenol-d5		2-Fluorophenol		2,4,6-Tribromophenol			
ecommended QC imits based on oil matrix	23-120		30-115		18-137		24-113		25-121		19-122		Number of constituents outside recommended range	Number of spikes outside recommended range
ncinerator test	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries		
001-Creosote	7	28-69	7	3.3-72	7	0-74	7	65-75	7	62-67	7	5-56	3	18
.001-PCP	3	92-102	3	85-90	3	87-88	3	132-134	3	124-127	3	72-89	2	6
.011/K013/K014	2	63-75	2	66-89	2	44-86	2	61-84	2	59-77	2	53-100	0	0
'019	6	72-84	6	63-72	6	98-110	6	74-91	6	81-92	6	63-78	0	0
024	3	70-87	3	45-61	3	23-105	3	10-65	3	21-57	3	13-44	2	3
.037	6	66-99	6	81-93	6	66-109	6	62-98	6	51-84	6	80-99	0	0
<048-K052	6	66-96	6	61-65	6	105-115	6	50-64	6	64-113	6	24-43	0	0
<087	5	40-67	5	58-76	5	20-48	5	36-61	5	31-57	5	19-47	0	0
<101	3	38-52	3	42-56	3	44-60	3	39-57	3	41-54	3	33-49	0	0
<102	4	58-95	4	70-98	4	66-99	4	64-92	4	64-88	4	60-68	0	0
'024	6	49-65	6	26-55	6	2-43	6	60-85	6	57-79	6	19-75	1	4
<015	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pesticides I	4	34-32	4	36-78	4	69-90	4	61-93	4	52-87	4	58-99	0	0
Pesticides II	4	26-66	4	28-40	4	0-46	4	38-81	4	36-72	4	14-49	3	5
Number of tests with surrogate outside limit		0		2		3		2		1		3		

Table 9. Surrogate Recoveries for Volatile Organics for Scrubber Water

	Toluene-d8		Bromofluoro-benzene		1,2-Dichloro-ethane-d4			
Recommended QC limits based on water matrix	88-110		86-115		76-114		Number of constituents outside recommended range	Number of samples outside recommended range
Incinerator test	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries		
K001-Creosote	7	107-125	7	99-109	7	94-107	1	3
K001-PCP	3	102-100	3	103-108	3	96-118	1	1
K011/K013/K014	7	97-102	7	90-96	7	96-110	0	0
K019	6	136-164	6	70-74	6	98-103	2	12
K024	6	88-111	6	99-105	6	65-103	0	0
K037	8	99-119	8	104-127	8	90-109	2	6
K048-K052	6	96-104	6	95-105	6	92-99	0	0
K087	6	97-108	6	69-101	6	95-97	0	0
K101	4	100-101	4	102-105	4	81-94	0	0
K102	6	100-102	6	100-105	6	85-96	0	0
F024	6	95-102	6	87-102	6	83-92	0	0
K015	4	87-190	4	84-115	4	92-129	2	4
Pesticides I	4	103-104	4	97-98	4	100-101	0	0
Pesticides II	4	100-103	4	95-98	4	93-97	0	0
Number of tests with surrogate outside limit	5		2		2			

Table 10. Surrogate Recoveries for Semivolatile Organics for Scrubber Water

	Nitrobenzene-d5		2-Fluorobiphenyl		Terphenyl-d14		Phenol-d5		2-Fluorophenol		2,4,6-Tribromophenol			
Recommended QC limits based on water matrix	35-114		43-110		33-141		10-94		21-100		10-123		Number of constituents outside recommended range	Number of samples outsid recommended range
Incinerator test	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries	# of samples	Range of recoveries		
K001-Creosote	7	7.5-74	7	63-89	7	79-89	7	1.8-69	7	0.5-64	7	2.6-80	4	8
K001-PCP	4	56-66	4	100-126	4	81-87	3	11-46	4	2-26	2	17-18	2	4
K011/K013/K014	2	63-82	2	78-81	2	99-103	2	63-84	2	74-84	2	106-116	0	0
K019	6	90-94	6	66-72	6	100-106	6	65-90	6	52-75	6	52-71	0	0
K024	7	81-117	7	54-61	7	93-102	7	8-52	7	4-46	7	31-57	2	6
K037	8	96-117	8	98-117	8	117-125	8	88-107	8	79-95	8	110-130	4	13
K048-K052	6	77-87	6	45-90	6	29-75	6	67-102	6	61-93	6	55-83	2	3
K087	6	59-113	6	56-83	6	75-141	6	6-75	6	4-86	6	10-102	2	6
K101	4	6-32	4	45-50	4	62-68	4	56-63	4	57-63	4	55-68	1	4
K102	4	88-122	4	67-80	4	87-117	4	70-117	4	79-106	4	52-126	4	4
F024	6	47-77	6	16-44	6	23-73	6	4-142	6	2-67	6	20-262	5	13
K015	4	13-59	4	56-99	4	70-86	4	63-117	4	58-108	4	39-71	3	3
Pesticides I	4	48-89	4	55-66	4	47-64	4	42-65	4	47-61	4	55-76	0	0
Pesticides II	4	30-36	4	24-50	4	26-42	4	30-71	4	52-72	4	25-86	3	6
Number of tests with surrogates outside limit	6		4		3		8		7		4			

To HERE

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Quality Assurance Oversight of Superfund Contract Laboratories Using GC/MS Raw Data Audits

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ABSTRACT

The monitoring of the quality assurance results produced by laboratories participating in the Superfund Contract Laboratory Program (CLP) is a task of the Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV). One element of this monitoring program involves the review of electronically stored data created by modern data systems during the analysis of environmental samples using gas chromatography/mass spectrometry (GC/MS). Utilizing this electronic raw data, quality assurance reviewers at EMSL-LV reconstruct the steps used by the original analyst to obtain a second set of final analytical results. The two sets of results (reviewer-generated and analyst-generated) are compared to determine the extent of laboratory or analyst variance.

EMSL-LV maintains a GC/MS raw data audit facility which includes stand-alone data systems for all of the commonly used GC/MS systems currently used in the Contract Laboratory Program. The laboratory includes systems from Hewlett-Packard, Finnigan, Extrel, and VG Instruments. The procedures used for the quality assurance review of GC/MS raw data will be discussed. Common quality assurance defects found during the raw data reviews will be surveyed.

Notice: Although the research described in this article has been supported by the Environmental Protection Agency under contract 68-03-3249 with Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

The use of trade names is for example only and does not constitute an official endorsement or recommendation.

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Testing and Quality Assurance for Hazardous Wastes Intended for Fixation and/or Land Disposal

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Abstract

By May 8, 1990, the so-called "third third" rule will be implemented by U.S.E.P.A.; thus, finalizing the land disposal restrictions for all listed and characteristic hazardous wastes.

Pre-screening and acceptance of any hazardous waste into a treatment facility or a hazardous landfill require specific analytical technology backed by relevant Quality Control/Quality Assurance practices, especially when conducting site clean-ups involving large volumes of hazardous waste.

This paper deals with the following:

1. Treatment (stabilization/fixation) facility requirements.

    a. Documentations such as Waste Characterization forms and analytical findings.

    b. Process assessment QA/QC by the introduction of a simulated treatment (bench scale) process to evaluate submitted wastes individually. Examples will be given for electroplating wastes. B.D.A.T. standards achievement in treated wastes: reporting and documentation.

2. Land Disposal

Wastes submitted for acceptance to a hazardous waste landfill require relevant certification backed with analytical findings and relevant QA/QC.

This paper will present the requirements and examples of hazardous wastes covered.

The practical limitations for such QA/QC programs will also be discussed based on the experience gained by a T.S.D.F. during the first and second third periods.

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STATISTICAL ANALYSIS FOR EVALUATION OF A GROUND WATER MONITORING PROGRAM

Biography of Authors:

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Abstract - Analytical data from an ongoing, regulatory-required groundwater monitoring program for a major west coast petroleum refinery have been statistically evaluated to justify reducing the scope of the monitoring effort without compromising the objectives of the program which were to:

- Monitor off-site contaminant migration during operation of a liquid hydrocarbon recovery and groundwater reinjection system;
- Monitor lower aquifers for indication of vertical contaminant migration; and
- Establish baseline conditions across the refinery.

The statistical analysis comprised the following steps:

1) Correlation analysis of the 114 analytes to select indicator compounds;

2) Principle component analysis of the indicator compounds to further group the indicator compounds by their relative variability;

3) Cluster analysis of the principle components, by well, to identify similar wells based on chemical properties, and

4) Further statistical review at the request of the regulatory agency to predict gasoline concentration from EPA 602 results (i.e., benzene, toluene, ethylbenzene, and xylene; BTXE). This approach involved the following statistical analyses:

   - o Summing BTXE concentrations and ranking them highest to lowest.
   - o Ranked values were input to the general linear model (GLM) to establish groupings of wells.
   - o Wells falling into multiple groups were evaluated and placed into a single group based on geological features. (As it turned out wells could be grouped according to the amount of free hydrocarbon present in the well.)
   - o) Regression analysis were performed on each the four groupings of wells to generate linear regression plots and equations for each group.

The equation generated from the linear regression was considered valid only if the plot was linear and the correlation coefficient was ≥ 0.70 with significance <0.1. The predictive value of the linear regression equation for each of the four groups was tested using recent field data and precision

estimates were calculated from the measured versus calculated results. In addition, an F-test was performed and it was shown that there was no statistical difference between the measured and calculated result.

The results of this statistical analysis were presented to the regulatory agency charged with overseeing the groundwater monitoring program, as justification for reducing the scope of the program. The agency accepted the approach and savings in sampling and analytical costs will exceed $150,000 per year. Since this groundwater monitoring program will probably continue for the next 20 years, savings of over a million dollars will likely be realized from this effort.

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RCRA Detection Monitoring Statistical Analysis for Volatile Organic Constituents: Part I, A Case Study

ABSTRACT

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As RCRA land disposal facilities have received final permits, one area which has required considerable effort has been the development of suitable alternate statistical procedures to be used in the analysis of volatile organic constituent (VOC) data. Concerned persons in both the regulated community and regulatory agencies have recognized that certain situations call for additional guidance beyond that presented in the EPA guidance document entitled: Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities: Interim Final Guidance {IFGD} (EPA, April 1989).

The challenge has been to develop a valid statistical test which satisfies the regulations contained in 40 CFR 264.97. A review of permits which have been granted reveals that some contain non-statistical comparisons which, although granted, do not technically satisfy the requirement for a statistical test. This is especially true in those permits which utilize a multiple of a PQL as a regulatory limit. Other permits have addressed the issue through groundwater waivers; the omnibus provisions of RCRA are invoked to allow a non-statistical test to be utilized to determine if contamination above background has occurred.

The authors have developed and negotiated a statistical test procedure for VOC data for which false positive and false negative rates can be determined and adequately balanced, and which meets the regulatory requirements for an alternate statistical procedure as set forth in 40 CFR 264.97.

INTRODUCTION

In order to obtain final operating status under RCRA, land disposal facilities must comply with regulations contained in 40 CFR §264. Specifically, 40 CFR 264.97 requires the use of a statistical test to determine if groundwater contamination may be present at the facility. Since the default test mandated in the former regulation (CABF test) was widely recognized as being inappropriate for this purpose, especially for VOC data, Envirosafe Services of Ohio, Inc., (ESOI) in applying for a Part B permit to obtain final status, presented several different alternative statistical methods. These different methods reflected changes in technology and regulatory guidance which occurred over the six years during which the permit application was finalized and a final permit drafted for the facility. The method which was developed and finally agreed to by both ESOI and USEPA utilizes a "Control Limit Value" against which analytical results are compared to determine if contamination may be present.

EVOLUTION OF A STATISTICAL TEST

In 1983, ESOI transmitted a Part B application to USEPA for operation of a RCRA land disposal facility. In that application, as allowed by regulation 264.97(b)(1)(ii), ESOI proposed an alternate statistical test to the CABF test originally required under 264.97(b)(1)(i). The primary reasons for requesting the alternate statistical procedure were:

- The incorrect assumption that all monitoring parameters follow a normal distribution
- The unreliable nature of the CABF test
- The high frequency of false positive findings
- The mandated use of a minimum of 16 values (4 sub-samples of one sample taken each of 4 quarters). Because these analytical results are not all independent the first condition of statistical analysis by a t-test is violated. In reality only 4 independent samples are collected and only 3 degrees of freedom are possible.
- The inability of this procedure to supply any other information outside of a finding of significance.

ESOI, in it's 1983 application, proposed the use of an ANOVA (Analysis of Variance) test to determine if a statistically significant increase in indicator parameters had occurred. These "indicator parameters" on the list of parameters initially proposed by ESOI are those initially proposed by ESOI with the addition a few naturally occurring anions and cations. The parameters selected were for the most part always found above the detection level and did have a definable data distribution. ANOVA offered the capability of partitioning the variance. Partitioning the variance allows the assignment of potential sources of the significance by structuring the subgroups by spacial, temporal or analytical attributes. The results of this type of analysis would narrow the scope of any subsequent investigation if one were needed. This procedure was rejected by USEPA due to the fact that it did not meet the regulatory requirement at the time of comparing "each" individual result from "each" down-gradient well to the background data pool.

During this period the focus was turned to the selection of "indicator parameters". At this time there was an increase in interest by the Agency to shift from gross indicators of migration to specific and more sensitive measures such as the volatile organic compounds (VOC's). An alternate list of monitoring parameters was proposed by ESOI in place of the default indicator parmaters cited in the regulations (pH, conductivity, Total Organic Carbon). The list is given in Table 1. These parameters were chosen due to their presence in the waste, the leachate, and their detectability in groundwater (264.98(a)). Primarily composed of volatile organics, the list also contains parameters which are of regulatory concern, such as cyanide. Many of these compounds have been demonstrated to migrate quickly in contaminant plumes at other facilities, and so are most likely to be detected first in case of a release. (Ironically, under the October 1988 revision of 40 CFR §264, the use of one-point-in-time comparisons and of one-way ANOVA's are now encouraged; see 53 FR 39719, October 11, 1988, and the IFGD.)

In its reponse to this finding of deficiency, and after studying data distributions of volatile organic compounds obtained from USEPA Groundwater Task Force Reports of

Table 1: ESOI Indicator Parameters

Xylene
Toluene
1,1-Dichloroethane
Chloroform
Ethylbenzene
Benzene
1,1,1-Trichloroethane
Trichloroethylene
1,2-Dichloroethane
Cyanide
Lead (Dissolved)
Cadmium (Dissolved)
Chromium (Dissolved)
Phenol
Methyl Ethyl Ketone
Methylene Chloride

contaminated facilities, ESOI proposed a statistical test based on a Poisson distribution of sample frequency indicators. The basis of this test is that at facilities where releases have occurred, more than one compound (usually several or many) are detected in the groundwater at higher concentrations than those usually present as a result of laboratory or sampling error. At that time, because false positive "hits" due to solvent contamination in laboratory ambient air were common, ESOI was concerned that one of these false positive hits could be erroneously interpreted as groundwater contamination due to the notification requirement under 40 CFR 264.98(g)(1). Therefore, this test required that a minimum number of detections above a certain concentration would be necessary to demonstrate that groundwater contamination may be present. This method was also denied by USEPA.

As a third statistical proposal, ESOI presented the 20-30-50 test. Using this method, contamination would be indicated by a detection of any three indicator parameters in excess of 20 µg/l, two at 30 µg/l, or one at 50 µg/l. At the time of the proposal, this method had already been accepted for use by USEPA Region 4 at a RCRA land disposal facility in Emelle, Alabama. ESOI had further justified the use of this method through empirical analysis of data obtained by USEPA Groundwater Task Force investigations at RCRA facilities nationwide. By comparing the determinations by Task Force officials as to the presence or absence of groundwater contamination involving parameters listed in Table 1 with the determination which would have been arrived at by the 20-30-50 method, ESOI demonstrated that the test would have also indicated contamination in the same wells. This method was rejected by USEPA for use by ESOI because the concentration levels were not statistically based.

At that time, USEPA was placing increasing emphasis on the use of Appendix IX PQL's in analysis of groundwater samples. Initially proposed as a check on laboratory methodology (52 FR 25945, July 9, 1987) Appendix IX PQL's were routinely being used as MCL's (Maximum Contaminant Levels) in groundwater. This created a dilemma, since 40 CFR §264.97(b)(1)(ii) called for a "statistical procedure...that...reasonably balances the probability of falsely identifying a non-contaminating regulated unit and the probability of failing to identify a contaminating regulated unit". The PQL "value" did not take into account laboratory errors, and therefore did not meet the requirements of the regulations to use a statistical procedure (40 CFR 264.98(f)). In addition, the majority of the numbers given as PQL's were not experimentally determined, but were arbitrarily assigned, and therefore were not statistically determined. ESOI felt that the adoption by a RCRA facility of a method clearly in contravention of the regulations would set a poor precedent, and might in fact not be fully protective of human health and the environment. ESOI therefore set out to develop a statistical test which, although similar to the use of PQL's, would meet the requirements of the regulations, and would be protective of human health and the environment.

DETERMINATION OF CONTROL LIMIT VALUES

Experimental Methodology

In order to develop a statistical test based on Control Limit Values (CLV's) which adequately balances the risks of false positives and false negatives, ESOI developed a series of experiments to determine the degree of laboratory error inherent in analysis of the indicator parameters to be used at the ESOI facility. The primary objective was to determine

the degree to which the concentration, as reported by the laboratory, of a constituent varied from the known concentration. This would be accomplished by spiking water samples with known concentrations of constituents and comparing the reported value with the known concentration.

The study is being conducted in three phases. In Phase I, spiked samples were made up using ultra-purified, organic free water. In Phase II, the spikes were repeated, but at levels more near the detection limit for each compound, and using natural groundwater from leak detection and bedrock wells. This added an additional element of variability to the process. Since nearly 100 of the monitoring wells to be sampled under the Part B permit were installed in clay formations, significant amounts of suspended solids are frequently encountered in samples obtained from these wells. The level of "siltiness" is variable, and its effects on measurements of low concentrations of organics have not been fully explored. Controlling the amount of siltiness of the spiked samples in Phase II was problematic, as using several different levels of siltiness combined with varying spiking concentrations could greatly increase the scope and cost of the experiment. Ulitmately, it was decided that the water obtained from several leak detection wells would be composited into one large sample, and any suspended solids would be kept in suspension with a magnetic stirring device as the vials were filled. No attempts were made at insuring that each vial would contain exactly the same amount of suspended solids, not only because it would have been very difficult to do this, but also because the levels would be uncontrolled in real-life scenarios as well. The suspended solids were not a factor for water obtained from bedrock wells, since this water is virtually free of suspended solids.

Phase III of the study, which is yet to be implemented, will use natural water samples spiked with levels of inorganic constituents found in Table I, in order to determine control limit values for those parameters as well.

Samples were to be sent to laboratories "blind" so they would be analyzed with the same level of care as any routine groundwater sample. This was important, since any attempt by a laboratory participating in the study to apply special consideration to the sample above what is normally provided would potentially bias the results. (The revised 40 CFR §264.97(i)(5) states that any pql approved by the Regional Administrator shall be the lowest level that can be reliably achieved during routine laboratory operating conditions.) In order to determine between-lab variation, at least two different laboratories would participate in the experiments. Since accuracy was extremely important, any source of outside contamination of the samples had to be avoided. This required that the spiked samples be prepared by a laboratory which had the expertise to produce, maintain, and accurately analyze them, without the time pressures presant in large commercial laboratories processing large numbers of samples. With these factors in mind, ESOI contracted the services of Battelle Memorial Institute in Columbus, Ohio.

Battelle has participated in Phases I and II of the study. It was the task of Battelle in both cases to produce a series of water samples spiked with various concentrations of VOC's found on Table 1. In Phase I, distilled water was further purified to insure that no residual VOC contamination was present which would bias the results. The laboratory was required to create spiked samples, and to analyze duplicates of the spikes to determine the relationship of the true concentration to the calculated spiked concentration. (The spiking concentrations to be used were determined through methods discussed elsewhere in this paper.) A total of 60 different samples would be used, requiring 300 vials to be prepared

(one for each participating laboratory, one for ESOI, and one retained by Battelle). Laboratory water was "ultra-purified" and spiked according to the following procedure:

1. Prepare a 5000 µg/ml stock solution of each analyte in methanol by adding a volume of the analyte calculated to weigh 500 µg to approximately 99 ml of methanol in a 100-ml volumetric flask. Add the analyte to the flask using a 500-µl or 1000µl syringe in such a manner that the drops of the liquid added drop directly into the surface of the methanol. Dilute to volume with methanol and mix thoroughly by inverting the flask at least 10 times. Transfer stock solutions to 20 ml septum-capped storage vials, filling the vials completely to ensure zero headspace. Store solutions at -10 to -20° C if they are not going to be used within one week.

2. Prepare calibration spiking standards containing 5, 10, 25, 50, 100 and 200 µg/ml of each analyte by adding the appropriate volume of stock solutions to a 10-ml volumetric flask diluting to volume, and mixing thoroughly. Transfer solutions to 2-ml septum-capped vials, filling the vials completely to ensure zero head space. Store solutions inverted at -10 to -20° C if they are not going to be used within one week.

3. Prepare spiked solutions containing the amount of each analyte required to give the spiking levels in water samples specified by ESOI when 100 µl of the spike solution is added to 500 ml of water. Add the appropriate volume of stock solutions to a 10-ml volumetric flask, dilute to volume and mix thoroughly. Transfer solutions to 2-ml septum-capped vials, filling the vials completely to ensure zero headspace. Store solutions inverted at -10 to -20° C if they are not going to be used within one week.

4. Equip a 12-gallon glass carboy with an aluminum plate on top with a glass tube extending to the bottom of the carboy for nitrogen purge gas and a glass tube extending to the bottom of the carboy for siphoning water from the carboy. Rinse the tubing thoroughly with acetone, methanol, and distilled water prior to use. Extend the siphoning tube outside the carboy to a level at least 10" below the bottom of the carboy and install a Teflon stopcock 6-8" from the end of the tube to control the flow of the water. Place the carboy in a foam-insulated cooler.

5. Prepare 12 gallons of volatiles-water by passing distilled water thorough a Millipore water purification system into the glass carboy, preserve by adding 360 ml of 6 N HCl as a preservative, and purge with high purity nitrogen at a flow rate of 1-2 l/min. for at least 16 hours. Add ice to the cooler to cool the water to 5° C or lower.

6. Analyze at least 3 replicates of each unspiked volatiles-free water by PTD GC-PID/Hall analysis using EPA Methods 8010/8020 to demonstrate that none of the analytes are present at levels greater than 1 ppb. If contamination is found, identify the source and correct the problem, if feasible.

7. Prepare at least three replicates of 40-ml water samples at each of six calibration levels by precalibrating the volume of 500-ml separatory funnel containing 10-12 glass beads, completely filling the separatory funnel with volatiles-free water

drained from the 12-gal carboy, spiking with 20 µl of calibration standard per 100 ml of water, mixing throughy by inversion at least 20 times, filling 40-ml vials by draining the samples into the bottom of a vial and gradually lowering the vial to permit the vial to become completely filled, sliding a Teflon-lined septum over the top of the vial and securing with a holed screw cap to give a headspace-free sample. Prepare blanks in a similar manner. Store the samples in an inverted position at 0-5° C until analyzed.

8. Prepare at least five replicates of 40-ml water samples spiked with each of the 60 spike solutions (total of 300 samples) using the procedure described in step 7. Transfer at least one replicate of each sample to ESOI.

9. Analyze the water samples spiked with the calibrations solutions in Step 7 by PTD GC-PID/Hall analysis and prepare an external standard calibration curve.

10. Analyze two of each of the 60 water samples prepared in Step 8 by PTD GC-PID/Hall analysis within seven days and tabulate the results.

In Phase II, the spikes were repeated, as discussed above, but with different spiking concentrations and different numbers of samples, using natural groundwater samples. This injected the element of natural variability into the process. This was important, since this variability could increase the false positive rate if not fully accounted for by the final control limit value as determined by the study. Water from bedrock and leak detection wells was prepared and spiked according to the following methodology:

1. Prepare a 5.00 mg/ml stock solution of each analyte in methanol by adding a volume of the analyte calculated to weigh 500 to 525 mg to a stoppered, 100-ml volumetric flask tared after addition of approximately 95 ml of methanol. Add the analyte to the flask using a 500-µl or 1000 µl syringe by injecting it directly into the methanol. Reweigh the stoppered flask, dilute to volume without mixing. Add sufficient methanol, using appropriate size syringes, to give a final concentration of 5.00 mg/ml and mix thoroughly by inverting the flask at least 10 times. Transfer stock solutions to septum-capped storage vials, filling the vials completely to ensure zero headspace. Store solutions at -10 to -20° C if they are not going to be used within one week.

2. Prepare calibration spiking solutions at 48 µg/ml for each analyte so that 500 µl of this mixture was spiked into 600 ml of reagent water to give a 40 ppb standard, 250 µl into 600 ml reagent water to give a 20 ppb standard, 125 µl into 600 ml for a 10 ppb standard, 62.5 µl into 600 ml for a 5 ppb standard, and 25 µl into 600 ml for a 2 ppb standard.

3. Prepare spiked solutions containing the amount of each analyte required to give the spiking levels in water samples specified by ESOI when 100 µl of the spike solution is added to 500 ml of water. Add the appropriate volume of stock solutions to a 10-ml volumetric flask containing approximately 5 ml methanol, dilute to volume and mix thoroughly. Transfer solutions to 2-ml septum-capped vials, filling the vials completely to ensure zero headspace. Store solutions inverted at -10 to -20 C if they are not going to be used within one week.

4. Equip three 12-gallon glass carboys with an aluminum plate on top, a glass tube extending to the bottom of the carboy for nitrogen purge gas and a glass tube extending to the bottom of the carboy for siphoning water from the carboy. Rinse the tubing thoroughly with acetone, methanol, and distilled water prior to use. Extend the siphoning tube outside the carboy to a level at least 10" below the bottom of the carboy and install a Teflon stopcock 6-8" from the end of the tube to control the flow of the water. Provide for magnetic bar stirring of 2 carboys.

5. Prepare 12 gallons of reagent water (RW) free of organic volatiles by passing distilled water thorough a Millipore water purification system into the glass carboy, preserve by adding 180 mL of 12 N HCl, and purify to ensure removal of organic volatile material by purging with high purity nitrogen at a flow rate of 1-2 l/min. for at least 16 hours. Use a Millipore system that has been modified by moving the carbon containing module to the final position in the flow stream in order to minimize the organic contaminants; use only glass, metal or Teflon lines, and flushing the lines thoroughly before use.

6. Prepare 10 gallons each of 2 ground waters by placing Bedrock water received from ESOI in one glass carboy and Till water in the other one, adding 150 ml of 12N HCl to each carboy as a preservative, and purging with high purity nitrogen at a flow rate of 1-2 L/min for at least 16 hours.

7. Analyze at least 3 replicates of each unspiked water by PTD GC-PID/Hall analysis using EPA Methods 8010/8020 to demonstrate that none of the analytes are present at levels greater than 1 ppb. If contamination is found, identify the source and correct the problem, if feasible.

8. Prepare spiked RW calibration standards at each of six levels:

i. Precalibrate the volumes of 500-mL separatory funnels containing four or more glass rectangles (to aid mixing), completely fill with RW drained from the 12-gal carboy and install the stopper in such a manner to give no headspace in the funnel;

ii. Place the filled separatory funnel in ice for a length of time pre-determined to ensure that the water is at or below 5° C;

iii. Spike with 20 uL of calibration standard per 100 ml of water and mix thoroughly by inversion at least 20 times;

iv. Fill at least three replicate 40-ml vials by draining the sample into the bottom of a vial and gradually lowering the vial to permit the vial to be completely filled, and seal with a Teflon-lined septum and a holed screw cap to give a headspace-free sample.

The separatory funnel filling and 40 ml vial filling are done in a N_2 filled cupboard. Prepare blanks in a similar manner. Store the samples in an inverted position at 0-5° C until analyzed (within 7 days).

9. Using the procedure described in Step 8, spike samples of Bedrock and Till water. Spiked samples are prepared at eight to ten day intervals until ten sets have been prepared. The first three sets will consist of six samples each: three of Bedrock water and three of Till water. The remaining seven sample sets will consist of four samples each: two of Bedrock water and two of Till water. Thus, the total number of samples spiked is 46 = (3x6)+(7x4). The set of analyte concentrations for these 46 spiked samples is unique and is provided by ESOI. Each spiked water sample is split into 10 replicate 40 mL samples. Four of the ten replicates of each spiked sample are shipped to ESOI by overnight delivery on the day they are prepared. Two of the ten samples are analyzed by Battelle (Step 11 below), and the remaining four samples are stored at 0-5° C for contingencies and for future analyses to assess storage stability (see step 12 below).

10. Analyze the water samples spiked with the calibration solutions in Step 8 by PTD GC-PID/Hall analysis and prepare an external standard calibration curve.

11. Analyze two or three replicates of each of the four spiked water samples prepared in Step 9 by PTD GC-PID/Hall analysis within seven days using EPA Methods 8010/8020. Process and tabulate the results within two working days of the analysis completion.

12. After two weeks of storage, analyze in duplicate at least four of the 46 samples prepared in Step 9 by PTD GC-PID/Hall analysis. Repeat this analysis on these sample spiked samples after an additional six weeks of storage.

Unspiked bedrock waters are generally free of suspended solids, but may have higher dissolved solids than water obtained from leak detection wells in the clay tills found at the facility. Typically, concentrations of dissolved sulfate and chloride can vary widely in bedrock wells, depending on the characteristics of the limestone in the vicinity of the well. Since waters obtained from leak detection wells typically have much higher levels of suspended solids than water from the bedrock formation, it is expected that these waters will exert a stronger influence on analytical data due to the presence of these solids. These effects may be specific to each well, depending on the level of "siltiness" typically found in water from that well.

Sample Shipment

The primary purpose of the study was to determine the magnitude of laboratory variability on analyses of water samples containing low levels of VOC's. In order to insure that the samples were analyzed in the same manner as any routine groundwater sample in the laboratory, the purpose of the sample was not revealed to the participants, since a laboratory knowingly receiving samples designed to determine the accuracy of that lab's analyses might, understandably, use more care in analyzing these samples than is normally the case. This could cause the data to show the laboratories to be more accurate than can be expected in routine analyses in the future.

In Phase I, the samples were sent to the two laboratories in one shipment containing all spiked samples, plus two controls consisting of groundwater samples from the facility which were not spiked. Battelle also analyzed control samples of the ultra-pure water

prepared for Phase I. After analysis of the data from Phase I, it was determined that sending the samples in at the same time did not necessarily insure that all the samples would be *tested* at the same time by both laboratories. As presented in the upcoming discussion concerning the statistical analysis of the data from Phase I, one laboratory ran the samples on three different days, whereas the other lab seems to have processed the samples in one run. Statistical analysis recorded a significant day-to-day component of variability for measurements of at least some of the indicator parameters. Since the experiment was to determine the amount of laboratory error present, it must also be sensitive to changes in laboratory conditions over time. A given laboratory may be "better" or "worse" on any given day, depending on the operating conditions of the instrument, the skill level of the operator, or the number of samples being processed that day. The presence or absence of ambient contaminants may also change from day to day. It is clear that in order to account for these variabilities, the samples in Phase II of the study would have to be delivered to the laboratories in small batches so that they would be run on separate occasions over a relatively long period of time. As discussed in Step 9 of the Phase II methodology, spiked samples were prepared at eight to ten day intervals until ten sets were prepared. The samples were sent to ESOI, whose staff immediately sent them to the participating laboratories. Since the maximum holding time on VOC samples analyzed under RCRA is 14 days, the eight to ten day interval insured that no more than two batches could be run at the same time, and that all batches would probably be run separately. In this way, an analysis could be made of actual laboratory error, including changing conditions over time.

Experimental Inconsistencies and Quality Assurance/Quality Control

Quality Assurance and Quality Control were provided by Battelle for the spiked samples and control samples in both Phases I and II. In both Phases, Battelle retained replicate samples which were analyzed by PTD GC-PID/Hall analysis to obtain the "true value" of the spiked sample, to demonstrate that the spiked values for each sample were correct for statistical comparison. In those few cases where the value of the tested replicate differed from the planned spiking concentration, the measured concentration value of the replicate was used as the "true" value for statistical comparison. In a couple of cases it is not possible to determine whether the spiked value or the analyzed value is accurate; these cases were omitted from the statistical analysis. The following test protocol was used by Battelle for Phase I as an internal check on the true spiking concentration:

> Two replicates of each sample were analyzed by PTD GC-PID/Hall analysis using EPA Methods 8010/8020 with a VOCOL column as the packed column equivalent. A Varian Model 3700 gas chromotograph fitted with Tracor PID and Hall detectors and interfaced with an O.I. Model 4460A PTD and autosampler system was used for the analyses. The analysis system was calibrated by analyzing three or more replicate water samples spiked with calibration standards at levels of 0, 2, 5, 10, 20, and 40 ppb. A blank, 5 ppb calibration check sample, and 20 ppb check sample were analyzed with every 10 samples was used for Phase I. Because of the one and one-half to two week interval for analysis of sample sets in Phase II, replicates of calibration standards at 2.0, 10, and 40 ppb levels were interspersed among the groundwater samples and a new calibration curve was generated for each set. Quantification was based on an external standard approach.

In any experiment of this size, errors may occur which do not affect the outcome. In Phase I, data from two sets of spiked vials must be considered suspect due to outlying data. In Phase II, there were 12 analyte data points flagged as outliers. Although a scenario can be constructed which explains the errors, there may be other scenarios which have not been considered which may have had the same affect on the data. It is interesting to note that in the QA/QC portion of the study as performed by Battelle, in over 2000 individual data points, there was not one false positive or false negative. Several vials were broken in both Phases; however, since the number of missing or incorrect analyses was very small in relation to the total number of samples, the CLVs, as determined by the study, were not affected.

The companion paper: "RCRA Detection Monitoring Statistical Analysis for Volatile Organic Constituents: Part II, Experimental Results and Statistical Techniques", describes the outcomes and conclusions of the experiment.

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RCRA Detection Monitoring Statistical Analysis for Volatile Organic Constituents: Part II, Experimental Results and Statistical Techniques

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ABSTRACT AND INTRODUCTION

To carry out the program described in Part I of this paper, a multi-laboratory experiment is progress. The goal is to characterize the statistical properties of GC/MS measurements of eleven specific VOCs, focusing attention on samples with known actual concentrations around and somewhat above the nominal detection limits or PQLs. Samples were spiked in ultra-pure reagent water as well as in "clean" upgradient bedrock and till ground water; analyses were performed on several occasions by different laboratories; and, of particular importance, laboratory analyses were performed "blind" under routine commercial laboratory conditions rather than as part of a calibration study.

Experimental data obtained consist of the known spiking concentrations and the resulting laboratory measurements, the latter including both rounded numerical values and "<DL" values. The data are used to evaluate several types of variability of these GC/MS measurements (within-lab-within-day, day-to-day within lab, and between-lab), the dependence of measurement levels and variability on actual concentrations and on matrix effects, and so on. Based on these evaluations, appropriate techniques are selected to produce Control Limit Values for RCRA detection monitoring, using statistical techniques related to those recommended in Analysis of Ground-Water Monitoring Data at RCRA Facilities: Interim Final Guidance. False positive and negative rates for detection monitoring using these control limits are estimated.

In this paper, the experimental design and statistical techniques used are discussed, along with general descriptions of the results obtained. Sample computations and plots are presented; supplementary materials, including more technical details, will be available from the authors. Finally, the degree to which these specific results may be extrapolated to other situations is discussed briefly.

CONTROL LIMIT VALUES

The EPA's recently released Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities: Interim Final Guidance (IFGD) suggests in Chapter 6 that an appropriate statistical procedure for comparisons with an MCL could use 98% confidence intervals for the mean concentration; so long as the lower end of the confidence interval is no greater than the specified comparison level (MCL), the level of that constituent is to be considered acceptable. If the lower limit of the confidence interval is above the MCL, contamination is suspected.

This confidence interval procedure is equivalent to a one-sided hypothesis test, which produces a critical value above the MCL; if the sample mean is below the critical value, the level of the constituent is considered acceptable; whereas if the sample mean is above the critical value, contamination is to be suspected, and notifications will be required, followed by appropriate resampling and testing.

For monitoring ten of the eleven VOCs specified as detection monitoring parameters at ESOI, the EPA's Regional Administrator has specified "Threshold Limit Values" of 5 µg/ℓ; for methyl ethyl ketone the TLV is 10 µg/ℓ. Due at least in part to the great number of monitoring wells and parameters involved (22 bedrock wells and around 95 till wells and trench sumps, with 16 parameters each, or around 1872 measurements for each monitoring occasion), with the attendant opportunities for sporadic false positives to occur, the Agency has agreed to allow the use of statistical comparisons with the TLV's, as described herein.

Control Limit Values (CLVs) will follow this principle. ESOI plans to take just one measurement (X) from each well on each monitoring occasion, so the sample mean will be X and the sample size 1; given a standard deviation estimate S, the lower limit of the confidence interval will then be

$$X - t_{.99}S$$

This decision criterion outlined above is, of course, equivalent to deciding that

no contamination is found if $X \leq TLV + t_{.99}S$, and

possible contamination is found if $X > TLV + t_{.99}S$.

The quantity $(TLV + t_{.99}S)$ is, in principle, the Control Limit Value (CLV).

To carry out this calculation, an estimate of the appropriate standard deviation is needed. First, one must

determine what standard deviation should be used. There are two principal considerations:

(1) for all of these compounds, the standard deviation increases as the true concentration increases; and

(2) there are many sources of variability in these measurements, such as measurement error, day-to-day laboratory variability, inter-laboratory variability, and matrix effects, and the appropriate standard deviation and CLV should incorporate all of these in an appropriate fashion.

Determining the appropriate standard deviation occupies much of our attention below. In addition, in some cases the average measurement obtained is not equal to the true concentration; the final CLV will incorporate a correction to allow for this.

PHASE I - DESIGN AND RESULTS

Sixty samples were prepared by spiking ultra-pure reagent water with specified VOCs, as follows: with probability 1/3, the spiking concentration was 0; with probability 1/6, it was 20 µg/ℓ; with probability 1/6, it was 40 µg/ℓ; and with probability 1/3, it was randomly distributed uniformly between 0 and 40 µg/ℓ. The samples were distributed to two laboratories, which were then to analyze these samples for the requested parameters in their usual fashion; subsequently, requests were made to examine the GC/MS traces to determine whether any readings reported as "<DL" (less than the detection limit) could in fact be quantified.

Due to a lack of communication and an urgency of some technical staff to proceed, all samples were sent to the two labs at the same time. Fortunately, lab W did analyze their samples on three separate (though consecutive) days, allowing for some insight into the existence of day-to-day variation. Lab E apparently analyzed all of their samples consecutively on the same day.

Therefore, the results from Phase I were used to give preliminary indications of the nature of the relationship between standard deviation and level and of the magnitudes of the several components of variance. Further, there is some indication in the Phase I data that successive measurements obtained on the same day have some positive autocorrelation, so that estimates of standard deviations based on that data would be expected to underestimate the true variability. Finally, based on prior experience as well as on information submitted to the public docket on the

new 40 CFR Part 264 ground-water monitoring regulation, rather more randomness at low spiking levels had been expected than was actually observed, and so there were relatively few samples obtained at spiking levels around 5 to 10 µg/ℓ; as a result, the preliminary estimates of the variability in that range are based on the assumption that the relative standard deviation is approximately constant, and that the relative standard deviation for the 5 to 15 µg/ℓ range may be extrapolated from that observed in higher ranges. There is some indication in the Phase I data that, with some compounds, the relative standard deviation may increase as the true concentration level decreases. (This indeed appears to be the case with the Phase II data.)

Interim CLVs based on the Phase I data were incorporated into the ESOI RCRA Final Permit, along with a description of the protocol for determining final CLVs in Phase II of the study (and in Phase III, for the inorganic compounds). The statistical analysis used for this purpose is similar to that given in the sample analysis below for benzene, treating the four groups of data as if they had been obtained at one lab on four separate days. It was impossible to sort out the difference between lab-to-lab and day-to-day variability, except with xylenes, where it was clear that the two labs measured xylenes quite differently.

Numerical or other results from Phase I will not be reported here, except for the following observations:

(1) The actual quantity analyzed (in both Phases) is the Relative error, R = (Measured - True)/True. Therefore, for any particular analysis, cases with T = 0 were omitted. There were no cases with R ≠ 0 when T = 0 for the compounds of interest, although there was one case of misidentification, in which 40 µg/ℓ of 1,2-dichloroethane was misidentified as concentrations of 50 µg/ℓ of 1,1-dichloroethene and 93 µg/ℓ of acetone. This data point was not included in the analysis of 1,2-dichloroethane. (Several other related compounds present in that sample were not misidentified.)

(2) In addition, those observations with T > 0 but M = "<DL" were omitted; this was a very small proportion of the total data. There was just one case with a quantified level which was less than the nominal detection limit of 5 µg/ℓ.

(3) Normal probability plots indicated distributions that were essentially normal, with a few outliers. Outliers are problematic, of course, and are one reason for strongly recommending a resample and retest whenever

suspected contamination is found (see below).

(4) The interim CLVs ranged from 6.5 (for benzene) to 16.0 (for 1,1,1-trichloroethane), with values of 8.5 for trichloroethene and 13.5 for methylene chloride.

(5) In spite of claims by both labs to have detection limits of 10 µg/ℓ for methyl ethyl ketone, only once was this compound detected, and that with T = 40.

PHASE II - DESIGN AND ANALYSIS PLAN

Phase II (using actual ESOI till and bedrock ground water rather than ultra-pure reagent water) was designed using the experience obtained in Phase I. Twenty samples each were prepared in till and bedrock waters; two samples of each water type were sent to the labs on each of ten days, separated sufficiently far in time as to virtually preclude analyses being performed on the same day. Three labs were used, designated as B, I, and W (the same W as before).

Each compound was present in each sample, at one of five fixed levels (chosen from 4, 8, 12, ..., 20 or 5, 10, 15, ..., 25 or 6, 12, 18, ..., 30, according to the size of the interim CLV). In addition, three samples each of till and bedrock water were spiked with rather higher levels of methyl ethyl ketone (70, 110, and 150 µg/ℓ).

The ten possible pairings of two spiking levels chosen from five available levels were randomly assigned to each of the ten days. This would have produced a statistical design known as a partially balanced incomplete block design (mixed model) for the basic twenty samples, for which some standard statistical theory exists; see, e.g., §9.5.2 of The Analysis of Linear Models by Ronald R. Hocking. The balance inherent in this design would be preserved across labs, so that extensions of that theory would apply. However, a few samples were spiked at the wrong levels, or were otherwise omitted from the analysis; some bottles broke; and some samples shipped the same day were analyzed on different days and vice versa. Therefore, the analysis described below was used instead, including the additional samples with the high methyl ethyl ketone concentrations. That analysis is approximate, being more nearly exact when the level and variability of the relative error R is nearly constant across levels of T and labs, and less so otherwise. There are four stages:

(1) For each VOC, perform preliminary analyses to decide what effects seem to be present. First, replace the few "<DL" measurements with DL/2; compute R = (M-T)/T; fit R

as a linear function of T (R = A + BT) for each lab; obtain residuals (i.e., actual - fitted R values); plot residuals against day and do a one-way ANOVA to see if day-to-day variation is present; compute $\sqrt{|\text{residual}|}$; plot it against lab and T and do two-way ANOVAs to see if there seems to be lab-to-lab variation in the size of residuals, or if the size of relative error seems to be changing with T.

(2) Decide on the treatment to be used for each VOC; in particular, decide whether labs can be treated as one, or if the labs can be pooled, with separate fitted lines, or if lines should be fitted separately, or if weighted regression analyses should be performed because of unequal variances across levels of T, and so on.

(3) Fit the R = A + BT model using the effects and for the subgroups decided on in step (2); obtain residuals again; if weighted regression is not used, do a one-way ANOVA (variance components analysis) on the residuals to estimate the overall standard deviation; compute a CLV.

If weighted regression is used, fit weights to |residual|, multiplying by $\sqrt{\pi/2}$ to estimate standard deviations; compute (new) weights; fit the line and obtain new residuals, and iterate until the fit converges; obtain standardized residuals; perform the one-way ANOVA (variance components analysis) on those, obtaining a multiplier for the fitted standard deviation (as a function of T); compute the CLV.

(4) Assume the fitted mean value of M at T = TLV and the fitted standard deviation (function) are the actual values; use these to estimate power curves.

PHASE II - EXPERIMENTAL RESULTS AND SAMPLE ANALYSES

It soon became clear that lab I is different from the others in the variability of its measurements. Lab I had initially reported a detection limit of 2 µg/ℓ for all VOCs involved, even methyl ethyl ketone, but had switched to the 40 CFR Part 264 Appendix IX PQLs; we felt that it would jeopardize the "blindness" of the experiment to intervene in that matter at that point. All labs had occasional anomolous values, or "outliers", but lab I had them rather more routinely than the others. Lab I initially reported different compounds than those requested; moreover, supplementary analyses supplied often indicated the presence of acetone, which was not present. Therefore, the data from lab I has been set aside for later inspection.

With labs B and W, one curious difference in reporting exists: lab B reports all values to three significant digits (i.e. 2.98, 13.4, or 115), whereas lab W rounds all values to integers (i.e. 3, 13, or 115 respectively). This rounding can have the effect of increasing the relative variability at the lower range of T values, and there does seem to some of this effect with some of the VOCs.

The conclusions reached in stage (1) of the analysis are summarized in the Table 1 below. R indicates bedRock and T indicates Till water, with Δ indicating the difference between these; an X indicates a sizable effect, definitely needing consideration, and an x indicates a smaller effect, probably worthy of consideration.

Conclusions were drawn on the basis both of formal analyses and graphs. With the formal analyses, p-values of around 0.25 or less, along with sizable effects, were taken as reasons for including an effect in the considerations at subsequent analysis stages. (This is actually conservative, but appropriate when the analyses that would be performed separately for different labs, for example, would be valid but perhaps not quite so sensitive as a pooled analysis if the labs were really not different.)

A indicates that the average measurement is greater or smaller than 100%,
L indicates lab differences in level of R,
T indicates overall curvature of the relationship of M and T,
LT indicates differences in curvature across labs,
D indicates a day-to-day component of variability in addition to within-day laboratory error,
S-L indicates a difference in size of variability across labs,
S-T indicates a difference is size of variability across levels of T, and
S-LT indicates that the S-T variability is different for different labs.

As most of the VOCs showed at least some differences between bedrock and till waters, it was decided to analyze these separately in each case. There will still be (nearly) 23 cases per laboratory, enough to carry out the analyses desired.

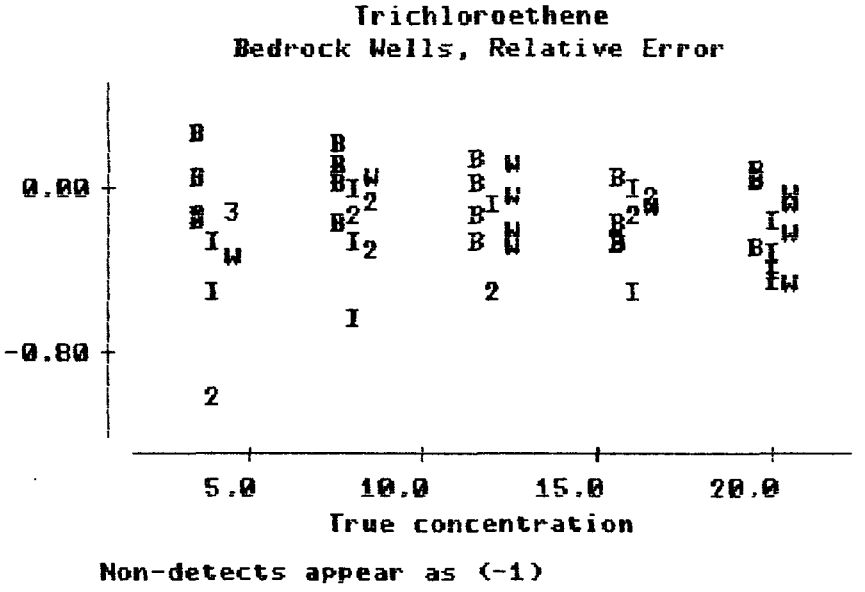
Sample analyses are given below for three examples: trichloroethene, bedrock wells; benzene, bedrock wells; and methylene chloride, till wells. These range from the simple to the difficult analyses, and will thus amply illustrate the techniques used.

Table 1

VOC		A	L	T	LT	D	S-L	S-T	S-LT	# separate CLVs
Methylene Chloride	R	X				X	x		x	4
	T	X			x	X	x	X	x	
	Δ	x			x			X	x	
Xylene	R		X							4
	T	x	X	X	X	X		x		
	Δ	x		X	X	X		x		
Toluene	R		X			X				3
	T	x	X			X				
	Δ	x	x							
Benzene	R	X	X			X				4
	T	x	X			X				
	Δ	x								
1,1-Di-chloro-ethane	R	X	X			X	x			4
	T	X	X	X		X	x			
	Δ			X						
Chloro-form	R		x			x				2
	T		x			x				
	Δ									
Ethyl-benzene	R	X	X	x		X				4
	T					x	x			
	Δ	X	X	x		x	x			
1,1,1-Tri-chloro-ethane	R	X	X		x	X	X		X	4
	T					x	X		x	
	Δ	X	X		x	x			x	
Trichloro-ethene	R					X				2
	T	X				X				
	Δ	X								
1,2-Di-chloro-thane	R					x				3
	T	x	X			x	X		X	
	Δ	x	X				X		X	
Methyl ethyl ketone	R	The detection limit for B is 10 µg/ℓ;								
	T	that for W is 50 µg/ℓ. This will be								
	Δ	handled separately.								

SAMPLE ANALYSIS - TRICHLOROETHENE - BEDROCK WELLS

A plot of the relative error R against the true concentration T is given here:



No effects were statistically significant, and none had estimates of a size that would be of consequence, except for the day-to-day variance component. Therefore the CLV will be of the form CLV = TLV + tS. S here should be the standard deviation of measurements on the original (M) scale, and s will denote standard deviation on the relative scale. In this case, S = sT.

The standard deviation on the relative scale is estimated from the R data by a variance components analysis: variance components are the day-to-day variance, σ_B^2 (B for "Between groups"), and within-days variance, σ_W^2 (W for "Within groups"). The variance of any particular measurement will then be

$$\sigma^2 = \sigma_B^2 + \sigma_W^2 .$$

This can be estimated as a linear combination of the mean squared deviation between groups and that within groups from a one-way analysis of variance (ANOVA). The fact that group sizes are not equal prohibits the use of standard formulas; however, it can be shown that the appropriate variance

estimator is

$$s^2 = \frac{1}{A} MS_B + (1 - \frac{1}{A}) MS_W ,$$

where MS_B and MS_W are the usual ANOVA mean squares between and within groups, respectively, and

$$A = \frac{\Sigma N_j - \frac{\Sigma N_j^2}{\Sigma N_j}}{k - 1} , \quad \text{where}$$

N_j is the number of observations in the j^{th} of the k groups. The distribution of linear combinations of mean squares is still an open question; however, one may approximate the distribution by a multiple of a χ^2 distribution with d degrees of freedom, where

$$d = s^2/c , \quad \text{and}$$

$$c = \frac{(\frac{1}{A})^2 \frac{MS_B^2}{k-1} + (1 - \frac{1}{A})^2 \frac{MS_W^2}{\Sigma N_j - k}}{s^2} .$$

(See, e.g, R. Hocking: The Analysis of Linear Models, §8.4.2.) The value of d will give an appropriate approximate number of degrees of freedom for the t value to be used in the resulting confidence interval.

Since σ is a relative standard deviation, the actual measurement standard deviation at a particular level of T is σT, and there remains the question of which value of T should be used in computing the CLV. If the confidence intervals of Chapter 6 of the IFGD were used, the standard deviation estimated would be that at the level of the measurements; therefore, for the present purpose, the standard deviation is estimated at the CLV.

That is, we will have

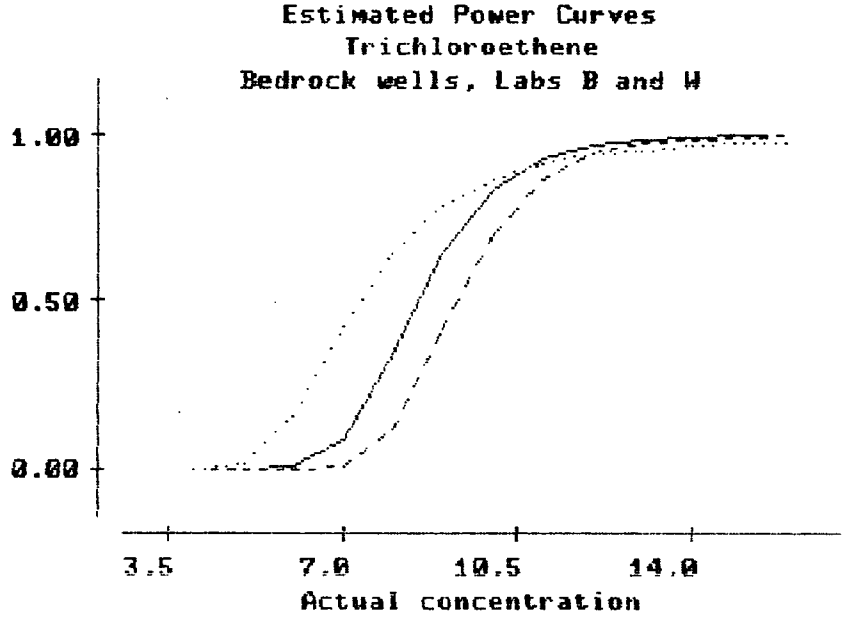
$$CLV = TLV + tsCLV, \text{ or}$$

$$CLV = \frac{TLV}{1 - ts}$$

With the trichloroethene data, d was 22.68, so the t value was 2.5025; s was 0.155113, and so the CLV was computed to be 8.1722, which was rounded up to 8.5 µg/ℓ.

Then, for a range of T values from 4 to 16, the power, or probability of obtaining a measurement exceeding the CLV, was estimated as $1 - \Phi(8.5 - T/(0.155113T))$, where Φ is the standard normal distribution cumulative distribution function.

In addition, the chance of obtaining two measurements in a row exceeding the CLV is estimated by squaring the previous power. The large number of measurements to be obtained on any given monitoring occasion at ESOI makes it highly advisable to do a resample and retest to confirm any suspected contamination. A retest lowers the sensitivity to real contamination, of course, as the site has to "fail the test" twice in order to be reported. This second power analysis estimates the chance of detecting such real contamination even with the retest. As the plot shows, using the retest gives up only about 1 µg/ℓ in sensitivity.



The third power curve is an estimate of that which the procedure in Chapter 6 of the IFGD itself would have. Recall that in the recently revised 40 CFR Part 264, the requirement is that four independent samples be obtained during each monitoring period; the confidence intervals suggested in the IFGD are thus based on samples of four observations (with an internal estimate of standard

deviation, using three degrees of freedom, rather than our external estimate from this study, with its approximately 22 degrees of freedom). The additional samples do give higher power, over much of the range of T; this shows the effect of the greater sample size, in spite of the loss of degrees of freedom. However, again, the improvement in sensitivity is only 1.5-2.0 μg/ℓ. The cost of just analyzing the additional three samples per well, at about $230 per sample, would be over $80,000 per monitoring period for this large facility.

SAMPLE ANALYSIS - BENZENE - BEDROCK WELLS

With benzene, the only significant effect present, other than the day-to-day component of variance, is the difference in values of A in the regression model R = A + BT. For lab B, we have a constant of -0.0264, meaning that lab B essentially finds nearly 100% of the benzene present, on the average. However, for lab W, A is -0.1856; lab W finds only about 80% of the benzene present.

With other VOCs, A can be positive, indicating that measurement levels are generally higher than the true values. In either case, an adjustment is appropriate.

The way chosen here to accomplish that adjustment is to replace the previous formula by

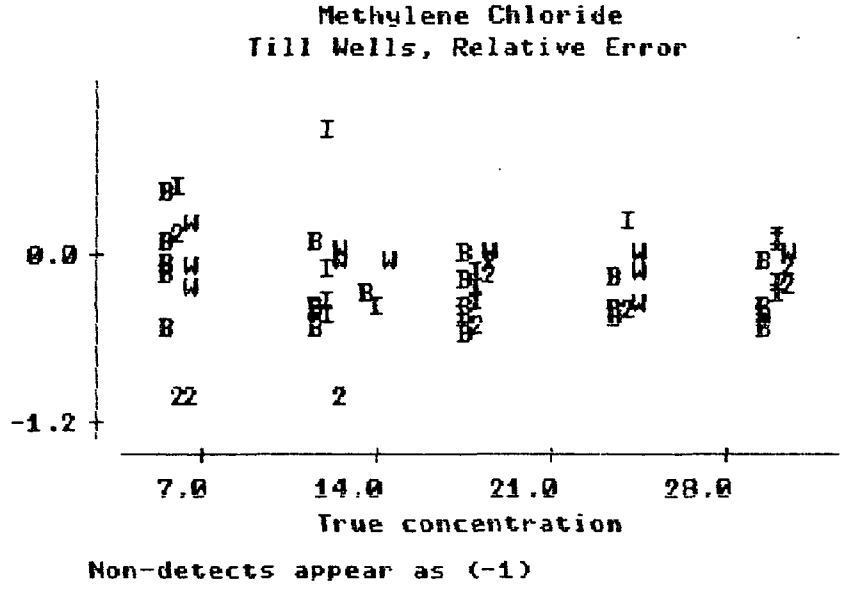
$$CLV = (1 + A)\ TLV + tsCLV, \text{ or}$$

$$CLV = \frac{(1 + A)\ \ TLV}{1 - ts} \quad .$$

This essentially replaces the TLV by the fitted mean value of M when the true value is the TLV. This approach can be carried our nicely with the more complicated cases, as well. In principle, one ought to allow for the uncertainty in the estimate of that mean value in some fashion. An alternate method, which does that, is to form 99% prediction intervals at T = TLV, using standard regression techniques. With our analysis, the additional variability will be adequately compensated for by evaluating the standard deviation at the CLV, rather than the TLV, in the spirit of the recommendations of the IFGD.

With our data, we get an estimate of relative standard deviation of s = 0.1514, with approximately 22.64 degrees of freedom. For lab B, then, the CLV becomes 7.838, rounded up to 8.0, and for lab W, it becomes 6.557, rounded down to 6.5. (We generally round up to the nearest multiple of 0.5, unless the value is just above such a multiple.)

SAMPLE ANALYSIS - METHYLENE CHLORIDE - TILL WELLS - LAB B



With methylene chloride, many effects are present, and CLV analyses will be done separately for the two labs. We present the lab B analysis as an example here. First, an iteratively reweighted regression of R on T is done. The weights used are $1/S^2$, where S is $\sqrt{\pi}/2$ multiplied by a quadratic fit of (non-standardized) |residual| as a function of T. (The $\sqrt{\pi}/2$ is the ratio between the square root of the expected value of the square of, and the expected absolute value of, standard normal random variables.) Both constant and linear terms in that regression were non-zero; the fitted value of R when T = TLV = 5 was -0.1648.

The fitted standard deviations work reasonably well: we have

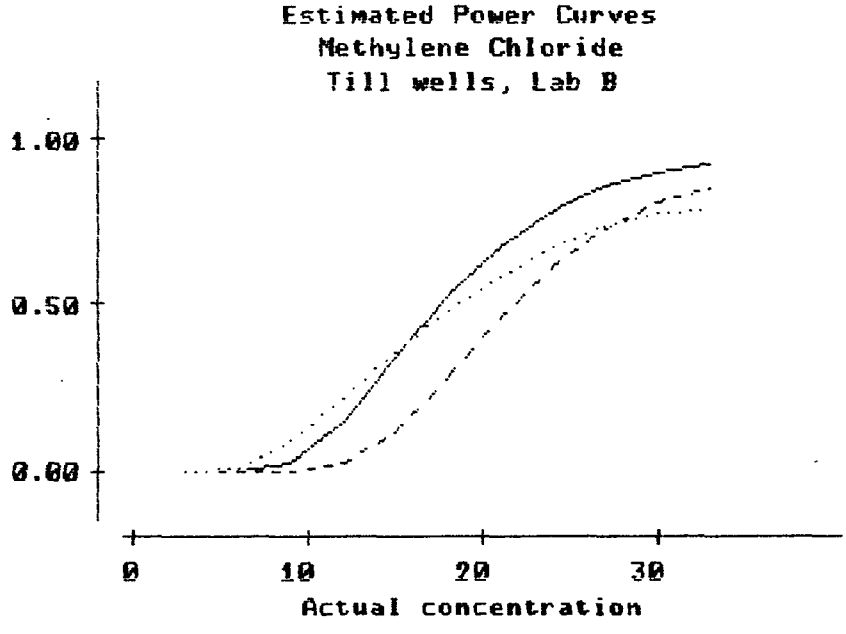
T:	6	12	18	24	30
observed s.d.:	.328	.253	.221	.146	.182
fitted s.d.:	.302	.244	.199	.167	.148

The reasons for fitting standard deviation as a function of T, rather than just using the estimated standard deviations at each value of T, are two: (1) we will need standard deviations at intermediate values for producing CLVs; and (2) each standard deviation is estimated with only a few degrees of freedom, so these can be rather variable, and smoothing is appropriate. Also, fitting absolute values of residuals rather than squares is less sensitive to outliers.

The standardized residuals (which have a variance of approximately one throughout the range of T), are then put through the variance components analysis. In this case, the relative standard deviation estimate (weighted) was 1.0654; a degrees of freedom adjustment increased this to 1.0904.

Then the previous formula for the CLV is used, except that now relative standard deviation is itself a function of T. The solution to the equation is found by search; an initial guess of T = 12 was made, and the expected value of M given T = TLV was computed as (1 - 0.1648) TLV. At T = 12, ts = 0.732372, and the first iterate gives a CLV of 15.6. We use T = 15.6/(1-0.1648) = 18.68 for the second iterate, obtaining CLV = 10.03. This iteration proceeds, possibly with some human intervention, until the fixed point is found; here with CLV = 12.4, which is rounded up to 12.5.

The power is estimated as before, except that the standard deviation used is T multiplied by the fitted relative standard deviation, which is itself a function of T.



The greater CLV value and much less satisfactory power curves for methylene chloride reflect mainly the rather greater relative variability of methylene chloride measurements, at least with this laboratory in this kind of

water. In spite of this, we still see a relatively small penalty (around 4 µg/ℓ, say) for allowing a retest, and relatively little superiority of the IFGD Chapter 6 procedure using four times as many observations in each sampling period.

SUMMARY AND CONCLUSION

In Phase II of this study, three laboratories were used. One of these proved to rather more erratic in its analyses than the others, and was temporarily discarded. The other two labs agree reasonably on CLVs for some of the VOCs, but not for others. Different VOCs have rather different modes of variability in measurements between labs, between types of waters (matrix effects), and across true concentration levels. All of these factors encourage the use of Control Limit Values (CLVs) which are both facility- and laboratory-specific.

Techniques illustrated above can be used to produce such CLVs, based in principle on the idea of statistical comparisons with an MCL as described in the IFGD. Producing such CLVs in this fashion involves some initial costs; the resulting detection monitoring procedures, however, can achieve nearly the same sensitivity with one observation per monitoring period as the IFGD procedure can with four. If this procedure would be permitted, the resulting savings would quickly compensate for that initial cost.

At this point in time, we find it difficult to imagine extrapolating our results to arbitrarily chosen laboratories. Our sample of labs is small, and each is quite different from the others. Perhaps similar studies and analyses, performed with enough other labs and other matrices, will be able to build up enough information so that one day such extrapolation will be possible.

REFERENCES

Hocking, Ronald R. (1985). The Analysis of Linear Models, Brooks/Cole, Monterey, CA.

U.S. EPA (1989). Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities: Interim Final Guidance, Washington, DC.

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QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES FOR HAZARDOUS WASTE INCINERATION

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ABSTRACT

Midwest Research Institute has developed for the Environmental Protection Agency (EPA), a handbook presenting guidance on quality assurance (QA) and quality control (QC) procedures for hazardous waste incineration. This paper presents the topics covered in the handbook and covers some of the major QA/QC issues.

INTRODUCTION

The EPA has promulgated regulations for hazardous waste incinerators under the Resource Conservation and Recovery Act (40CFR:264, Subpart O). These regulations require the permit applicant to conduct trial burns to demonstrate compliance with the regulatory limits and provide data needed to write the operating permit for the hazardous waste incinerator. Trial burns require a QA Project Plan (QAPjP) with QA/QC procedures to control and evaluate data quality. Both permit writers and applicants are in need of specific, consistent guidance in preparing QAPjPs and for designing the necessary QA/QC procedures in order to ensure consistency and adequacy of plans, report, and overall data quality.

Although considerable information is available on sampling and analysis for hazardous waste and its incineration, guidance on specific QA/QC procedures has not previously been available. To meet this need, a handbook was developed by MRI for the Center for Environmental Research Information (CERI) under subcontract to Eastern Research Group. The title of the handbook is Handbook on Quality Assurance and Quality Control Procedures for Hazardous Waste Incineration. It is a free publication available from CERI (publication number EPA/625/6-89/023; for copies call 513-569-7562). This paper will present a brief overview of the handbook and its key concepts.

THE HANDBOOK

The handbook presents guidance on the preparation and review of QAPjPs, establishment of QA objectives, design of QA/QC procedures and assessment of trial burn results. QA/QC procedures are defined for process monitoring, sampling and analysis for both the initial trial burn and for later continuing operation of the incineration facility. The handbook covers sampling and analysis for: principal organic hazardous constituents (POHCs), metals, chloride, heating value, ash viscosity,

particulates, continuous emission monitors, volatile organics and semivolatile organics. Matrices covered are; incinerator waste feeds, air pollution control device emissions, ash, and stack gas. The table of contents is given in Table 1.

The handbook is intended for a diverse audience: engineers, chemists, environmental scientists, facility personnel and EPA staff at all levels. It has been written with the EPA or state permit writer's information needs in mind, but would be, by extension of considerable value to the permit applicant. The handbook assumes the reader understands the technical approach to incineration and is familiar with the basics of most sampling and analysis methods. Many of the handbook sections are somewhat independent to allow the book to be used as a reference document. The user may go directly to their area of interest (e.g. continuous emission monitors for oxygen) and obtain the information needed.

The handbook is divided into four general areas. The first area covers the QAPjP and general issues associated with a trial burn. The need for a QAPjP is discussed and a general format for a QAPjP is presented. This format is discussed in detail with recommendations for each section of a QAPjP. The second area is sampling. The general QA/QC procedures associated with the sampling of wastes, scrubber waters, stack gases, etc are discussed in relation to the standardized EPA sampling methods. The third area is analysis. Specific QA/QC procedures are recommended for the standardized EPA methods and guidance is given on general QA/QC methods for non-standard methods (e.g. HPLC). The fourth area is QA/QC for routine incinerator monitoring and permit compliance and has different requirements and objectives from those of the trial burn. The trial burn is viewed as a short-term project with a defined beginning and end, while compliance monitoring is considered an ongoing process.

The handbook covers a wide variety of sampling and analytical methods and virtually all are standardized EPA methods. Based upon practical application of the methods, specific QA/QC procedures have been delineated which are beyond those in available written protocols. Key QC procedures of each method are addressed but some minor QC procedures have not been covered. The overall goal is to provide the user of the handbook with a way to control and/or determine the precision and accuracy of all critical measurements. Each determination of precision and accuracy must have an associated acceptance criteria. If the QC data are within the acceptance criteria, the accompanying trial burn results should be of sufficient quality to meet the needs of the data users. If trial burns and routine monitoring are designed using the QA/QC procedures indicated in the handbook and follow the guidance on QAPjP, the level of precision and accuracy will be documented and acceptance limits for all data will be defined. This should make the process of preparing and reviewing permit applications easier, more effective and hopefully more standardized.

Table 1. Contents of the Handbook of QA/QC Procedures for Hazardous Waste Incineration

CONTENTS (continued)

The QA/QC procedures presented in the handbook should be considered the minimum necessary for assessing data quality and ensuring the attainment of the permit writer and applicant's objectives. For some facilities, regions or states, the guidance in the handbook may not be sufficient due to the complexity of a given trial burn; in these cases, the handbook guidance should constrain neither the applicant nor regulatory agency. It should also be noted that the handbook contains suggested criteria for virtually all of the associated QA/QC procedures (e.g. recommended surrogate recovery limits). These suggested criteria are based upon the general performance of the specific sampling or analysis technique and should not be viewed as generic acceptance limits for all data. The permit applicant and permit writer must tailor the QA/QC procedures and especially the acceptance criteria to meet the specific data quality needs of each individual incinerator.

QA PROJECT PLANS

Trial burns of hazardous waste incinerators are complex activities requiring operation of the incinerator under rigorously controlled conditions in conjunction with environmental sampling and analysis of constituents in diverse matrices. This complexity is reflected in the permit application and trial burn plans (TBP) which must cover facility design, theoretical design of the trial burn, incinerator operating conditions (waste streams, temperature, etc.), complex sampling methods (e.g. VOST, SVOST etc), and finally preparation and analysis of samples ranging from high concentration waste feeds to low concentration stack gas samples. All of the data generated must have a documented, known level of precision and accuracy sufficient to support decisions based upon those data.

The procedures needed to ensure quality data are vital in presenting the technical design of the trial burn and should be discussed in a QAPjP. The QAPjP should assure that precision and accuracy are documented and provide criteria to assess the overall quality of the trial burn. EPA QA policy stipulates that every monitoring and measurement project must have a written and approved QAPjP (EPA QAMS-005/80). This document should present, in specific terms, policies, organization, overall objectives, functional activities and tailored QA/QC activities designed to achieve the data quality goals of the particular project or continuing operation. The QAPjP must be prepared by the organization responsible for the project work and approved by the appropriate federal, regional, or state agency.

The QAPjP and TBP should be considered companion documents and should be reviewed at the same time. They may be presented as a single document if that is the applicant's preference. Generally, the TBP covers topics related to the experimental design of the trial burn (e.g. incinerator type, waste feeds, test schedules), sampling design and methods plus analytical methods. The QAPjP covers all the QA/QC procedures necessary to fulfill the objectives of the trial burn. In

many areas there will be overlap between the TBP and QAPjP, or areas will be repeated in both documents; however, the TBP is considered the primary document, and the QAPjP should summarize or specifically cite subjects already considered in the TBP.

The general format and required topics in a QAPjP are outlined by the EPA in Interim Guidelines for Preparing Quality Assurance Project Plans (QAMS-005/80). There are 16 elements that "must be considered and addressed in each QAPjP. If a particular element is not relevant to the project under consideration, a brief explanation of why the element is not relevant must be included.

The permit writer should not accept a QAPjP which does not cover all the elements in the QAMS guidance. Most researchers take the 16 elements and make them into separate sections of the QAPjP. However there is no standard format for a QA plan. To aid in the review of QAPjPs, ensure comparable data quality for permits written by different agencies or personnel, and ensure that the QAPjP is complete, the handbook presents a recommended outline for a QAPjP which is given in Table 2. The only modifications to the 16 EPA elements is the addition of staff qualifications to the fourth section and a combination of audits, corrective action and QA reporting into a single section. The handbook offers a brief discussion of what each section of the QAPjP should address.

Table 2. Recommended Outline for a Trial Burn Quality Assurance Project Plan (QAPjP)

Section 1.0	Title Page (with approval signatures)
Section 2.0	Table of Contents
Section 3.0	Project Description
Section 4.0	Organization of Personnel, Responsibilities, and Qualifications
Section 5.0	Quality Assurance and Quality Control Objectives
Section 6.0	Sampling and Monitoring Procedures
Section 7.0	Sample Handling, Traceability, and Holding Times
Section 8.0	Specific Calibration Procedures and Frequency
Section 9.0	Analytical Procedures
Section 10.0	Specific Internal Quality Control Checks
Section 11.0	Data Reduction, Data Validation, and Data Reporting
Section 12.0	Routine Maintenance Procedures and Schedules
Section 13.0	Assessment Procedures for Accuracy, Precision, and Completeness
Section 14.0	Audit Procedures, Corrective Action, and QA Reporting

GENERAL QA/QC PRINCIPLES FOR SAMPLING

The handbook covers the most common stack sampling methods; EPA methods M1 (location), M2 (velocity), M3 and M3A (gas analysis for carbon dioxide, oxygen and excess air), M4 and M5 (moisture and particulates), 0030 (Volatile Organic Sampling

Train - VOST), 0010 (Semivolatile Organic Sampling Train - SVOST), and the draft EPA methods for hydrogen chloride and metals. Most of these methods have specific procedures for assuring precise and accurate measurements.

The handbook guidance for sampling is based upon three primary QA/QC concepts. First, and most important, is that the standard methods must be followed in detail. Any and all modifications to the standard methods must be explained in the TBP or QAPjP. The TBP must delineate all choices of method options (e.g. sampling probe type). The use of a standardized method assures the data users that the stack gas samples are representative and comparable to other emission measurements. For trial burns where situations are so unique that standard methods do not apply, the sampling method should be validated before use. This is particularly important when the VOST and SVOST methods are used for analytes for which the methods have not been evaluated.

The QA/QC aspects of sampling waste, ash, fuel, and air pollution control device (APCD) effluent are much more subjective than those of stack sampling. Stack sampling enjoys the luxury of established procedures with relatively long histories of satisfactory performance. The wide diversity of waste feeds, POHCs, incinerators, APCD and trial burn experimental design precludes the establishment of firm sampling procedures applicable in all situations. To address this difficulty, the handbook states that the media to be sampled must be described in terms of physical characteristics, method of generation, any time related phenomena and any potential change in the media brought about by the act of sampling. This description must be of sufficient detail to provide justification that the sampling method of choice will provide a representative sample. Then general sampling method must be translated into specific procedures for sampling each media. Generic procedures (e.g. composite of 15 minute grabs) is not sufficient. A specific procedure should be written detailing the equipment, the frequency of sampling, the actual operations of sampling and the data to be recorded.

The second QA/QC concept regarding sampling is the calibration of sampling equipment according to the methods. The handbook discusses the required methods of calibration and also provides recommended calibration procedures for method 0030 (VOST) which does not have specific required procedures for calibration. Calibration of sampling equipment is essential in assuring that the methods are properly utilized and that samples are representative. Calibration also assures that the data used in the final calculations for corrected stack gas emissions is accurate and precise.

The third QA/QC concept is submission of complete field records and calibration records with the trial burn results. These records are needed to assure the data users that all stack samples and stack emission measurements are valid. If these records

indicate that sampling was conducted according to the methodology and that all method requirements were met, then the samples and measurements will be considered valid and usable.

The handbook contains specific guidance in each of these three areas for every method. Common quality problems associated with the methods are discussed. In general, most suggestions for QC and calibration criteria are taken from the standardized methods.

GENERAL QA/QC PRINCIPLES FOR ANALYSIS

This area is the largest in the handbook and takes up about half of the discussions. As stated before, the handbook gives specific QA/QC procedures to control and/or determine the precision and accuracy of virtually all measurements conducted for a trial burn. However, these specific procedures are all founded on similar basic principles and share similar QC techniques.

Objectives of the Analysis - Choice of a Methodology

Knowing the objectives of a specific measurement is a basic concept but one which cannot be overlooked in trial burns. Three of the most common determinations in a trial burn are VOST, SVOST and multiple metals in stack gas. VOST and SVOST can often have 3 to 5 primary analytes with up to 30 to 50 secondary analytes, while metals usually has 5 to 10 analytes. These multiple analytes can be present at concentrations varying several orders of magnitude. Due to the regulatory objectives of a trial burn, some analytes and concentration ranges are more critical than others. Which measurement are critical depends upon the overall objectives of the trial burn.

There are a factors about a trial burn which aid the researcher. Since the incinerator is being controlled to meet specific regulatory related objectives, the number of analytes is known in advance, the physical properties of the samples are known and a fairly good estimate can be made of the analyte concentration in each sample matrix. The sampling and analysis methods of VOST, SVOST and multiple metals are then tailored to optimize results for specific analytes and specific concentration ranges. However, without a clear idea of the objectives of the data user, there is a real possibility of generating data of insufficient quality for permitting decisions.

The permit applicant must approach each measurement in a trial burn with a clear grasp of the following:

- What will the final data be used for? What regulatory decisions or permit operating conditions depend upon these measurements?
- What are the analytes of interest? Which analytes are more critical than

others?
- What is the expected concentration range of the analytes in the samples?
- What sampling and analysis technique will allow quantitation of those analytes at the desired concentrations? How does sample concentration relate to final concentration after sample preparation? Is this final concentration within the reliable calibration range of the analysis technique? Are there severe sample matrix effects which will preclude successful analysis?

These issues must be clearly discussed for all major trial burn measurements either in the TBP or QAPjP.

Demonstration of the Capability of the Measurement Technique and Firm Conducting the Trial Burn

The VOST, SVOST and multiple metals methods are complex procedures and require the choice of various options to optimize the method for the analytes and concentrations of interest. For example, in SVOST the extraction solvent can be chosen to optimize analyte recovery and in multiple metals, the digestion procedures have options that can be chosen to provide lower detection limits. Sometimes the analytes of interest have not been validated for the specific methods and the general method has to be modified to meet a special analysis technique (e.g. HPLC) or concentration range (e.g. selected ion monitoring for GC/MS).

These procedures are complex requiring integration of sampling and analysis activities and are generally not routine methods. The firm conducting the trial burn must have a relatively high degree of capability in order to successfully undertake the project. Discovering that the methodology does not work or that the firm employed to do the trial burn is not capable after the trial burn has been completed is extremely wasteful. Both the permit applicant and the regulatory agency invest significant amounts of time and money into each permitting process. Thus the handbook takes the position that all trial burn plans should demonstrate the capabilities of both the chosen measurement technique and the firm conducting the work. This can be done in three general ways:

- The applicant can present QC data from past trial burns indicating that the methodology is acceptable. This could be a simple as surrogate recovery data from previous SVOST analysis of samples for the same or similar analytes.
- The applicant can generate QC results in the laboratory to prove that the methodology will be acceptable. This could be done through the sampling and analysis of a VOST audit cylinder. It could be done by spiking the components of a SVOST train in the laboratory and extracting and analyzing the components to prove acceptable recovery.

- In cases where unusual problems are expected or the sampling/analysis methods are novel, a preliminary "mini" trial burn conducted at the facility prior to the actual trial burn would provide the needed information. This is particularly important if the stack gas matrix could present serious interference problems.

The purpose of the initial demonstration is to assure the regulatory agency that the analytical method is capable of providing usable data. Researchers must exercise caution when reviewing the development of alternative analytical methods or sampling approaches. The accuracy of a POHC determination is highly dependent on adequate method development. Analytical method performance cannot be assumed from theoretical postulates, but must be demonstrated in advance using actual data obtained by the firm conducting the trial burn.

General QA/QC Principles for All Analysis Techniques

There are specific topics discussed in the handbook for each type of analysis and can be grouped into the categories of calibration, overall accuracy, overall precision, and absence of contamination. The general principles followed by the handbook for each of these areas are discussed below:

Calibration

For most analytical methods, initial calibration is done by demonstrating the behavior of the measurement system at different levels and determining the quantitation constants used to convert instrument response to final results. This is done before sample analysis usually by comparing the measurement system's response to reference standards at different concentrations levels. Demonstration of the "correctness" of the mathematical system used to convert instrument response into results should be judged by quantifiable acceptance criteria for initial calibration such as linear correlation coefficients, standard deviation of response factors or the demonstrated relative error of reference standards.

Initial calibration should be verified by the analysis of an independent standard (sometimes called a check standard or QC standard). This standard is analyzed following the initial calibration and is not prepared from the same standard solutions used in initial calibration. Preferably this standard is purchased at a certified concentration or prepared independently by QA personnel. The verification is demonstrated by comparing the standard concentration determined instrumentally to the certified concentration. For initial calibration to be valid, the check standard concentration must meet predetermined criteria for accuracy.

The measurement system's stability must demonstrated by the routine analysis of the

same standard material and blanks used in initial calibration. The stability of the system should be judged by criteria associated with the routine check. Each sample analysis should be bracketed by at two successful analyses of a calibration standard.

Overall Accuracy

The accuracy of the complete sample preparation and analysis method needs to be determined by one of three methods: (a) surrogate compounds added to every sample, (b) fortifying a sample split with the analytes of interest or (c) analysis of control samples of known composition. For the first two cases accuracy is measured by the recovery of the surrogate compounds or the analytes of interest. For the last case accuracy is measured by comparing the observed results to the reference values of the control samples. In all cases, accuracy must meet predetermined acceptance limits for associated sample data to be acceptable. The guiding principle is that the samples used in accuracy determinations should be subjected to all the preparation and analysis steps plus match the matrix of the trial burn samples as close as possible.

For most organic analyses, the addition of surrogates to the samples provides the most efficient method of measuring the overall accuracy of the measurement system. For analyses employing mass spectrometry, the isotopically labeled analogs of the target analytes are usually employed, while other analysis techniques use compound of similar structure to the target analytes. The surrogate is added at the beginning of sample preparation and the amount found in the sample is compared to the amount added and accuracy is expressed as recovery.

Surrogates are strongly recommended for GC/MS methods and particularly for VOST and SVOST, organic analyses where samples cannot be split for accuracy determinations by fortification. Since surrogates provide an accuracy measurement for every sample, they are one of the best methods for determining accuracy. The handbook elaborates on the use of surrogates required in the standard EPA methods and provides guidance on surrogate spiking levels.

For some kinds samples, surrogates are not appropriate (e.g. metals or ash analyses) are not readily available (e.g. unusual target analytes) or might not be possible due to sample matrix interferences. Where possible the sample is split, with one portion being spiked or fortified with the target analytes of interest and the other portion is analyzed without fortification. The amount of analyte found in the spiked sample is adjusted for the amount native to the sample and compared to the amount spiked for a determination of accuracy expressed as recovery.

Analysis of waste feed, ash, APCD samples for organic compounds and metals are particularly amenable to spiking. Usually sufficient sample is collected to allow multiple split of the samples. At least one spike samples is recommended for each

applicable sample matrix. However, unlike surrogates which provide an accuracy determination for every sample, spikes only provide accuracy results for a specific sample matrix. Guidance is provided in the handbook on the use of spikes for particular determinations and the choice of spiking levels.

In cases where both spikes and surrogates are not possible (e.g. metals determination in stack gas), reference samples are suggested. Reference samples are samples of known composition which will give a gross indication of overall accuracy. Accuracy is measured by comparison of the determined amount to the theoretical amount. Reference samples are carried through the entire sample preparation and analysis procedures; however since they are not actual trial burn samples, they usually do not faithfully mimic the sample matrix and as such are usually represent a "best case" for accuracy. For some analysis techniques this is the only option for an accuracy determination. The handbook provides guidance on reference samples and when they are appropriate.

Overall Precision

Precision determinations follow the same design as those for accuracy. For samples which are spiked with surrogates, the surrogate recovery for multiple samples is used to measure precision. For samples which can be split and spiked, one sample is split three ways, one split is spiked for an accuracy determination and the other two are prepared and analyzed as regular samples. The results of the two splits are used to determine overall precision. For analysis methods which employ reference samples, multiple reference samples are prepared at the same concentrations and the results are used to determine overall precision.

Absence of Contamination

The absence or extent of contamination of field samples and measurement system is verified by the analysis of blanks. The handbook gives specific guidance on the use of field blanks, trip blanks, method blanks and calibration blanks for every analytical measurement. In general, the handbook does not recommend routinely correcting sample data for blank results.

AUDITS AND ASSESSMENT OF TRIAL BURN RESULTS

The position is taken in the handbook that proper planning and implementation of QA/QC procedures for a trial burn will result in a data set of known and demonstratable quality. All measurement systems will have an agreed upon level of precision and accuracy as well as QC procedures to indicate achievement of this level. Most QA/QC procedures (e.g. calibration, accuracy determinations, etc.) will have a measurable level of quality. This level of quality must be within limits defined by the

methodology and/or TBP/QAPjP. If the QA/QC procedures are within the applicable criteria, associated sample results should be acceptable. When QA/QC data does not meet criteria, the problems must be investigated and sample data will not be acceptable without technical justification provided by the permit applicant.

The handbook recommends which QA/QC should be reported for a trial burn. The handbook also recommends that the permit applicant have their QA personnel conduct an audit of data quality on the trial burn results. This should include inspecting field records, raw analysis data, and project records as well as assessing overall data quality based on reported QC data. The QA personnel should inspect all the data for at least one run and ensure traceability from field records through analysis records to final results. In this audit, the performance of the experimental work must be compared with the TBP and QAPjP for compliance. Selected data should be independently recalculated and verified by the auditor. In addition to the audit, all QC data should be examined and compared to the criteria for data acceptance given in the QAPjP. All data which do not meet the QC criteria must be discussed in the trial burn report in terms of acceptance of sample results, given the failure to meet criteria. A brief summary of the audit results and data quality assessment should be prepared by the auditor and included as an appendix to the report.

The purpose of the audit and quality assessment is to provide an independent review of trial burn results and supporting documentation before submittal to the regulatory agency. This internal audit should ensure that data are usable, which will save time during permit application review. Data quality problems and possible incomplete or missing sections of the trial burn report should be addressed before the report is submitted. The EPA requires a similar review and narrative summary in other programs for acceptance of experimental results. A complete report with an honest and open assessment of data quality, should benefit all parties involved in the permitting process.

SUMMARY

In summary, the handbook should provide valuable practical guidance for all people involved in hazardous waste incineration. The authors hope that the document will mature and be revised as new regulations, new technologies and new ideas come about in the future. If trial burns and routine monitoring are designed following the guidance on QAPjP development and using the QA/QC indicated in the handbook, the level of data quality will be documented, and acceptance limits for sample data will be defined. This should make the whole process of reviewing and assessing trial burn results and permit compliance easy, effective and standardized.

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PRACTICAL QUANTITATION LIMITS

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ABSTRACT

A statistical method for computing practical quantitation limits (PQL) is developed. The PQL is operationally defined following Currie (1968) as the concentration at which the instrument response signal is ten times it's standard deviation (*i.e.*, 10% rsd). The response signal is defined as the ratio of analyte to internal standard peak areas. 95% confidence limits for the PQL are also derived. The PQL is estimated directly from calibration data, and uncertainty in the parameters of the calibration function are incorporated. Following Clayton *et al.*, (1987), the non-constant variance problem is dealt with using variance stabilizing transformations. The method is illustrated using 199 calibration samples for 10 volatile organic priority pollutant compounds. The results of these analyses suggest that USEPA estimates of PQL's for these compounds correspond to a 20% relative standard deviation and not the traditional 10% rsd definition.

1 Introduction

In the course of developing detection monitoring programs for hazardous waste disposal facilities (Gibbons 1987a, Gibbons 1987b, Davis and McNichols 1987, Gibbons, 1989), it became necessary to determine limits of quantitation for various analytical procedures when dealing with trace-level measurements. For example, volatile organic priority pollutant compounds are rarely detected in background or upgradient ground-water quality samples and when they are detected, their concentrations are often so low that they may provide limited quantitative information. While USEPA (1985) has identified "Practical Quantitation Limits" (PQL) for some compounds these limits are often based on consensus rather than operational definitions and experimental evidence

and in fact typically take on the two values, 5 and 10 $\mu g/l$. Indeed, in the new USEPA statistical regulation (USEPA, 1988), we are told that,

> The Appendix IX rule (52 FR 25942, July 9, 1987) listed practical quantitation limits (PQL's) that were established from "test methods for evaluating solid waste" (SW-846). ... The PQL's listed were EPA's best estimate of the practical sensitivity of the applicable method for RCRA ground-water monitoring purposes. However, some of the PQL's may be unattainable because they are based on general estimates for the specific substance. Furthermore, due to site specific factors, these limits may not be reached. For these reasons the agency feels that the PQL's listed in Appendix IX are not appropriate for establishing a national baseline value for each constituent for determining whether a release to ground-water has occurred. Instead the PQL's are viewed as target levels that chemical laboratories should try to achieve in their analysis of ground-water. In the event that a laboratory cannot achieve the suggested PQL, the owner or operator may submit a justification stating the reasons why these values cannot be achieved (*e.g.*, specific instrument limitations). After reviewing this justification, the Regional Administrator may choose to establish facility specific PQL's based on the technical limitations of the contracting laboratory.

The purpose of this paper is to develop an operational definition for the PQL and a corresponding statistical methodology for obtaining facility-specific PQL estimates and regions of confidence.

2 Practical Quantitation Limits

Currie (1968) defined the determination limit (L_Q) as the concentration "at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate". This definition is similar to that used by Adams, Passmore and Campbell (1966) who defined a "minimum working concentration" as that for which relative standard deviation (rsd) was 10%. The determination limit has since been described by several names, most notably "Practical Quantitation Level" (USEPA, 1985) and "Limit of Quantitation" (USEPA, 1987). USEPA defines the PQL as "the lowest level achievable by good laboratories within specified limits during routine laboratory operating conditions." This rather vague definition has been operationally defined by USEPA as 5 or 10 times the method detection limit, or the concentration at which 75% of the

laboratories in an inter-laboratory study report concentrations ± 20% of the true value, or the concentration at which 75% of the laboratories report concentrations within ± 40% of the true value (USEPA, 1987). The first operational definition is arbitrary, and depends completely on the validity of the corresponding method detection limit, about which serious questions have been raised (see Clayton *et al.*, , 1987). The second and third operational definitions are somewhat better, however, the inter-laboratory studies are often done at a single concentration (*e.g.*, maximum contaminant level - MCL) in experienced government laboratories that "knew they were being tested with standard samples in distilled water without matrix interferences." USEPA (1985) points out that,

> Actual day-to-day operations in a wide variety of laboratories using real samples in natural water would be expected to produce poorer results, *i.e.*, wider performance ranges especially at the lower concentration levels.

(see Koorse, 1989 for an excellent review of the legal implications of these definitions). Furthermore, it is unclear whether all measurements made by a single laboratory must be within ± 20% or if this criterion can be satisfied by just one or two measurements.

3 A Statistical Estimate of the PQL

To determine the PQL of a given compound in a given laboratory using a particular methodology, we must begin by obtaining calibration data for a series of concentrations in the range 0 to 2-5 times the hypothesized PQL. The following hypothetical example illustrates the required data collection.

Figure 1 illustrates the least squares calibration line for the relationship between actual concentration and instrument response (defined as the peak area ratio of analyte to internal standard). Inspection of Figure 1 reveals that as concentration increases so does variability. One solution to this problem is to obtain a suitable transformation of the observed data, so that variability is constant throughout the calibration function. Clayton *et al.*, (1987) suggest,

$$\text{response} = y = \sqrt{\frac{\text{peak area for compound}}{\text{peak area for internal standard}}}$$

and

$$\text{concentration} = x = \sqrt{x' + 0.1} - \sqrt{0.1}$$

Actual Concentration ($\mu g/l$)	Peak Area Ratio
2	.2
2	.3
2	.4
2	.1
10	.7
10	.9
10	.5
10	1.1
20	1.2
20	1.5
20	1.8
20	2.1
40	2.3
40	2.8
40	3.7
40	3.2

where x' is the original analytic concentration (*e.g.*, in $\mu g/l$). Figure 2 illustrates the effect of this transformation on the hypothetical dataset. The variability is now relatively constant throughout the range of the calibration study and the calibration function is clearly linear.

As a first step, we will follow Adams, Passmore and Campbell (1966) and Currie (1968), and operationally define the PQL as the concentration at which the relative standard deviation is 10%. Working with the transformed data, we therefore, require the concentration that corresponds to a response signal that satisfies,

$$\hat{y}^* = \frac{\hat{y}}{s(\hat{y})} = 10 \tag{1}$$

that is, the predicted response which is 10 times it's estimated standard deviation. Of course, to obtain the predicted response and corresponding standard deviation, we must also know the slope of the calibration line for which the least-squares estimate is,

$$\hat{b} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{2}$$

and the relationship between predicted response $\hat{y}$ and predicted concentration $\hat{x}$ is,

$$\hat{x} = \bar{x} + \frac{(\hat{y} - \bar{y})}{b} \tag{3}$$

Given these two estimates we can now obtain the standard deviation of $\hat{y}$ as,

$$s(\hat{y}) = s_{y.x}\sqrt{1 + 1/n + (\hat{x} - \bar{x})^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{4}$$

where $s^2_{y.x}$ is the sum of squared deviations from the calibration line; that is,

$$s^2_{y.x} = \frac{\sum_{i=1}^{n}(y_i - \bar{y})}{n - 2} \tag{5}$$

and

$$\hat{y}_i = \bar{y} + b(x_i - \bar{x}) \tag{6}$$

The PQL in the transformed metric is therefore,

$$\text{PQL}' = \bar{x} + (\hat{y}^* - \bar{y})/b \tag{7}$$

The 95% confidence limit for the PQL in the transformed metric is

$$\text{PQL}' \pm (t_{[n-2,.05]} s_{y.x}/b)\sqrt{1 + 1/n + (\text{PQL}' - \bar{x})^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{8}$$

In order to express the PQL′ and corresponding confidence limit in the original metric (*e.g.*, $\mu g/l$), we compute

$$\text{PQL} = (\text{PQL}')^2 + 0.632456(\text{PQL}') \tag{9}$$

This same equation can be used to untransform the upper and lower confidence limits, substituting LCL′ and UCL′ from equation (8) for PQL′ in equation (9).

There is still one missing ingredient. In order to compute the PQL′ value in equation (7), we require an estimate of $\hat{y}^*$ from equation (1), that is, the predicted transformed response signal for which the relative standard deviation is 10%. One solution to this problem is to compute $\hat{y}$ and $s(\hat{y})$ for various values of $\hat{x}$, using equations 4, 5, and 6, until the ratio $\hat{y}/s(\hat{y})$ equals 10. To obtain a more direct solution, we can solve equation (1) for $\hat{y}^*$ and obtain:

$$\hat{y}^* = \frac{10 s_{y.x} b \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2[\bar{y}^2 + (1 + 1/n)\sum_{i=1}^{n}(x_i - \bar{x})^2 b^2 - (1 + 1/n)100 s_{y.x}^2]} - 100 s_{y.x}^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2 b^2 - 100 s_{y.x}^2} \quad (10)$$

(see the Appendix for the derivation of this result). Substitution of $\hat{y}^*$ into equations 7, 8, and 9 will yield the PQL and its confidence interval in both transformed and original metrics.

Of course, the derivation described here applies to any required level of precision. For example, if we had defined the PQL as that concentration for which the rsd was 20%, then the values 10 and 100 in equation (1) and (10) would be replaced by 5 and 25 respectively.

Returning to our example data set, and applying the transformations to both peak area ratios and concentrations, the summary statistics are $b = .26$, $s_{y.x} = .16$, $\sum_{i=1}^{n}(x_i - \bar{x})^2 = 51.12$, $n = 16$, $\bar{x} = 3.55$, $\bar{y} = 1.09$, and $t_{14,.05} = 2.145$. The transformed response signal that is 10 times it's standard deviation is then computed as:

$$\hat{y}^* = \frac{10(.16).26\sqrt{51.12[1.09^2 + (1 + 1/16)51.12(.26^2) - (1 + 1/16)100(.16^2)]} - 100(.16^2)1.09}{51.12(.26^2) - 100(.16^2)} = 1.74$$

The PQL in the transformed metric is,

$$\text{PQL}' = 3.55 + (1.74 - 1.09)/.26 = 6.05$$

and in the original metric,

$$\text{PQL} = 6.05^2 + 0.632456(6.05) = 40.43 \mu g/l.$$

The 95% confidence interval in the transformed metric is,

$$6.05 \pm (2.145(.16)/.26)\sqrt{1 + 1/16 + (6.05 - 3.55)^2/51.12}$$

which has the roots 4.61 and 7.49, and in the original metric,

$$\text{LCL} = 4.61^2 + 0.632456(4.61) = 24.17 \mu g/l$$

and

$$\text{UCL} = 7.49^2 + 0.632456(7.49) = 60.84 \mu g/l$$

4 Illustration

In order to examine the PQL estimator developed here, calibration data were examined for 10 volatile organic priority pollutant compounds, obtained from a major environmental monitoring laboratory. Multiple analysts and instruments were used over a period of several weeks. The data consisted of 199 standard analyses, at concentrations of 2, 4, 10, 20, 30, and 40 $\mu g/l$. All 10 volatile organic compounds were included in each sample at the same concentration. The 10 compounds were.

1. methylene chloride
2. chloroform
3. trichloroethylene
4. tetrachloroethylene
5. trans 1,2-dichloroethene
6. benzene
7. chlorobenzene
8. carbon tetrachloride
9. 1,1-dichloroethane
10. chloromethane

4.1 Standard Preparation

Standards were prepared from commercially available stock solutions in laboratory reagent water. To 25 ml of each standard solution, internal standards were added at a concentration of 10 $\mu g/l$. The internal standards used were bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5.

4.2 Analysis

Standards were analyzed by capillary gas chromatography using an HP-5890 GC with Mass Selective detector and a TEKMAR purge and trap sample concentrator with autosampler in accordance with EPA December 1987 draft method 8260. Column conditions and instrument operating conditions were optimized for each of the four systems used. Data were collected on HP-1000 computers, and AQUARIUS software was used for qualitative and quantitative analyses.

5 Results

Estimated PQLs and 95% confidence limits for the 10 compounds are displayed in Table 1. Table 1 contains PQL estimates for definitions based on 10% and 20% relative standard deviations. Inspection of Table 1 reveals that there is considerable variability in PQL's for the 10 compounds. This, of course, is directly related to the fact that measurements for some compounds are highly reproducible whereas others are not. For example, Figure 3 displays the transformed calibration data for chlorobenzene for which the PQL is 5.24 $\mu g/l$ and Figure 4 displays the transformed calibration data for chloromethane for which the PQL is 114.04 $\mu g/l$.

The transformation appears to be reasonably effective for chlorobenzene (See Figure 3), particularly at concentrations above 2 $\mu g/l$, and somewhat less effective for chloromethane (see Figure 4), although it performs reasonably well for concentrations above 4 $\mu g/l$. In the context of estimating PQL's, this is not a problem, since we are interested in variability at concentration levels above the method detection limit. As such, we desire an estimator for which the rsd is 10% at the PQL and less than or equal to 10% for concentrations that exceed the PQL. It is, of course, possible to imagine a spiking concentration so close to zero, such that the instrument response is relatively constant. At this point the standard deviation is zero as is the %rsd. At a slightly higher concentration, however, the %rsd could be 50% or more. This is an improper solution, and one that is clearly avoided by the method described here. For computing method detection limits (MDL's), in contrast to PQL's, the inability of the transformation to bring about constant variance at very low concentrations is a problem. An analogous procedure for computing MDL's has been developed by Gibbons *et al.*, (1989), and there the non-constant variance problem is solved using a weighted least-squares procedure.

Comparison of the results for the two PQL definitions (*i.e.*, 10% rsd and 20% rsd) also reveal striking differences. (see Table 1). For the 20% definition the PQL's are in the range of 1 $\mu g/l$ to 25 $\mu g/l$, and most of the PQL's and/or upper confidence limits correspond closely to those suggested by USEPA (1987). For the traditional 10% definition, however, only chlorobenzene and trichlorethylene even approach the levels suggested by USEPA.

6 Discussion

The PQL estimator described here has several advantages over existing procedures. First, it has a clear operational definition based on the %rsd, that has been proposed in the literature for the last 25 years. Second it can be determined empirically using data from a single laboratory. Third, the uncertainty

in the calibration function is incorporated in both the statistical estimate of the PQL and corresponding confidence limits. Fourth, the operational definition may be modified to reflect the degree of required, or reasonably achievable precision, with only the most minor modifications to the estimation equation (*e.g.*, 10% rsd versus 20% rsd). Fifth, variability throughout the working range is considered instead of simply relying on an estimate of variability obtained from a single fixed point on the calibration line.

Using this PQL estimator, it is now possible to provide laboratory specific PQL's, and in the context of ground-water detection monitoring, for example, the regional administrator may now "establish facility-specific PQL's based on the technical limitations of the contracting laboratory", rather than relying on a national baseline that reflects ideal target levels that may not be achievable in routine laboratory practice.

References

[1] Adams, P. B., Passmore, W. O., & Campbell, D. E. (1966). Symposium on trace characterization - chemical and physical. *National Bureau of Standards,* (October, 1966).

[2] Clayton, C. A., Hines, J. W. and Elkins, P. D. (1987). Detection limits with specified assurance probabilities. *Anal. Chem.* **59,** 2506-2514.

[3] Currie, L. A. (1968). Limits for qualitative decision and quantitative determination. *Anal. Chem. 40,* 586-593.

[4] Davis, C. B. & McNichols, R. J. (1987). One-sided intervals for at least p of m observations from a normal population on each of r future occasions. *Technometrics,* **29,** 359-370.

[5] Gibbons, R. D. (1987a). Statistical prediction intervals for the evaluation of ground-water quality. *Ground Water,* **25,** 455-465.

[6] Gibbons, R. D. (1987b). Statistical models for the analysis of volatile organic compounds in waste disposal facilities. *Ground Water,* **25,** 572-580.

[7] Gibbons, R. D. (1989a). A general statistical procedure for Ground-Water Detection Monitoring at waste disposal facilities. *Ground Water,* **in press.**

[8] Gibbons, R. D., Jarke, F. H., & Stoub, K. P. (1989b). Method detection Limits. Proceedings of *Fifth Annual USEPA Waste Testing and Quality Assurance Symposium,* Vol. **2,** 292-319.

[9] Koorse, S. J. (1989). False positives, detection limits, and other laboratory imperfections: The regulatory implications. *Environmental Law Reporter,* **19,** 10211-10222.

[10] USEPA (1985). *Federal Register,* **50** 46906, (Nov. 13, 1985).

[11] USEPA (1987). *Federal Register,* **52** 25699, (July 8, 1987).

[12] USEPA (1988). 40CFR Part 264: Statistical methods for evaluating ground-water monitoring from hazardous waste facilities; final rule. *Federal Register,* **53, 196,** 39720-39731.

Table 1

Practical Quantitation Limits
and 95% Confidence Limits

Analyte	10% rsd			20% rsd		
	PQL	LCL	UCL	PQL	LCL	UCL
Chloromethane	114.04	73.36	163.63	25.08	9.07	49.02
Methylene Chloride	16.28	10.31	25.59	3.84	1.24	7.80
Trans-1,2 DCE	19.39	12.59	27.64	5.04	1.89	9.67
1,1 DCA	21.58	13.96	30.84	5.52	2.03	10.67
Chloroform	13.72	8.87	19.60	3.52	1.28	6.82
Carbon Tetrachloride	36.03	23.24	51.61	8.98	3.27	17.46
Benzene	12.19	7.88	17.42	3.12	1.13	6.06
Trichloroethylene	8.90	5.74	12.75	2.25	0.79	4.41
Tetrachloroethylene	12.44	8.00	17.84	3.13	1.10	6.13
Chlorobenzene	5.24	3.40	7.47	1.35	0.48	2.62

APPENDIX

Derivation of the PQL

We require,

$$\hat{y}/s(\hat{y}) = 10$$

where

$$\hat{y} = \bar{y} + b(\hat{x} - \bar{x})$$

and

$$\hat{x} = \bar{x} + \frac{(\hat{y} - \bar{y})}{b}$$

and

$$\begin{aligned} s(\hat{y}) &= s_{y.x}\sqrt{1 + 1/n + (\hat{x} - \bar{x})^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2} \\ &= s_{y.x}\sqrt{1 + 1/n + (\bar{x} + (\hat{y} - \bar{y})/b) - \bar{x})^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2} \\ &= s_{y.x}\sqrt{1 + 1/n + [(\hat{y} - \bar{y})/b)]^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2} \end{aligned}$$

then

$$\hat{y} = 10 s_{y.x}\sqrt{1 + 1/n + [(\hat{y} - \bar{y})/b)]^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2}$$

To solve for $\hat{y}$, let

$$\hat{y}^2 = 100 s_{y.x}^2 \left[1 + 1/n + [(\hat{y} - \bar{y})/b)]^2 / \sum_{i=1}^{n}(x_i - \bar{x})^2\right]$$

and define

$$s' = 100 s_{y.x}^2$$

$$x' = \sum_{i=1}^{n}(x_i - \bar{x})^2$$

$$n' = 1 + 1/n$$

then

$$x'\hat{y}^2 = s'n'x' + \frac{s'}{b^2}(\hat{y}^2 - 2\hat{y}\bar{y} + \bar{y}^2)$$

$$x'\hat{y}^2 - \frac{s'}{b^2}\hat{y}^2 + \frac{2s'}{b^2}\hat{y}\bar{y} - \frac{s'\bar{y}^2}{b^2} - s'n'x' = 0$$

$$\left(x' - \frac{s'}{b^2}\right)\hat{y}^2 + \left(\frac{2s'\bar{y}}{b^2}\right)\hat{y} - s'\left(\frac{\bar{y}^2}{b^2} + n'x'\right) = 0$$

The solution of this quadratic equation (*i.e.*, the positive root) is therefore,

$$\frac{\frac{-2s'\bar{y}}{b^2} + \sqrt{\frac{2s'\bar{y}}{b^2} + 4s'(x' - \frac{s'}{b^2})(\frac{\bar{y}^2}{b^2} + n'x')}}{2(x' - \frac{s'}{b^2})}$$

After a little algebra, a somewhat more computationally tractable form is,

$$\hat{y} = \frac{10s_{y.x}b\sqrt{x'(\bar{y}^2 + n'x'b^2 - n's')} - s'\bar{y}}{x'b^2 - s'}$$

substituting for s', x', and n' yields equation 10, which is the peak area ratio that is 10 times it's standard deviation.

FIG 1: EXAMPLE DATA SET - LINEAR CALIBRATION

ACTUAL CONCENTRATION VERSUS PEAK AREA RATIO

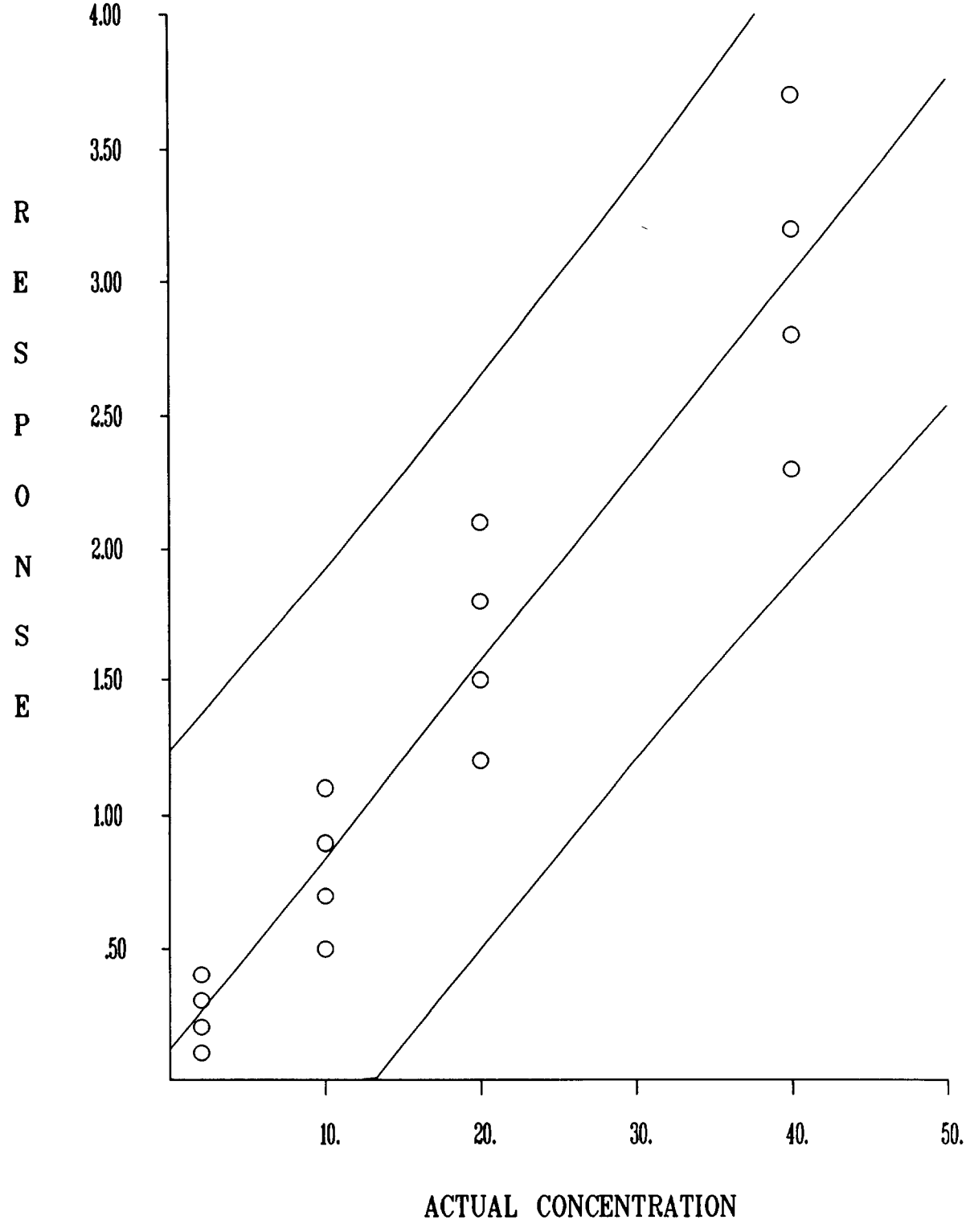


FIG 2: EXAMPLE DATA SET - LINEAR CALIBRATION

TRANSFORMED CONCENTRATION AND PEAK AREA RATIO

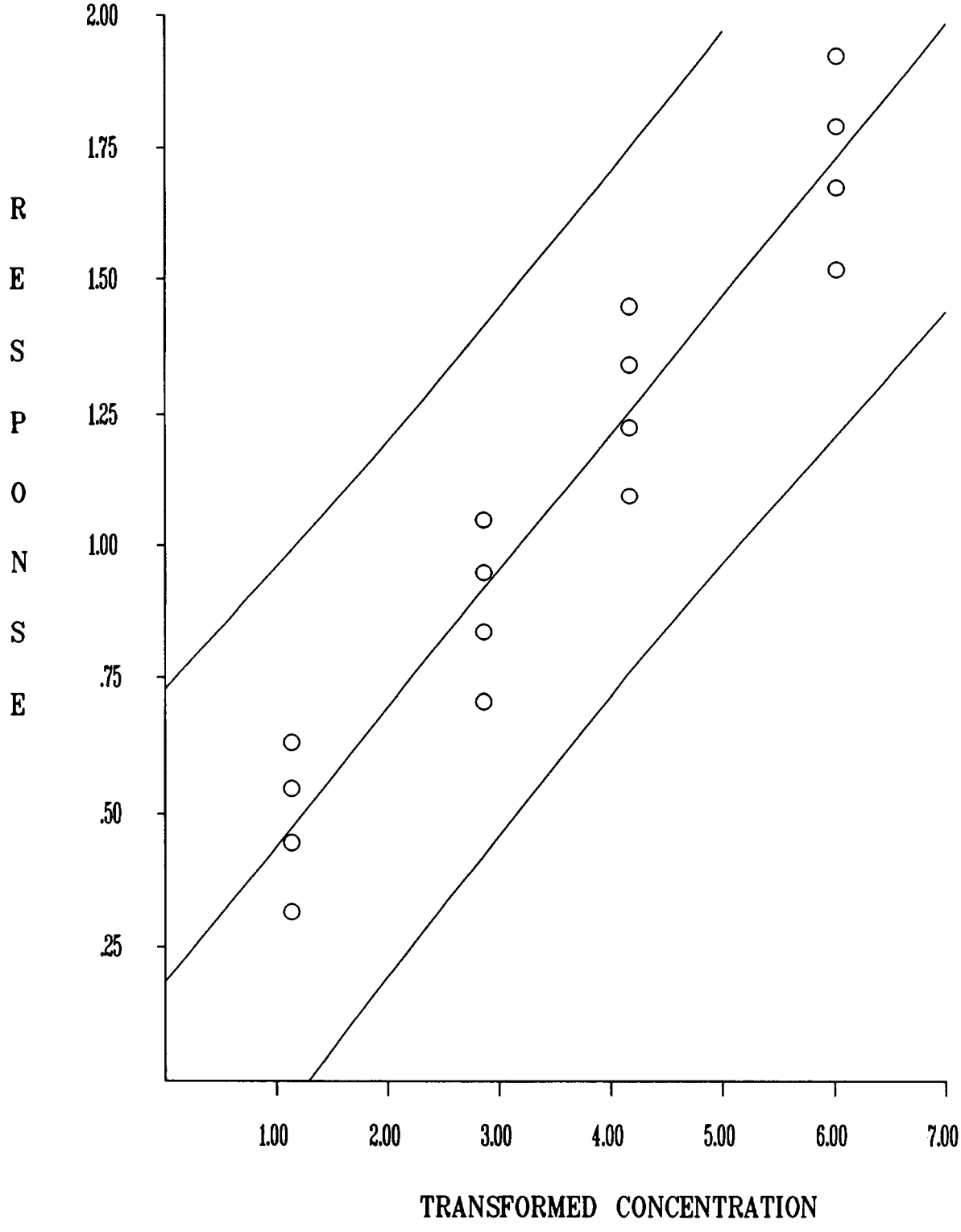


FIG 3: METHOD DETECTION LIMIT - LINEAR CALIBRATION CHLOROBENZENE (PPB) - 1 OUTLIER REMOVED

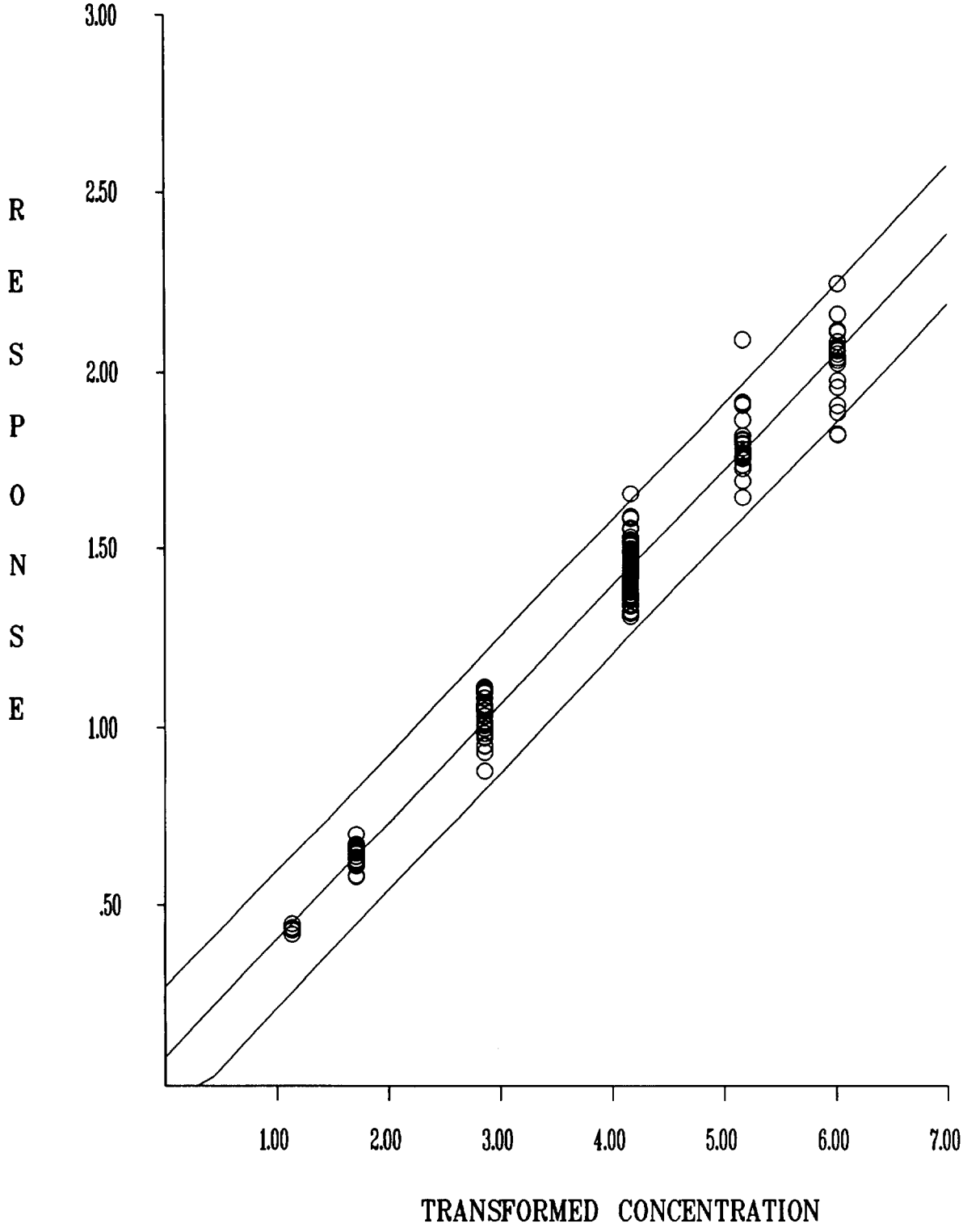
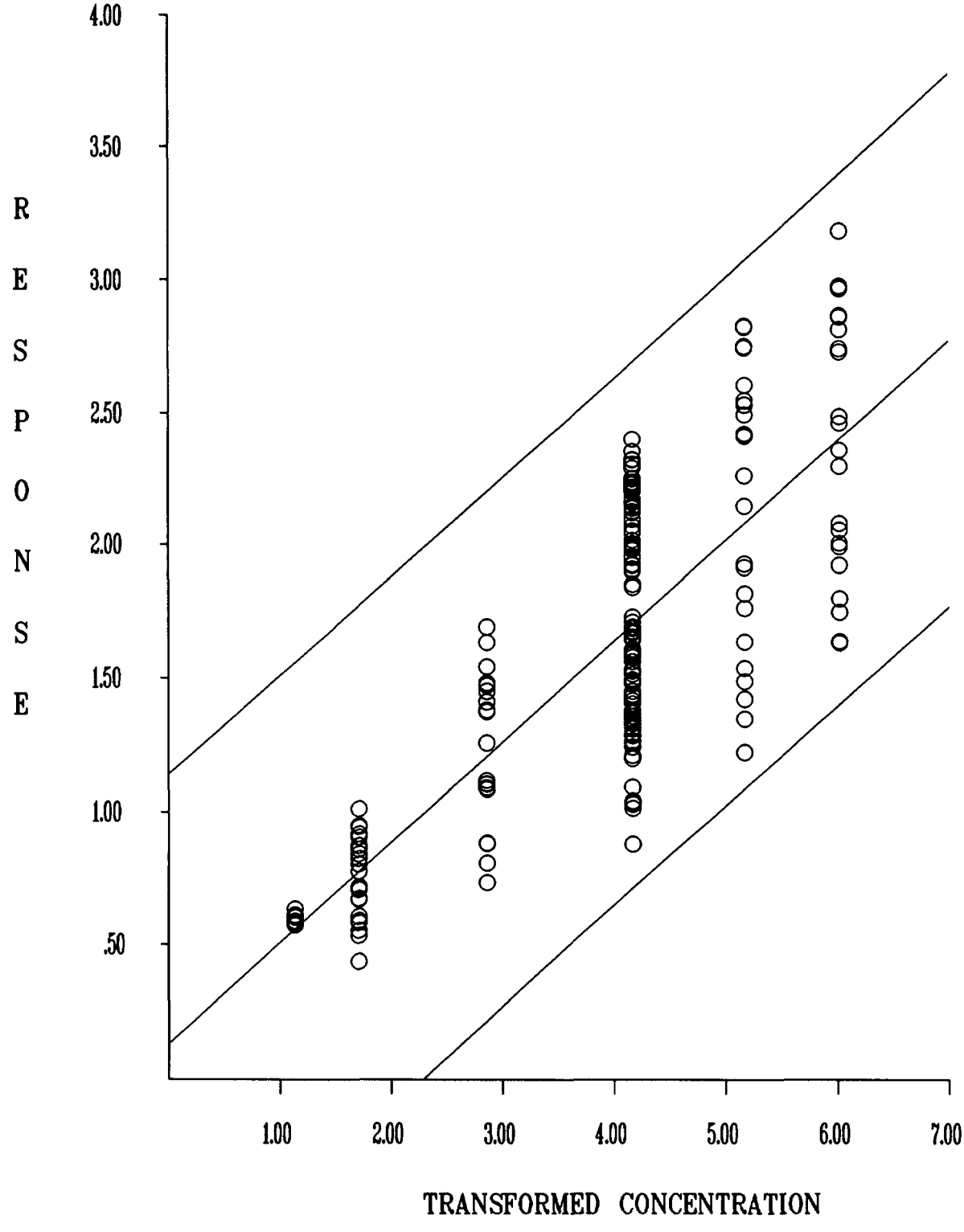


FIG 4: METHOD DETECTION LIMIT - LINEAR CALIBRATION CHLOROMETHANE (PPB) - 1 OUTLIER REMOVED



20 DATA IN STATISTICAL ESTIMATION OF THE METHOD DETECTION LIMIT

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ABSTRACT

The data used as input to a statistic, and the statistic itself, are equally important to the calculation of the method detection limit estimate (MDL). The effect that the data can have on the calculated MDL value should not be discounted or ignored. No matter how powerful a statistical estimator is, if the data that are used as input are not representative of the method, the result will be poor. Since data embodies the magnitude, variability and bias characterisitic of the method itself a first consideration must be how well the data represent routine method conditions. This may be evaluated by utilizing the concept of assignable sources of error. Assignable sources of error are all persons, equipment, materials and procedures that bear an effect on the precision and accuracy of the method. When assignable sources of error are acting on routine samples, but not on the input data to the MDL statistics this may result in the variability and the bias of the method being under-represented in the data, and therefore result in the MDL being underestimated. The opposite is also possible. Evaluating data that have different assignable sources of error acting on them, while holding the statistical approach and other variables as constant as is possible, can be useful in understanding how much effect a particular assignable source of error has on the MDL. Examples of this approach are provided using a method of analysis for volatile organics by purge and trap GC/MS.

INTRODUCTION

The Method Detection Limit (MDL), and statistics used to estimate this characteristic of a method, have undergone much scrutiny in recent years. There is serious concern about the appropriateness of the various statistics for estimating the MDL and about the use of these estimates as reporting or enforcement limits.

While the approach to the null hypothesis, the inclusion of false positive and false negative rates, and the importance of various mathematical assumptions is appropriately debated, it is often not emphasized enough that estimation of an MDL depends not only on the mathematics chosen, but also on the analytical data that are the input to these statistics. The analytical data "characterize" the method, and "encodes" the precision and accuracy of the method that may then be utilized by the statistics.

The MDL, as defined by the EPA, is the minimum concentration of an analyte at which there is 99% confidence that the concentration is different from zero. (1) Additional qualifications that are often added to this definition include specifying conditions of routine operation and acknowledging the effect that sample matrices may have on the MDL.

In evaluating MDL estimates, it should always be remembered that the real MDL is unknown and dynamic. Statistics, and input data to these statistics, are used to periodically estimate this unknown moving target. In this light, it becomes clear that using alternative approaches to calculating the MDL will not change method performance. It does not decrease effects of method procedures on the routine

sample data and MDL. And, it does not change the true confidence of the method at the low-end of the dynamic range. It will only improve or diminish the quality of the estimate of the real MDL, and will only increase or decrease the false positive and/or the false negative detections that are made. In conclusion, data which most closely reflect the variability and bias experienced by routine sample data where detection decisions apply, will provide the most representative input to the statistics.

Why not use sample data itself as input data? The difficulty encountered is that there is no known value to compare the result data with to quantitate the magnitude, variability and bias. So what are the options? An experiment could be performed where known samples are substituted for unknown samples into routine operation, and the data generated is used as input for the statistics. The known samples could be prepared in reagent water or a particular matrix of interest, and the analyte concentration could be known to the analyst, it could be blind (concentration unknown, experiment known), or it could be double blind (concentration unknown, experiment unknown). Alternatively, standard and/or quality control analyses required by methods during routine analysis could be used. There are advantages and disadvantages to each data type, and there are specific attributes of the different data that, based on the observer's opinion, may be considered to be either an advantage or a disadvantage.

ASSIGNABLE SOURCES OF ERROR

To discuss the role of the data in MDL estimation, it is important to first introduce the concept of assignable sources of error. Each routine matrix sample analyzed by a method will be "exposed" to "errors" that cause imprecision

and inaccuracy, and that result in variability about, and bias from, the "true" value in the sample. By way of example, sample storage, detector noise, and injection technique, may be assignable sources of "error" in a sample's result. Each of these sources of error acts in consert with all the other sources from the method, to produce the total variability and bias in the sample result data. This "error" from the true amount of analyte in samples is not directly quantifiable, because the true value is unknown.

However, even though one cannot directly measure the error associated with routine sample analysis, indirect evaluation can be made by comparing the assignable sources of error acting on sample analysis with the assignable sources acting on the known analyses (experimental samples or routine standard and/or QC samples) where precision and accuracy can be measured. By doing this comparison, a judgment can be made of how representative input data are of routine sample data. If the procedures, equipment and personnel that are assignable sources of error to routine samples are not assignable sources to the input data for the MDL estimate, then that estimate can not reflect the contribution of these sources or error.

SOURCE DATA

The available data for use in statistical analysis are either known data generated routinely as required by the analytical methods, or experimental samples, analyzed as if they were samples. A common example of the experimental approach to data, is used in the 40 CFR Part 136 Appendix B MDL estimator. In this approach, a portion of reagent water, or optionally, a portion of matrix water, is spiked with a known amount of analyte at a concentration near, but above the

expected MDL. Replicates of this single standard are then processed together using a single instrument on a single day. (1)

Utilizing volatile organics as an example, let us compare the assignable sources of error acting during routine sample analysis, with the experimental data used with this statistic. In this type of method, routine samples are removed from the environment and placed in sample vials, often preserved in some way, transported, stored under refrigeration, warmed, decanted, prepared, concentrated, separated, detected, identified, and quantified. Then the data are evaluated, reviewed and reported. Also, in many laboratories, where samples for a single method are processed using multiple instruments and/or multiple analysts, other assignable sources could potentially be identified that affect the method as a whole. Finally there is the assignable source of sample matrix.

Which assignable sources of error acting on routine samples are not acting on the MDL experimental samples for the 40 CFR estimator? Are these unaccounted for sources contributing significantly to variability and bias in routine sample data? If so, is the contributed variability and bias acting at concentrations approximating the actual MDL? And finally would this disparity in accounting for sources of error cause the MDL estimate to significantly underestimate or over-estimate the true MDL of the method?

Using the volatile organic analysis example, generally, the placement of samples into storage vials, the preservation step, and storage are omitted when experimental, known samples are prepared for an MDL study. The known sample that is used for this experiment is generated just prior to the

sample introduction step. This known sample is then processed and quantified using the same procedures that would be utilized for samples, with some qualifications. First, the standard is prepared at a low concentration with all analytes of the method included and analyzed in replicate. Secondly, the analyst is generally aware of this, and of the expected concentration. Also, the analyst generally knows that an MDL evaluation is being done, that low levels of variability equate to a lower MDL, and that a lower MDL is a positive attribute. Qualitative analysis is somewhat altered from routine sample analysis because the analyst knows what analytes should be present, and if any expected analytes were missing, the analyst would know to make additional investigation. Finally, in practice commercial laboratories use laboratory reagent water as the matrix for the MDL experiment, not an environmental sample.

In summary, the data typically generated in this approach to the MDL, encodes the variability and bias associated with the preparation of a single low concentration standard analyzed in replicate as if it were a sample, using a single instrument, calibration, and analyst, on a single day.

ROUTINE ANALYTICAL DATA

An example of an alternative source of input data, is calibration standard data. As demonstrated by Clayton and coworkers in work for the EPA (2), and as utilized by Gibbons (3), these data, routinely produced for other purposes, may utilized as a source of data for MDL estimation. Standards may include initial and continuing calibration standards, and optionally other types, such as external reference standards, QC standards and performance evaluation standards for which the true value is known. Typically, standard data are

accumulated over a period of time and the data may include multiple instruments and multiple analysts.

Looking again at our volatile organic method example, and comparing assignable sources of error between routinely analyzed standards and routine unknown samples, the sources of error associated with sampling, preservation, or sample storage and the source of sample matrix are not being encoded in the standard data. However, since standards are being routinely analyzed, and are not part of a special testing event (as is the case with known experimental samples), routine operations are more closely represented in the procedures that do affect standards, and therefore in the data. This approach allows the inclusion of data variability over time, and variability resulting from multiple analysts and multiple instruments. As an outgrowth of routine generation of data, this approach can allow the MDL estimate to be continually up-dated and tracked in the same manner that laboratories now chart matrix precision and accuracy using a moving "window" of the most recent data to calculate the current acceptance limits.

As a note, the effect of calibration and use of calibrated data as input to the statistics should be considered with respect to assignable sources of error. Calibration can affect the variability and the bias that are encoded. Table 1 illustrates this effect. The data are the lowest level (4 ug/l) of the multi-point calibration curves that were generated for initial calibration of a single GC/MS instrument for chloroform. The column "Concentration" is the value determined for that standard analysis based on the calibration factor that was the outcome of the individual calibrations. Each data point is from a different calibration performed on a different day. The "Relative

Response" column is the "raw" data for the same analyses. It is the ratio of chloroform response to internal standard (pentafluorobenzene) response, both in units of area counts. Multiplying the relative response values in column 2 by the calibration factor for the particular calibration would produce the calibrated concentration in the first column.

Table 1 - Effect of Calibration on Standard Data

Calibrated Concentration (ug/l)	Relative Response (area counts/area counts)
3.58	0.2592
4.16	0.2554
3.94	0.2424
4.07	0.2501
4.10	0.2521
3.81	0.2342
4.27	0.2627
4.09	0.2515
4.13	0.3503
3.80	0.2672
Mean Value 3.995	0.2625
Stand. Deviation 0.2093	0.0323
% Rel. Std. Dev. 5.2%	12.3%

It can be seen that the percent relative standard deviation, which is the ratio of the standard deviation to the mean, is significantly less in the calibrated data than it is in the uncalibrated data. If the calibration procedure (a simple multiplication of the uncalibrated response ratio with a calibration factor) had not affected the variability encoded in the data, the percent relative standard deviation would be the same for both columns in the table. Calibration, itself, can be thought of as an assignable source for error (in this example, a negative source), and this attribute of the data, where present, should always be considered.

There are alternative sources for data, and alternative ways to design experiments, beyond the examples provided here. The two examples utilized are the most common sources used in the environmental laboratory industry. Other sources should not be summarily dismissed. Routine matrix spike data, for example, has the required attribute of both a known and determined value, though the assignable sources that apply are clouded by the necessity to subtract the response of the spiked sample from the response of the unspiked sample. Also, experiments can be designed to incorporate additional assignable sources, by such techniques as making the samples double blind, submitting them to multiple analysts, or randomizing the presence of the analyte and its concentration.

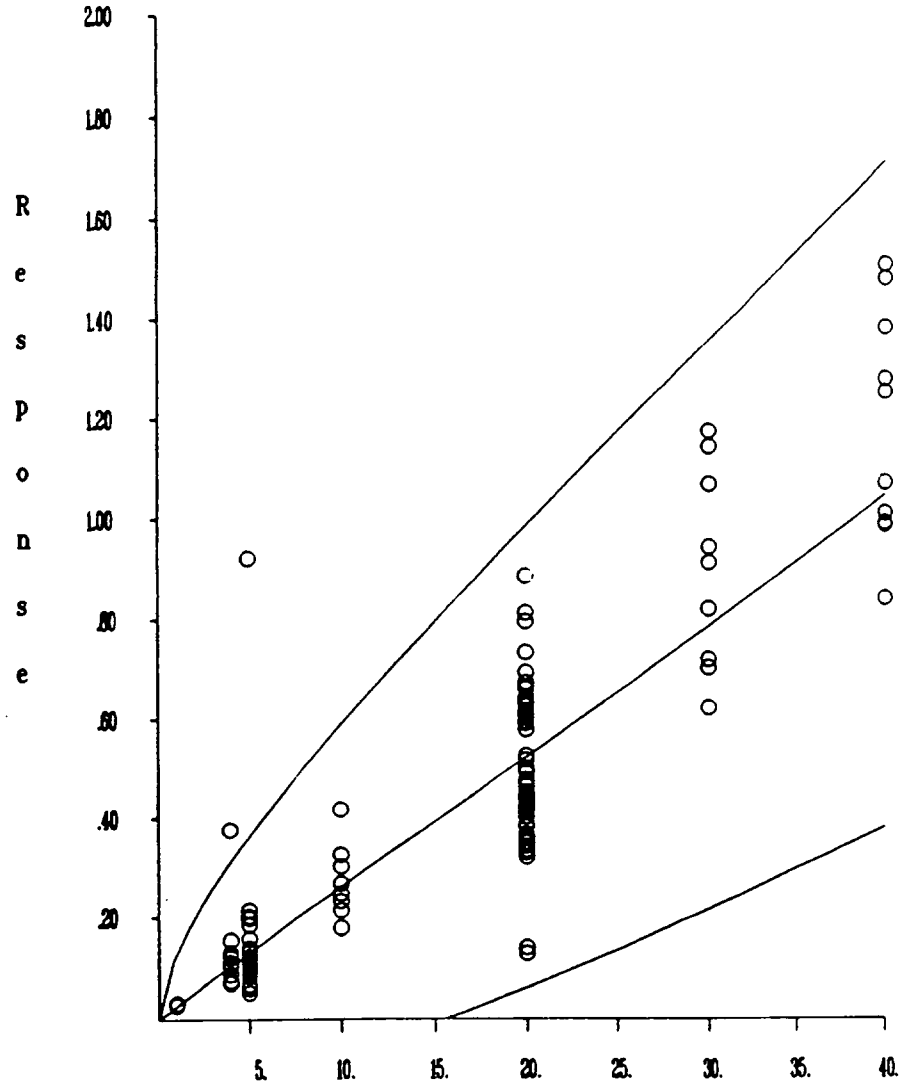
In evaluating sources, availability of data is one attribute that should be considered. The greater the number of data, the more routine will be its generation, and therefore the more representative of routine operation. Also, the greater the data availability, the more frequently the estimation of the MDL can be repeated.

THE STATISTICS AND SOURCE DATA

Two general statistical approaches to estimation of the MDL are commonly applied to analytical methods in environmental laboratories. (4) The first is a correlation of standard deviations of blanks and/or sample responses, that utilizes the concept of signal to noise. The second is calibration curve regression statistics. Experimental known samples are typically used for the standard deviation approach to MDL calculation and are generally prepared at a concentration near the expected MDL. When standard data are used in calibration curve regression, concentrations over the working range of the method are used. These different input data characterize the method in different ways, encode the error of different assignable sources, and the information encoded in them is used differently by the statistics.

Figure 1 is a graph of volatile organic standard data from four GC/MS instruments and analysts over the period of one month, using 25 ml purge and trap concentration technique and capillary columns. 174 data points are charted for one analyte of this method, bromoform. The vertical axis is relative response (ratio of analyte response to internal standard response). The horizontal axis is the concentration at which the standard was prepared, in units of micrograms per liter. The data at the 1 microgram per liter level is one set of 40 CFR MDL experiment data. Initial calibration data, are represented at the concentrations of 4, 10, 20, 30 and 40 ug/l. Continuing calibration analyses are at a concentration of 20 ug/l. A QC spiked blank standard is represented at 5 ug/l. And two sets of operator validation studies (four replicates each) were analyzed at 4 ug/l. The curved lines are the weighted least squares estimate of the confidence of the data.

Figure 1 - Standard Data for Bromoform



The information from this graph that was utilized for the 40 CFR MDL estimation are represented by the data at 1 mg/l on this graph. All of the 174 data points on this graph were used for calculation of the calibration curve regression MDL. (?) The values of the MDL, as determined by these two statistics, are 0.12 and 6.21 ug/l, respectively.

ISOLATING ASSIGNABLE SOURCES OF ERROR

Given that analytical data can only encode the error of the assignable sources that are acting on it, if we hold the statistical method constant and vary the assignable sources that are acting on the data, an evaluation of the effect, or lack of effect, that a particular assignable source of error has on the estimate of the MDL can be made.

Table 2 are results from method detection limit experiments performed in accordance with the 40 CFR MDL estimation procedure. The first column of figures are MDL values when the experimental known sample was prepared in reagent water. The next column is data for an experiment that was done the same instrument by the same analyst, on the next day, using a ground water matrix. The assignable source of error that has been changed is that of matrix.

Table 2 - 40 CFR MDLs in Reagent Water and Ground Water

Analyte	Reagent Water (Concentration in ug/l)	Ground Water
Chloromethane	0.4	0.2
Bromomethane	0.8	0.2
Vinyl Chloride	0.4	0.2
Chloroethane	0.5	0.1
Methylene Chloride	0.3	0.4
Trichlorofluoromethane	0.4	0.2
1,1-Dichloroethene	0.3	0.3
1,1-Dichloroethane	0.3	0.1
trans-1,2-Dichloroethene	0.2	0.1
Chloroform	0.2	0.3
1,2-Dichloroethane	0.3	0.1

Table 2 - Continued

1,1,1-Trichloroethane	0.4	0.1
Carbon Tetrachloride	0.6	0.2
Bromodichloromethane	0.4	0.1
1,2-Dichloropropane	0.2	0.1
cis-1,3-Dichloropropene	0.4	0.1
Trichloroethene	0.3	0.1
Benzene	0.2	0.1
Dibromochloromethane	0.3	0.2
1,1,2-Trichloroethane	0.4	0.3
trans-1,3-Dichloropropene	0.4	0.1
Bromoform	0.3	0.3
1,1,2,2-Tetrachloroethane	0.6	0.3
Tetrachloroethene	0.2	0.2
Toluene	0.2	0.2
Chlorobenzene	0.3	0.2
Ethyl benzene	0.3	0.2
1,3-Dichlorobenzene	0.4	0.4
1,2-Dichlorobenzene	0.4	0.4
1,4-Dichlorobenzene	0.4	0.4

Another assignable source of error that has been evaluated using this technique, that may be of interest to many laboratories, is that cause by multiple instruments and analysts. For the MDLs represented in Table ?, the calibration curve regression statistical approach was applied to standard data for three different analyst/instrument combinations and to the combined data from all three analyst/instruments that was acquired over a period of one month. The two data columns are MDL estimates determined using the statistic for 99% confidence as presented by Clayton (2) and for that of 99% confidence and 99% coverage as presented by Gibbons. (3)

Table 3 - Chlorobenzene MDLs - Effect of Multiple Systems

Analyst/ Instrument	Number of Data Points	99% Confidence Limit	99% Confidence-99% Coverage Limit
		(Units are micrograms per liter)	
#1/A	65	0.87	1.02
#2/B	59	1.20	1.40
#3/C	38	2.16	2.57
ALL	162	3.36	3.93

SUMMARY

It is very important to first consider the representativeness of the data used when evaluating the quality of a statistical estimate of a method's detection limit. If the data are not representative of routine analysis of samples by the method, and do not encode the actual variability and bias of the method that are acting on routine samples it can not extract that information from the data, no matter the attributes of a statistical approach. The concept of assignable sources of error is a tool that is useful in describing the representativeness of data. When an assignable source for error acts on routine samples but does not act on the source data for the MDL statistical estimation, then the question of whether or not this discrepancy creates a significant difference in the quality of the estimated MDL becomes an issue. Experiments can be designed to investigate what the magnitude of the error contributed by a particular assignable source is by developing parallel sets of data, one set encompassing the assignable source of interest, and one encompassing all of the assignable sources acting on the first set except the assignable source of interest.

ACKNOWLEDGEMENT

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REFERENCES

1. U.S. Government (1985). Definition and Procedure for the Determination of the Method Detection Limit. 40 CFR 136, Appendix B, p 504.

2. Clayton, C. A., Hines, J. W. and Elkins, P. D. (1987). Detection limits with specified assurance probabilities. Anal. Chem 59, 2506-2514.

3. Gibbons, R. D., Jarke, F. H., and Stoub, K. P. (1990). Detection Limits: For Calibration Curves with Increasing Variance and Multiple Detection Decisions, ASTM in press.

4. Kkoehn, J. W. and Zimmerman, A. G. (1990). Method Detection Limits: How Low Can You Really Go? Environmental Lab Feb/Mar p 36.

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DATA-QUALITY EVALUATION FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

The massive amount of data obtained when using inductively coupled plasma mass spectrometry (ICP-MS) could have quality assurance value if it could be evaluated in a convenient and timely manner. An effort is underway at EPA in Las Vegas to assess ICP-MS interferences and to develop ICP-MS data-evaluation software to ensure that data of known quality are obtained. This work has begun as a spreadsheet effort that inspects ICP-MS data, flags suspect values, and provides recommendations.

INTRODUCTION

Since data inspection by humans is a time consuming process, much information is not extracted from routine ICP-MS analyses. Some of this unused information has value for evaluating the quality of the analyte data. For example, a solution could appear to contain copper because signals at m/z 63 and m/z 65 are present in the appropriate proportions. However, the solution may only contain sodium and sulfur in such amounts that $ArNa^+$ ions at m/z 63 and SO_2H^+ ions at m/z 65 mimic the copper ratio. Such interferences could be eliminated by measuring pertinent ions and using appropriate correction formulas. For example, sodium can be measured at m/z 23 and related to the $ArNa^+$ signal at m/z 63. Although the $^{32}S^+$ signal in ICP-MS is confounded by the O_2^+ signal, sulfur combines with oxygen, hydrogen and nitrogen to provide other ICP-MS signals that can be used to assess sulfur interferences. For example, the $^{32}SO_2H^+$ signal at m/z 65 has been observed for our instrumental conditions to be 34 $\pm$ 3% of the $^{34}S^{16}O^+$ signal at m/z 50. When suspect values are identified, a benefit is achieved because data of known quality are obtained and because those samples needing matrix separation or other work are identified.

Notice: Although the research described in this article has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

DISCUSSION

Spreadsheet macros and lookup tables provide a convenient means to program computer inspection of ICP-MS data. When the signal value in a spreadsheet cell fits certain criteria, cells containing appropriate text can be displayed on the computer monitor and printed. The spreadsheet containing the macro software has blank fields allocated to receive imported unprocessed (raw) ICP-MS signal data to be evaluated.

Computer-monitor displays from the software evaluation of ICP-MS data could include the following:

ICP-MS Data Evaluation

Copper data for samples #10 and #11 may be affected at m/z 63 by high amounts of sodium and at m/z 65 by high levels of sulfur .

RECOMMENDATION: Determine the degree of sodium and sulfur interferences, or apply matrix separation before reanalysis of these samples.

ICP-MS Data Evaluation

Manganese data for samples #3 and #56 may be affected by high amounts of iron at adjacent m/z location.

RECOMMENDATION: Determine the degree of iron interference on Mn for samples #3 and #56, or reanalyze these samples after improve resolution between Mn and Fe.

ICP-MS Data Evaluation

Chromium and vanadium data for samples #42 and #43 may be affected by high carbon content.

RECOMMENDATION: Redigest these 2 samples by a more rigorous procedure to remove more of the organic content, or apply matrix separation to original digests, before reanalysis.

ICP-MS Data Evaluation

Cadmium value for sample #22 is affected by MoO^+ interference, and correction applied is more than 80% of the gross signal.

RECOMMENDATION: Consider cadmium value suspect, and apply matrix separation before reanalysis.

ICP-MS Data Evaluation

Lead value for sample #16 appears to include contamination because the lead isotope ratio ($^{208}Pb/^{206}Pb$) is typical of local dust and does not match ratio for duplicate (sample #18).

RECOMMENDATION: Reject lead value for sample #16, and analyze another portion after lead contamination is mimimized.

SUMMARY

Appropriate software offers a rapid means to achieve data-quality evaluation and guidance for ICP-MS analyses. It could prove useful for implementing "conditional quality control," in which interference corrections would only be applied when data evaluation indicates a need.

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ASSESSMENT OF ROUTINE LABORATORY PERFORMANCE IN THE CONTRACT LABORATORY PROGRAM

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INTRODUCTION

The Contract Laboratory Program (CLP) has developed a number of procedures to monitor CLP laboratory performance. Intermittent checks of performance are accomplished through the use of Quarterly Blind Sample analyses and laboratory audits. Routine performance checks are accomplished through Contract Compliance Screening (CCS) reports and the limited use of the data validation summary reports provided by regional data reviewers.

Both the organic and inorganic CLP statements of work were developed to provide the analysis of a large number of target analytes in a consistent, cost effective manner. While specialized analysis methods exist which can resolve matrix or detection limit problems, the CLP analytical methods were not designed to address these unique situations. Consequently, under routine CLP analysis conditions, some compounds are more troublesome than others.

Each EPA region has a Contract Laboratory Program Technical Project Officer (CLP-TPO) who must oversee the performance of the laboratories located in his/her region. The CLP-TPO must be able to identify which analytes represent problems for the chosen method and which are indicative of an individual laboratory's performance. The Region VIII CLP-TPO, with support from the Environmental Services Assistance Team (ESAT), has developed a laboratory performance tracking system that utilizes information generated from the review and evaluation of laboratory data, in the form of data validation summary reports. Although the Regional formats of data validation reports might vary, the same guidance documents are used to evaluate the data, nationally. Guidance documents for these reviews exist for all routine analyses performed in the CLP.

The primary objective for the development of this program was to aid the CLP-TPO in monitoring routine laboratory performance of Region VIII CLP laboratories.

It became clear that data reviewers consistently find both technical and contractual deficiencies in laboratory performance. Even laboratories which routinely score 90-100% on performance evaluation sample analyses, have deficiencies in routine analytical data production. The computerized

tracking system provides a mechanism by which the CLP-TPO can identify changes in laboratory performance that require immediate attention.

In the process of designing this system, it became evident that other uses could be made of this information. These secondary objectives include: (1) evaluation of the technical sufficiency of the CLP Statement of Work (SOW), (2) identification of problem areas for individual laboratories and for the analytical method as a whole, (3) evaluation of the suitability of the method as a function of sample matrix, (4) comparison of technical problems with contractual problems, and (5) evaluation of potential new contractual requirements and their impact on the data.

METHODS

The computer program was developed utilizing dBase language (i.e., DBXL, Quicksilver, and dBaseIII+). The dBase languages were chosen for their flexibility, memory capability, and report generation potential. As a compiled program, 'R8LAB' can be used as a stand-alone application program on any IBM-compatible computer.

It was necessary to develop standardized encoding forms to work with the various review formats used in each Region. Encoding forms were designed to include each element or compound found in the routine analytical services (RAS) menu for inorganics, volatile, semivolatile, and pesticide/PCBs, as well as the organic surrogate compounds. A field for all possible QC problems, including field QC (i.e., blank, duplicate, blind standard), is provided.

Where possible, values or alpha codes (i.e., H = high, L = low, OOC = out of control), are transferred onto the encoding sheets when QC problems are reported. The actual encoding task is performed by chemists to reduce the possibility of overlooking relevant information.

RESULTS AND DISCUSSION

There are five organic Contract Laboratory Program (CLP) laboratories in EPA Region VIII. Information from data validation summary reports forwarded to the Region VIII TPO by her counterparts in other regions since 1988 have been included in the data base.

The number of QC problems found was strongly influenced by the nature of the compound and fraction being analyzed. Statistical evaluation of the results is planned as a future effort.

From the CLP-TPO's perspective, the main utility of the data validation

summary is in the evaluation of the types of QC problems resulting from use of CLP protocols. For all the compounds, holding time violations represented the majority of the QC problems identified by the reviewers. However, the QC problems found are not the same for all the fractions. The low response factor for 2-butanone in the volatile fractions was a problem in many data reviews.

It is also possible to compare overall laboratory performance between the five organic laboratories in Region VIII. The three measures of laboratory performance, Quarterly Blinds, Contract Compliance Screening, and the Region VIII CLP Laboratory Performance Tracking data base do not correlate well within Region VIII. It is possible that these measures would correlate better using a national data base, but the data in this data base suggests that total reliance on the traditional indicators may not provide sufficient markers of routine analytical performance.

One of the main laboratory follow-up problems is distinguishing between method-specific problems and laboratory-specific problems. Since both the number and type of problems vary from laboratory to laboratory, Region VIII theorized that the laboratories might have varying success with the different compounds and fractions. The data base evaluation showed that for some compounds there were few differences between individual laboratory performance, yet for others significant differences appeared. Laboratory-specific problems can be brought to the laboratory's attention during audits or visits with the CLP-TPO.

The program also has the capability of segregating the data by sample matrix. The type of sample matrix (i.e., soil or water) influences the number of QC problems found in each case. All laboratories had fewer QC problems overall with water samples than with soil samples. The sample matrix had a profound effect on the nature of the QC problems reported.

Region VIII designed the program and the report formats to serve the needs of regional CLP-TPOs and aid in their laboratory oversight duties. The program has shown the potential of specifically identifying laboratory QC problems and, with sufficient data, can aid in determining whether these QC problems are laboratory-specific or whether all the laboratories in the region are having difficulty; an indication of an analysis method/field collection related problems.

For the CLP, the full capabilities of this concept could be incorporated into the national QA program with a little help from the regions. For example, the current checksheet required by the National Program Office (NPO) could be replaced with an encoding form and delivered either in hard copy or diskettes. It would allow a comparison of ongoing laboratory performance on a nationwide basis and could provide reports to the regions on a quarterly basis. The advantages of this system are (1) the NPO would have data which could rapidly identify method/field-related problems that could be targeted for methods research; and (2) the NPO could identify

laboratories which seem to perform better with a particular method than others. These laboratories with better performance, would be invited to make presentations at caucuses where they could be recognized for their success and share the secrets of their success with other CLP participants.

CONCLUSIONS AND RECOMMENDATIONS

With a small investment of time and effort, Region VIII has developed a technique to evaluate on-going laboratory performance in the Contract Laboratory Program. The results of the method have already proven to be very useful to the Region VIII CLP-TPO in carrying out the duties of monitoring on-going laboratory performance and have yielded preliminary information concerning analytical method performance. The full utility of the concept and the method could be achieved by adoption of this system on a nationwide basis. Moreover, since this represents only an improvement to the current QA services provided by the NPO, implementation should be straight-forward. EPA Region VIII recommends this approach as a starting point for long-term evaluation of laboratory performance.

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QA TRAINING SUPPORT TO OSWER PROGRAMS: CBT MODULES IN FIELD AND LABORATORY OPERATIONS

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PURPOSE OF PRESENTATION

The poster session is proposed to demonstrate a series of Computer-Based Training (CBT) modules that focus on Quality Assurance issues in data collection and data analysis.

PURPOSE OF TRAINING

This CBT project is part of an ongoing effort by the Quality Assurance Management Staff (QAMS) to provide technical and management training support to EPA's Quality Assurance program. Specifically, the CBT lessons are designed to help meet the urgent need for QA training in the RCRA and Superfund programs, which carry out some of the Agency's largest and most important data collection and data analysis activities.

In analyzing the QA training needs of these programs, QAMS determined that because of the size and complexity of the programs, new RCRA and Superfund staff had to absorb an enormous amount of basic information on procedural and technical subjects. Additionally, some programs with large oversight responsibilities have a continuing staff turnover, so this need for basic informational training remains consistently high. Because of these priorities, QAMS has focused much of its efforts on providing packaged, self-instructional materials that would minimize instructor time and travel costs associated with traditional classroom training.

These computer modules are intended for use by newly employed RCRA and Superfund staff and are designed to convey basic information on data collection and data analysis activities.

DESCRIPTION OF CBT MODULES

Each of the computer modules to be demonstrated at the OSWER Symposium is a stand-alone lesson that focuses on a topic related to environmental data collection activities. Graphics, animation, and games are implemented to provide a highly interactive, and visual learning environment. Each lesson has the same format:

1. Introduction - Describes the objectives of the module and explains how to move through the program using the appropriate function keys.

2. Menu - Allows the student to choose which topic to investigate and gives a quick outline of the areas to be covered in the lesson.

3. Tutorials - Provides individual units dealing with one subject to be learned in the module.

4. Challenge Exercise - Tests the student's knowledge of the material just covered in a game format.

Below is a description of three of the modules that would be available for demonstration. Participants will have the opportunity to go through the first three sample lessons during the poster session.

1. Field Sampling Equipment

   This CBT lesson deals with the uses and limitations of equipment used in sampling activities. It covers three topics: Augers, Bailers, and Containers. The equipment described includes the augers and bailers most commonly used in field sampling activities.

2. Decontamination Procedures

   This lesson covers decontamination methods used in the field and focuses on: Site Operations, Decontamination Methods, Verifying Decontamination, and Decontamination Documentation. Topics covered include decontamination of sampling equipment and peripheral equipment, as well as verifying decontamination and documenting decontamination procedures.

3. Chain of Custody Procedures

   This lesson deals with Sample Identification, Sample Transfer and Shipment.

4. This lesson focuses on sample preparation, preservation, and packaging.

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INCORPORATING PROPAGATION OF ERROR IN THE CALCULATION OF THE PRECISION FOR PERCENT RECOVERIES WHEN DOING ANALYTICAL METHODS DEVELOPMENT

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Most methods development studies published cite percent recoveries for the isolation of organic contaminants without reference to exactly how the calculation was done. A 90.5% recovery of benzo(a)pyrene from spiked water does not inform the reader as to the correctness of the precision for that analyte within the context of the developed method. The wide range of acceptability of percent recoveries in many EPA methods makes little mention on exactly how precise these recoveries actually were.

If percent recoveries are calculated based on a control or reference standard whereby the amount of analyte is measured along with the amounts from extracts of the spiked samples then the statistical concept of propagation of error should be incorporated since the percent recovery result is merely a division of two numbers.

We recently reported on our percent recoveries for selected organophosphorous pesticides that were isolated and recovered from spiked deionized water utilizing a propagation of error as well as a standard deviation

for the replicate sets of solid-phase extractions. (1) A computer program in BASIC was developed and used to generate the results which included estimates of confidence intervals (student's t), percent relative standard deviations (RSDs) and standard errors of the mean(2).

Our results for selected organophosphorous pesticides percent recoveries will be presented along with the mathmatical relationships used. These findings have universal applicability to other percent recovery studies with respect to trace environmental analyses.

References:

(1) Loconto, P.R. and A.K. Gaind, "Isolation and Recovery of Organophosphorous Pesticides from Water by Solid-Phase Extraction with Dual Wide-Bore Capillary Gas Chromatography", Journal of Chromatographic Science, 27 (1989) 569.

(2) Peters, D., J. Hayes and G. Hieftje, "Chemical Separations and Measurement: Theory and Practice of Analytical Chemistry", 1974 , Saunders, Philadelphia, p. 21.

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electronic Data Validation and Transfer System (eData)

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Abstract

eData is a personal computer (PC)-based system designed to allow the US EPA Environmental Response Team to manage, validate, report, and communicate hazardous waste sample information generated through sample collection and analytical activities.

The system consists of three distinct modules which reflect the needs of the site manager, the laboratory, and the data validator, respectively. A Central Node module serves as a centralized electronic repository and controls the file transfers between modules.

The site manager specifies the Quality Assurance Levels and Data Quality Objectives (DQOs) to be associated with any given batch of samples. eData includes pre-established QA/QC criteria and limits for volatiles, semi-volatiles, pesticides, PCBs, dioxins, and inorganic metals. These criteria and limits can be modified, deleted, or expanded to meet project specific needs. Sample collection (e.g., chain of custody) and DQO information is transferred electronically via a Central Node. Once the laboratory completes the analyses, the data may be evaluated (in the lab) against the QA/QC criteria previously established by the site manager. Preliminary data with qualifiers is uploaded to the Central Node where the data validators and the site manager have simultaneous access. The data validators draw upon other QA/QC information (e.g., PE limits, DQOs) not available to the laboratory and perform second level validation and usability determinations.

Introduction

There is a perpetual call for data of known quality to be available on an as-soon-as possible basis throughout the hazardous waste management business. Typically, delays in producing such data in a timely manner begin with the selection of appropriate analytical methods and performance criteria. This is a complicated task because of the wide selection of analytical tools available and the different performance criteria needed for different decisions. Where standardization has been encouraged (e.g., EPA's Contract Lab Program, CLP), the most appropriate data for the specific use is sometimes not generated or there is generation of excessive unutilized information. Even when appropriate methods and controls are selected, there is often miscommunication between the sampling team and the laboratory personnel. Errors may go unnoticed until after the expenditure of significant resources (i.e., time and money). Miscommunication and loss of time are impediments managers must endure because hardcopy information (e.g., chain of custody, logbook records, lab engagement agreement letters, analytical result packages, resubmittal data packages, correspondence, etc.) must be moved among the site, laboratory, and data validation personnel.

The US EPA Environmental Response Team (ERT) supports the Superfund Removal Program. The primary objective of the Removal Program is to identify and mitigate imminent hazards in a

timely and effective manner. Hence, there is a programmatic need for rapid turnaround of reliable data to support critical decisions. This need is best served through tools which facilitate communication, ensure consistency, and improve the efficiency of information handling and management. ERT has supported this objective through the development of eData, a PC-based computer program which is designed to assist the communication, management, evaluation and reporting of hazardous waste sample information generated throughout the sample collection and data assessment processes.

The three primary players in the data generation triangle are the site manager (who defines the needs and provides the samples for analysis), the laboratory personnel (who analyze the samples within required methods and performance criteria), and the data validators (who evaluate the analytical and performance criteria results against the defined data quality objectives and make recommendations on usability). Sometimes these three entities are under one corporate banner; however, more often they represent three distinct organizations. eData was developed to compliment these three perspectives, regardless of their organizational or geographical proximity.

The eData System

The eData system consists of three distinct modules which meet the information and activity needs of the site manager, the laboratory, and the data validator. There is also a Central Node module (an electronic bulletin board system, (EBBS)) which provides the centralized repository and controls the file transfer between modules. Future plans for eData include a module that will act as a central database repository for archiving data and evaluating data trends (Figure 1). The system can be set up to run all three modules at the same location, as in the case where the site manager has mobile field lab and data validator resources on-site. More commonly, the site manager and data validator are in close proximity and the laboratory is remote.

Module Characteristics

The appropriate eData system modules are installed at each location and communicate via the Central Node. Each module contains features which compliment the activities of the respective program user (Figure 2).

Installed at the site location (site manager's office/trailer), the site module: 1) assists the site manager in identifying samples, data quality objectives, analytical methods and their associated QA/QC criteria and limits, 2) assists with communication through the Central Node to provide the laboratory and the data validator with the appropriate information, and after sample analysis, 3) assists in the display of analytical results that include information added by data evaluation. This module also affords a local database for further data reduction activities (e.g., geostatistics, sample tracking, data archiving).

Installed at the laboratory, the lab module: 1) retrieves the information provided by the site manager, 2) captures the analytical and QC results after testing, and 3) evaluates the analytical results based on the criteria provided by the site module and internal lab QC criteria.

Installed at the data validator's location, the validation module: 1) provides an interface with the information provided by the site manager and the data transmitted from the laboratory, 2) provides utilities for evaluating the analytical results, including QC data not available to the laboratory (e.g., identification of blanks and acceptance windows for performance check samples) and 3) performs a preliminary data usability analysis.

System Features

- o Easy to use, menu driven user interface with pull-down menus and pop-up windows.
- o Lookup tables provided at data input prompts to facilitate data entry and retrieval.
- o Generation of electronic or hardcopy chain of custody forms for sample batches.
- o CLP default analytical methods and QC criteria/limits.
- o Flexibility to create non-CLP methods and QC criteria/limits.
- o Automated and manual analytical data handling capability.
- o Automated data evaluation routines.
- o Capability to view analytical results of specific samples in unique multi-window display.
- o Generation of a wide variety of reports with capability of previewing reports on screen, printing, and saving.
- o Electronic mail messaging via the Central Node.
- o Ability to track samples throughout analytical and validation processes.
- o Complete hardware setup and maintenance package, including archiving and de-archiving, indexing, backup, etc.

Data Flow Scheme

Following is a characterization of the interrelationship among the various modules as a batch of sample information is transferred through the eData system (Figure 3).

The site module enables the site manager to identify samples within batches. To these batches, the site manager will ascribe data quality objectives, analytical methods and QC performance criteria and limits. eData maintains a full library of CLP default information on Target Compound List parameters which the site manager may import directly or modify to create non-CLP methods and requirements. Once analytical requirements have been affixed to the appropriate sample batches, including the addition of performance evaluation samples and sample specific comments, the site manager is ready to create a hardcopy Chain-of-Custody (COC) form to include with the sample shipping container.

An electronic COC is also ready for upload to the Central Node module, where the information is accessible to the laboratory and the data validator. The site manager may communicate directly to the lab and data validation personnel through the messaging features of eData and the electronic bulletin board. This communication eliminates the need for extensive phone conversations regarding which methods apply to which samples and redundant written communication regarding commitments and requirements. Through the messaging feature, the site manager may advise the lab that on a given day they will receive 20 samples instead of an originally planned 35 samples and that the remaining samples will be added to the 30 samples planned for the next day. The data validator may also be simultaneously apprised of the sampling status without the need to directly contact the site or lab, as this information is accessible on a 24 hour basis to authorized parties. All communication files are protected by security features which prevent unauthorized access.

The laboratory module retrieves the information provided by the site manager. The communication feature provides the laboratory the opportunity report on the status of samples upon receipt in a timely and convenient manner, which in many cases may permit the field team to compensate for damaged samples without remobilization costs. When the analyses requested through eData are completed by the laboratory, eData will accept the analytical and QA/QC results through two primary interfaces. The system currently handles CLP diskette deliverable Format A information through automatic and manual interface features.

Once the results are in the databases, eData may be utilized by the laboratory to run a preliminary validation against the site manager provided QA/QC criteria and limits. It is also possible for the laboratory to add additional performance criteria for its own internal checks. These features allow the laboratory to check their data quality through an automated capability prior to delivery to the client (EPA or industrial). Data which does not meet client or internal lab performance criteria will be flagged by eData with up to ten unique flag codes and may be reanalyzed prior to exceeding holding times. When the laboratory is ready to release the data, eData affords electronic transfer capability through data export features to diskette or the Central Node. Throughout the sample analyses, the laboratory may communicate with the site manager regarding status or complications through the eData communication menu.

Once the laboratory uploads the analytic results, QC results, and preliminary validation results, the information is accessible to both the site manager and the data validator simultaneously. This feature affords the site manager the opportunity to evaluate preliminary data with qualifiers for any imminent threat abatement or cleanup decisions while the data validator initiates a more indepth second level validation with QC information not afforded to the laboratory (e.g., PE results).

The data validation module provides an interface with the information provided by the site manager on data quality objectives and QC data (e.g., which samples were blanks, performance check samples, etc.) and the laboratory generated results. The data validators may automatically perform various assessment routines on this data through eData. The inclusion of QC data not afforded the laboratory allows the data validator to run a second level validation and ascribe additional qualifying flags, if necessary. Validators can also draw upon sample/data quality objectives to perform preliminary data usability analyses.

The communication features of eData allow three way or select discussions among the three modules. This is useful where the validators need to communicate directly to the lab regarding missing data, additional data, or requests for reanalysis. Likewise, communication with the site manager may be restricted from the laboratory as in the case of data usability determinations. As mentioned previously, communication files are protected from unauthorized access.

Finally, if discussions with the site manager warrant, the data validators may adjust the ranges on the QA/QC performance criteria limits to be wider or more narrow and rerun the validation routines to assess the implication on results with respect to data usability. It is possible to print validation reports illustrating various batch, sample, holding time, and other information. Final qualified results are uploaded from the data validation module through the Central Node for access by the site module. Therein the site manager may view results, print reports, or export to local data application packages for alternate reduction activities.

Summary

eData was designed to facilitate interaction among the three primary players (site managers, lab personnel, data validators) in the hazardous waste data generation triangle.

This objective is achieved through the following major accomplishments:

1) Improving the transfer of analytical information by utilizing a widely available electronic delivery medium (i.e, EBBS) with 24 hour accessibility.
2) Resolving inconsistency of terms and frequent problems of miscommunication by standardizing criteria, while preserving flexibility to choose criteria and alter performance requirements, into one system delivery mechanism available/accessible to all appropriate users.
3) Maintaining linkage from DQO intention to result by incorporating usability assessment routines.

4) Providing data management/handling capability in an electronic form for current and future use options.
5) Improving the communications concerning sampling and analysis with all parties.

The system, which is currently being tested, was developed to support EPA's Superfund Removal Program; however, the features and flexibility of eData make it readily adaptable for handling other EPA program data handling responsibilities.

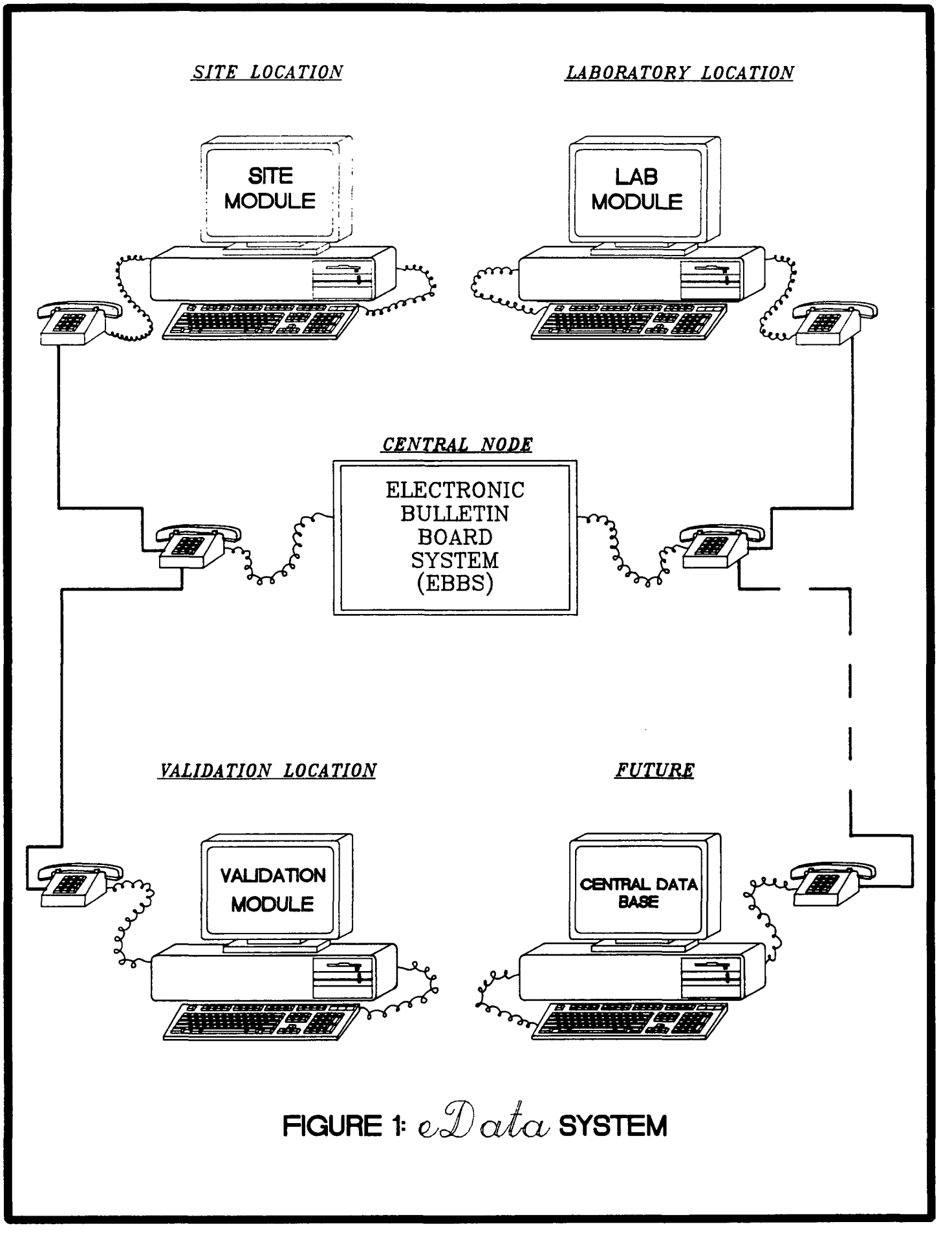

FIGURE 1: eData SYSTEM

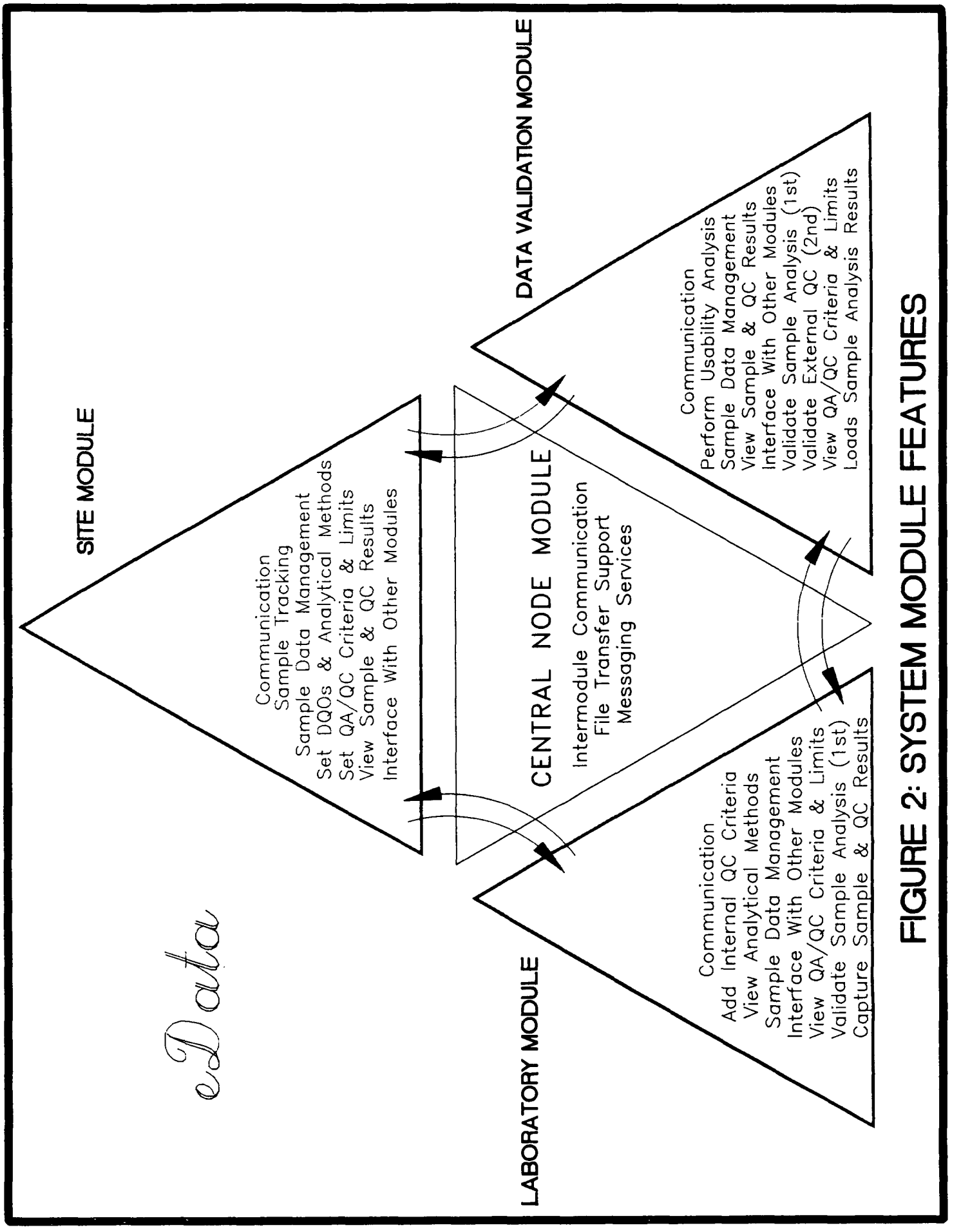

FIGURE 2: SYSTEM MODULE FEATURES

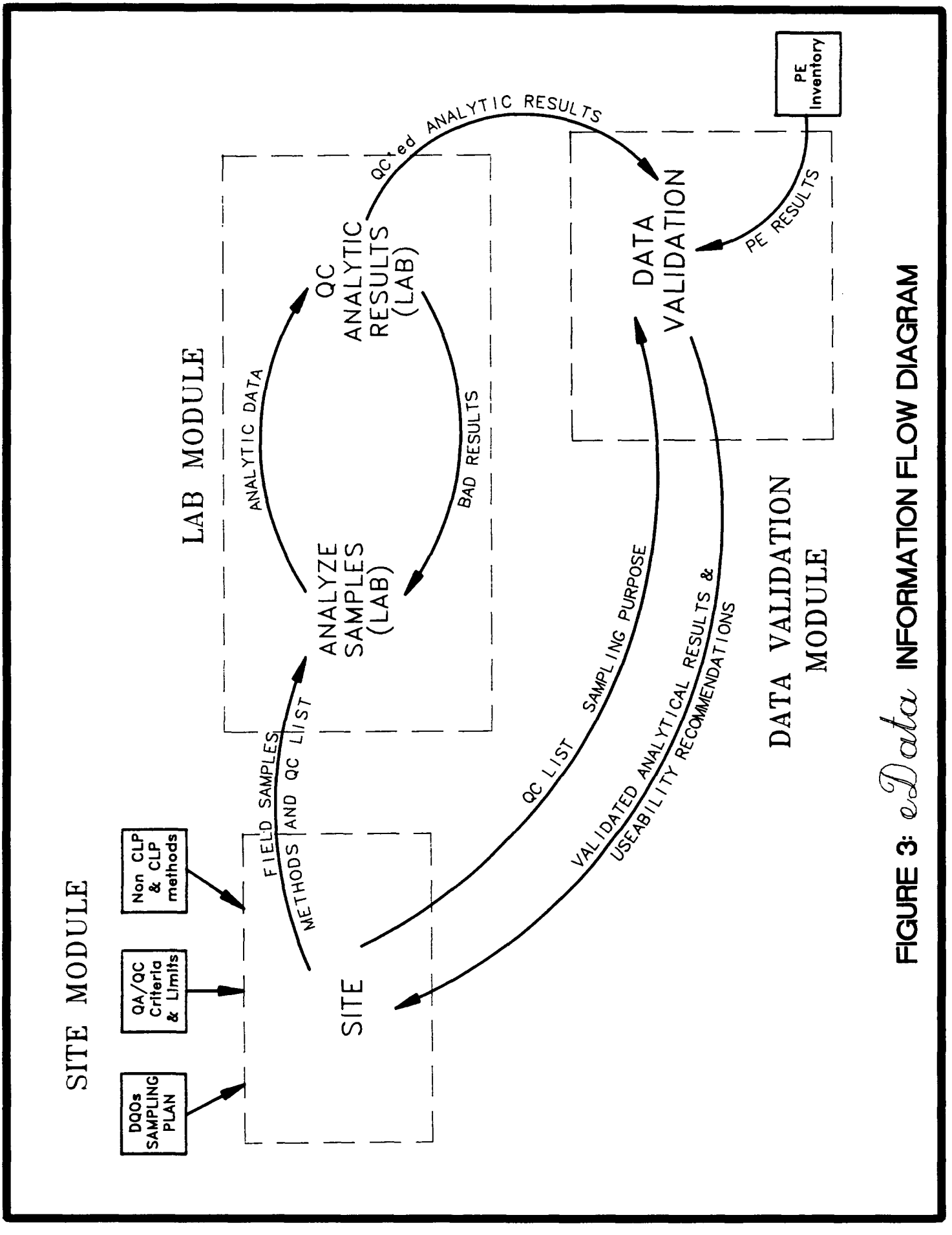

FIGURE 3: *Data* INFORMATION FLOW DIAGRAM

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STANDARDIZATION OF QUALITY ASSURANCE PROJECT PLANS: A WAY TO INCREASE QUALITY

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ABSTRACT. A trend has emerged during the last several years that points toward a possible decrease in the quality of environmental data. While the current policy and guidance documents supplied by the U.S. Environmental Protection Agency provide a comprehensive guide for developing Quality Assurance (QA) Project Plans, the details involved in developing such a plan are often not well understood by the firms generating and ultimately using them.

The discrepancies in many plans are created by

- Inappropriate selection of analytical methodology to meet data quality objectives
- Inappropriate selection of data review or validation procedures
- Inappropriate selection of sample containers, size, and preservation technique
- Lack of communication between engineering/consulting firms and laboratories

Discrepancies and variances in these plans raise numerous questions about the accuracy and suitability of data generated using many of these QA Project Plans.

The possibility of creating a "standardized" QA Project Plan that covers the entire scope of data quality objectives, analytical methods, and appropriate quality assurance techniques will be evaluated. This standardized QA Project Plan would form the basis of a plan that could be used and applied on a nationwide basis.

In addition to creating greater uniformity among QA Project Plan preparers and users, preparation time, review time and rewrite/rework time will be decreased. The end result being data that are adequate for its intended purpose at a lower cost.

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AN INTERLABORATORY STUDY TO EVALUATE LABORATORY PERFORMANCE ANALYZING HAZARDOUS WASTES USING EPA SW846 METHODS 3050 and 6010

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ABSTRACT

An interlaboratory study to evaluate laboratory performance using EPA SW846 methods 3050 and 6010 was conducted using homogenized industrial wastes. In this study, thirteen laboratories were used with each laboratory performing fifty determinations for a total of 650 data points. The results indicate that interlaboratory variability is extreme, with 52.8% of the data points outside a 95% confidence window. Use of independently developed QA/QC reference materials is recommended to detect erroneous or biased analytical results.

INTRODUCTION

Laboratory analysis directly influences the decisions on how industrial waste streams and remediation of contaminated sites are managed. Laboratories receiving environmental samples are asked to perform analyses on a wide variety of materials for analytes at concentrations ranging from the method detection limits to percent levels. To compound the difficulty of obtaining accurate analytical results, many of the laboratory technicians responsible for critical steps of the analyses are inadequately trained and have very little experience.

The inaccuracies occurring in analytical data can be traced to a number of potential areas. Contaminated reagents, cross contamination of samples, and biased methods are often the cause of erroneous data, resulting in a wide disparity in reported values. Errors can occur at any step in the procedure from sample preparation, to data reduction into a final report. However, the most common source of laboratory data inaccuracies can be traced back to errors committed in the performance of the method.

The consequences of inaccurate laboratory analyses may have an adverse impact on both public health and the environment, as well as financial liabilities for all parties involved. Decisions based on erroneous analytical data may result in huge financial expenditures for remediation or waste treatment/disposal that is not necessary. Conversely, inaccurate data may not identify a potential hazardous material that may endanger the public and environment. As a result, the generator and potentially the laboratory that performed the analysis, may assume a considerable future liability.

The Environmental Protection Agency (EPA) has implemented programs to improve the accuracy of analyses performed by environmental laboratories. Quality Assurance/Quality Control (QA/QC), required in current EPA analytical methodologies such a SW846 and the Contract Laboratory Program

(CLP) addresses the issues of laboratory contamination from reagents and cross contamination of samples by the use of blanks. Analyte recovery is evaluated, to some degree, by the use of matrix spikes and duplicate analysis. Instrument performance is monitored by the use of traceable standards and continued calibration of the instrument during analysis.

The one issue currently not evaluated is that of interlaboratory variability. Current QA/QC protocols only address internal laboratory control by using the methods described previously. These QA/QC methods tell us how precise the analysis is, but do not address the accuracy of the reported values.

INTERLABORATORY STUDIES

The EPA has investigated the errors associated with the analysis of waste materials. A multi-laboratory evaluation of SW846 methods(1) 3050 (acid digestion of solids) and 6010 (inductively coupled plasma or ICP) was conducted by the EPA(2) to determine the precision of the methodologies and associated errors (Table 1). It was concluded that the median percent relative standard deviation (RSD) for the combined methods was 6.7 percent with a range for RSD from 52 to 2.6 percent using quality control solutions. The study also evaluated the precision of the laboratories in analyzing spiked and unspiked materials (Table 1) that required digestion by SW846 method 3050 and analysis by method 6010. For spiked solids, the median percent RSD is approximately 15 percent. For unspiked solids the median percent RSD increases to approximately 22 percent. These data show that the methods are capable of good precision for most elements routinely analyzed by ICP, when the materials are analyzed under controlled conditions such as a collaborative study (i.e.,laboratories exercise more control when analyzing quality control samples).

The study also investigated the EPA's mine tailing sample that is used by the Contract Laboratory Program (CLP). The data are presented in Table 3. Data from Table 1 and Table 2 suggest that the methods are capable of good precision, however, the control limits for this sample suggest that the interlaboratory variation is much greater than regulatory requirements can tolerate. Examination, of the values obtained for chromium, reveals that a mean value of 12 mg/Kg was obtained with a standard deviation of 12 and a RSD of 104 percent. The control limit for chromium is 0 to 46 mg/Kg.

A collaborative study of the Toxicity Characteristic Leaching Procedure (TCLP) for metals, pesticides and semi-volatile organic compounds was also undertaken by the EPA(3). The results from the collaborative study for the metals analysis is given in Table 4. Three samples at two different pH levels were analyzed. The results of this study indicates that a questionable situation arises as to how the waste streams should be managed. Sample A-2 had a determined mean value for chromium of 3.79 mg/Kg with a standard deviation of 3.79 and an RSD of 100 percent. With the proposed regulatory limit for chromium in a TCLP extract set at 5.0 mg/Kg, the results indicate a range from 0 to 7.58. Without an outside reference to evaluate laboratory performance, the laboratory could report a value that

could impose huge financial and legal penalties.

Because these data were collected via a collaborative study, a true representation of actual laboratory variability was not possible. Our objective is to determine the actual method variability by an inter-laboratory method study without informing the laboratories of the application of the collected data.

EXPERIMENTAL DESIGN

An interlaboratory study was conducted to determine laboratory performance with real world hazardous waste materials. Eleven different hazardous wastes were selected for their matrix and level of metals present. The matrices included soils, sludges and incinerated materials. The levels of metals analyzed, ranged from low ppm (< 10), to percent levels. None of the analyzed materials were spiked or altered beyond normal sample preparation, such as grinding an/or sieving. The matrices were homogenized, verified for homogeneity, and submitted to 13 different laboratories for analysis by SW846 Methods 3050 and 6010. Each laboratory performed 50 determinations for a total of 650 data points.

RESULTS AND DISCUSSION

Each material was homogenized, sampled and analyzed for specific elements by one independent laboratory. The resultant data was tested for homogeneity by an adaption of Hartley's F-max test for homogeneity of variances. All eleven samples were found to be homogenous.

With the determination of homogeneity completed, each material was subsampled and submitted for analysis to thirteen laboratories. The laboratories were requested to determine the specified constituents for each matrix by SW846 methods 3050 and 6010.
The collected data was verified for normality by Geary's Test at a 5% level of significance before statistical analysis of the data. All of the collected data was determined to be normally distributed. Statistical outliers were determined by Grubb's Discordancy Test at a 5% level of significance. Of the 650 data points collected, 73 data points (11.2%) were determined to be statistical outliers, 307 data points (47.2%) were within a 95% confidence window of the mean, 400 data points (61.5%) were within one sigma of the mean, 572 (88%) data points were within 2 sigma of the mean and 577 (88.8%) were within 3 sigma of the mean (Table 5).

The resultant data was subjected to both simple linear regression and multiple linear regression tests. The simple linear regression tests showed that the number of statistical outliers reported had a significant linear trend to both, the number of data points that were within a 95% confidence window (Figure 1), and to the number of data points that fell within one sigma (Figure 2) of the reported mean. A test of the hypothesis that the data were related, confirmed the results. The data were not shown to have a significant linear trend when 2 and 3 sigma deviations were included in the calculations.

Multiple linear regression tests also supported the findings from the simple linear regression tests. The number, of statistical outliers, was compared to the 95% confidence window and to the one sigma window. The results were subjected to an analysis of variance, to test the regression relation. The results indicate that the number of statistical outliers is related to both the number of data points within a 95% confidence window and a one sigma window (table 6). No solution was possible with the 2 and 3 sigma results.

CONCLUSIONS

The results of this study indicate that there is a major problem that has not yet been solved; how can you be sure that the analytical values reported are a true representation of the material that was analyzed? Laboratory bias and errors in analyses are not adequately detected with current QA/QC protocols. The use of an independent reference sample will provide analytical laboratories and their clients an additional quality control check on laboratory performance.

A report by the Commission of the European Communities(4), which has investigated the use of reference materials since 1973, finds that the routine use of reference materials can improve the accuracy of analytical measurements. Other literature(5) supports this observation and has found that in some instances, the RSD can be decreased by 50% when a reference material is used in the analysis.

The data generated from this study shows that reference samples are excellent indicators in determining overall laboratory performance. The statistical analysis of the study data reveals that the number of statistical outliers each laboratory reported is inversely related to the number of analytes each laboratory reported in a 95% confidence window, and a one sigma window (Figures 1 & 2). Laboratory performance could not be correlated to a 2 or 3 sigma window. If analysis of a reference sample is evaluated, preferably, at the 95% confidence window and not exceeding a one sigma window, a strong indication of overall laboratory performance on the sample set can be derived. Data accepted beyond a one sigma window includes potentially invalid results, especially at or near regulatory limits, which will skew the interpretation of the laboratory's performance.

The results of a reference sample analysis should be used to evaluate the rest of the analytical data set, for consistency and accuracy, prior to reporting any determined values on unknown samples. The data also indicates that in order to determine overall laboratory performance, a reference sample should be used with all sample sets.

The statistical analysis demonstrates the ability to evaluate individual laboratory performance by analyzing a reference sample. Reference samples provide a mechanism to evaluate laboratory performance from sample preparation to report generation. Their routine use provides the user with pertinent information regarding the validity of data generated from the analysis of real world samples.

The use of reference samples provides a common reference on which to evaluate analytical data independent of the laboratories internal QA/QC. When large databases are being compiled, and data is being submitted by a number of different laboratories, there is no common reference point on which to evaluate the results other than internal QA/QC. When analyses are being conducted to determine the nature of a problem, an undetected error in the laboratory could create a injurious situation at a later time.

One of the primary factors relied upon in determining how to address and manage environmental issues are the results of a laboratory analysis. The use of reference samples in laboratory analyses, is inexpensive insurance against a costly mistake, and one that may have far reaching ramifications for the users of laboratory data as well as for the laboratories themselves.

LITERATURE CITED

(1) Test Methods for Evaluating Solid Wastes; U.S. Environmental Protection Agency. Office of SWER. U.S. Government Printing Office; Washington, DC, 1986; EPA SW846.

(2) Hinners, T.A. et al. Results of an Interlaboratory Study of ICP Method 6010 Combined With Digestion Method 3050. In Proceedings of Third Annual United States Environmental Protection Agency Symposium on Solid Waste Testing and Quality Assurance; U.S. Government Printing Office; Washington, DC, 1987.

(3) Blackburn, W.B. et al. Collaborative Study of the Toxicity Charac teristic Leaching Procedure(TCLP) for Metals, Pesticides and Semi-Volatile Organic Compounds. In Proceedings of Second Annual United States Environmental Protection Agency Symposium on Solid Waste Testing and Quality Assurance; U.S. Government Printing Office; Washington, DC, 1986.

(4) Marchandise, H. et al. New Reference Materials Improvement of Methods of Measurement. Commission of the European Communities, Brussels, Belgium, 1985. ISBN-92-825-5304-3, Available from the National Technical Information Service, Springfield, VA 22161.

(5) Accuracy in Trace Analysis; Sampling, Sample Handling, Analysis. NBS Special Publications 422, Gaithersburg, MD.

Table 1. SW846 Method 3050 and 6010 Precision Values Determined by Quality Control Solutions

ELEMENT	%RSD
Ag	52
As	13
Cd	11
Se	10.1
Tl	9.5
Mo	8.9
V	8.4
Sb	7.7
K	7.2
Zn	6.8
Ba	6.8
Ca	6.7
Ni	6.6
Mg	6.2
Na	5.8
Pb	5.6
Fe	5.3
Cr	5.2
Mn	4.5
Co	4.3
Al	4.0
Be	2.9
Cu	2.6

Table 2. Percent relative Standard Deviation of Analytes Recovered from Spiked Industrial Wastes

ELEMENT	FLY ASH	INDUSTRIAL SLUDGE	ELECTROPLATING SLUDGE
Al	20	14	18
Sb	25	28	40
As	16	19	20
Be	7.6	18	7
Cd	9.5	20	18
Ca	12	13	14
Cr	9.7	18	10
Co	11	17	13
Cu	11	19	9.1
Fe	44	18	15
Pb	9.6	20	19
Mg	17	16	10
Mn	11	17	19
Mo	23	18	43
Ni	9.8	20	16
Se	10	15	18
Ag	50	46	52
Tl	40	28	39
V	12	17	41
Zn	11	20	8.2
Ba	7.2	16	30
Na	25	22	15
K	17	22	5.7
Median Percent RSD	12	18	18

Table 2 (continued). Percent Relative Standard Deviation of Analytes Recovered from Unspiked Industrial Wastes

ELEMENT	FLY ASH	INDUSTRIAL SLUDGE	ELECTROPLATING SLUDGE
Al	19	15	23
Sb	0	47	68
As	32	83	44
Be	27	42	70
Cd	57	17*	22
Ca	10	10	17
Cr	28*	12*	12*
Co	23	21	47
Cu	16*	17	12*
Fe	52	15	12
Pb	33	16*	17*
Mg	20	17	14
Mn	20	18	21
Mo	20	57	49
Ni	34*	16	20*
Se	0	43	74
Ag	49	37	54*
Tl	0	38	45
V	15	28	35
Zn	20	12	9.0
Ba	4.1*	23*	38
Na	34	16	17
K	20	32	19
Median Percent RSD All data	20	18	22
Mean Percent RSD * only	20.5	17	23

Table 3. Multi-Laboratory Performance on the EPA CLP Unspiked Mine Tailing Sample[2]

ELEMENT	MEAN	STD.DEV.	%RSD	CLP TRUE	LCL[1]	UCL[2]
Al	13900	1580	11	15200	7500	22900
Sb	12	19	158	<20	0	44
As	618	161	26	680	380	980
Be	0.5	0.2	49	<1	0	1.6
Cd	1.7	1.4	83	<1	0	7.8
Ca	9850	718	7	10520	7850	13200
Cr	12	12	104	17	0	46
Co	7.2	2.1	29	6.9	0	19
Cu	215	63	30	265	220	310
Fe	10300	1580	15	11200	5910	16500
Pb	5660	1050	19	5830	4310	7340
Mg	14200	1040	7	14730	10910	18560
Mn	92800	926	1	91735	68600	114900
Mo	56	16	29			
Ni	21	8.9	43	22	5	39
Se	43	51	117	<1	0	11
Ag	8	6.8	85	<2	0	26
Tl	73	107	146	3.8	0	9.1
V	13	7.2	54	19	0	46
Zn	362	71	19	425	317	535
Ba	397	43	11	430	360	510
Na	3390	374	11			
K	8130	2620	32	8150	4540	11770

[1] LOWER CONTROL LIMIT
[2] UPPER CONTROL LIMIT

Table 4. Results of Interlaboratory Analysis on TCLP Method. [3]

SAMPLE	ELEMENT	MEAN	STD. DEV.	%RSD	SAMPLE	ELEMENT	MEAN	STD.DEV.	%RSD
	Cd	52.6	31.4	60		Cd	27.6	14.8	54
A-1	Cr	1.54	1.43	93	A-2	Cr	3.79	3.79	100
	Pb	2.97	2.67	90		Pb	3.89	2.59	67
	Cd	4.59	2.82	61		Cd	0.48	0.37	77
B-1	Cr	56.1	22.7	40	B-2	Cr	105	41.4	39
	Pb	3.12	3.13	100		Pb	12.4	13.6	110
	Cd	87.1	67.4	77		Cd	86.7	17.7	26
C-1	Cr	18.5	14	76	C-2	Cr	84.1	23.7	28
	Pb	8.69	7.40	85		Pb	45.7	8.3	18

Table 5. Results of the Interlaboratory Study on Laboratory Performance

LAB CODE	NUMBER OF DETERMINATIONS	NUMBER OF STATISTICAL OUTLIERS	INSIDE 95% CI	INSIDE 1 STD DEV	INSIDE 2 STD DEV
A	50	4 (8)*	28 (56)	31 (62)	45 (90)
B	50	4 (8)	28 (56)	35 (70)	46 (92)
C	50	6 (12)	21 (42)	29 (58)	43 (86)
D	50	3 (6)	26 (52)	32 (64)	47 (94)
E	50	10 (20)	16 (32)	23 (46)	39 (78)
F	50	10 (20)	12 (24)	19 (38)	41 (82)
G	50	4 (8)	33 (66)	38 (76)	46 (92)
H	50	10 (20)	17 (34)	24 (48)	38 (76)
I	50	7 (14)	19 (38)	27 (54)	43 (86)
J	50	2 (4)	31 (62)	39 (78)	48 (96)
K	50	7 (14)	19 (38)	30 (60)	42 (84)
L	50	5 (10)	25 (50)	32 (64)	45 (90)
M	50	1 (2)	32 (64)	41 (82)	49 (98)
TOTALS	650	73 (11.2)	307 (47.2)	400 (61.5)	572 (88)

()* = percent of total analyses

Table 6. Results of Multiple Regression Test

Dependent Variable is Percent Outliers

Variable	Coefficient	St. Error	t-value	p(2 tail)
Intercept	37.596	5.689	6.608	0.0001
95% Window	-0.1968	0.247	-0.798	0.4437
1 Sigma Win.	-0.2649	0.256	-1.037	0.3243

R-Square = 0.8045 Adjusted R-Square = 0.7654

Analysis of Variance to Test the Regression Relation

Source	Sum of Squares	df	Mean Sq	F	p-value
Regression	437.653	2	218.827	20.577	0.0003
Error	106.347	10	10.635		
Total	544.000	12			

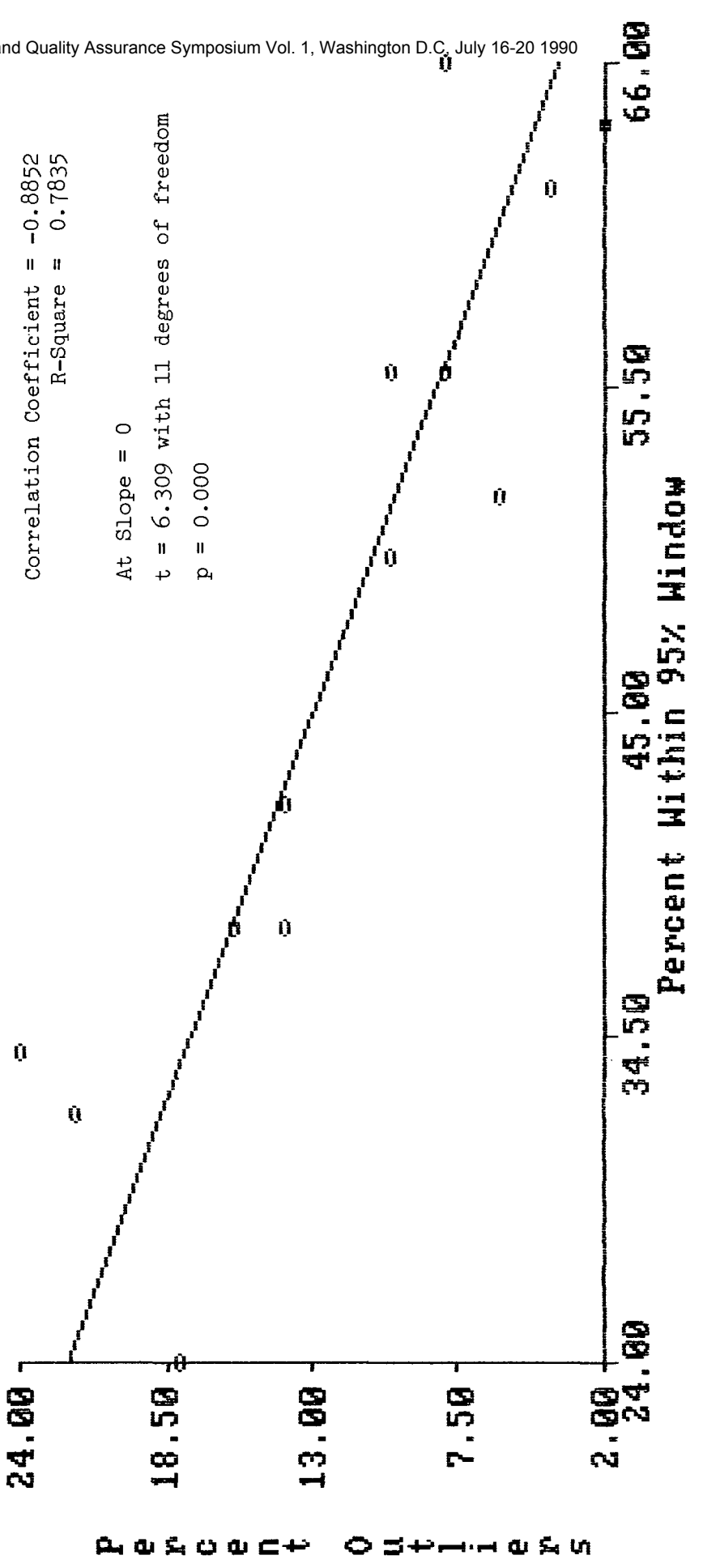
Correlation Coefficient = -0.8852
R-Square = 0.7835
At Slope = 0
t = 6.309 with 11 degrees of freedom
p = 0.000
Percent Outliers
24.00
18.50
13.00
7.50
2.00
Percent Within 95% Window
24.00
34.50
45.00
55.50
66.00

Figure 1.

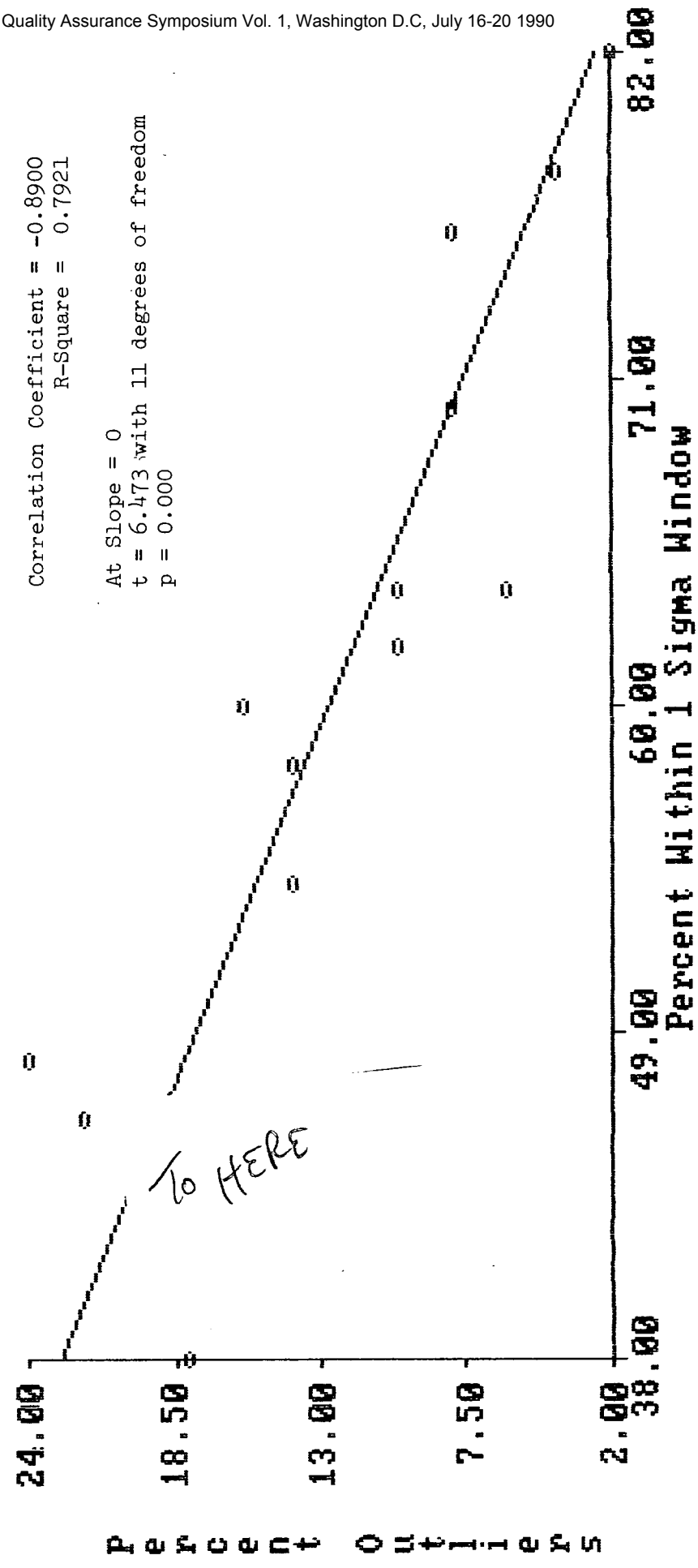
Correlation Coefficient = -0.8900
R-Square = 0.7921
At Slope = 0
t = 6.473 with 11 degrees of freedom
p = 0.000
TO HERE
Percent Outliers
24.00
18.50
13.00
7.50
2.00
Percent Within 1 Sigma Window
38.00
49.00
60.00
71.00
82.00

Figure 2.

28

A MODEL SYSTEM FOR LABORATORY SPC

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INTRODUCTION

Quality assurance is an essential aspect of operation for environmental laboratories. As the number and complexity of analytical tests performed in laboratories increases, so does the demand for quality.

Automation has enhanced the ability of laboratories to accommodate the increase in the volume and sophistication of analyses and the vast amounts of data generated. While automation has been readily adapted to the functions of instrument operation, data reduction, sample tracking, and reporting, it has historically been applied with much less frequency to the quality assurance and quality control functions in laboratories.

The increased efficiency of automated laboratory instrumentation challenges traditional approaches to laboratory quality assurance.

In manufacturing industries a concept known as statistical quality control (SQC) or statistical process control (SPC) has been used extensively for monitoring and improving quality.

Because successful application of SPC requires "real time" implementation, numerous products for automating SPC procedures have been developed and used for many years. Many of the principles of SPC can be adapted for use in laboratories, as can much of the available computer hardware and software.

STRATEGIES FOR AUTOMATING LABORATORY QUALITY

Science has been defined as "organized knowledge". A computer is basically a powerful "information organization machine" which, when equipped with the proper software, can organize even the most complex matrix of information in a manageable and useful way. Automating laboratory QA/QC information is a perfect application for computers.

There are two basic approaches which can be used to reach a decision about how best to automate any activity:

THE "HARDWARE DRIVEN" APPROACH

1. What are the intended applications or purposes for the computer?

2. What performance specifications are required?

3. What types of computer hardware will meet the performance specifications?

THE "SOFTWARE DRIVEN" APPROACH

1. What are the applications for which automation is called for?

2. What kinds of applications software are available to fit the needs?

3. What operating system does the software require?

4. What types of computer hardware are compatible with the operating system?

If the intention is to develop your own computer application, (i.e. write a computer program from scratch, custom tailored to your own specific needs) then the hardware driven approach is correct. If you are not a programmer and you do not have the resources of a programmer at your disposal, then the software driven approach is a necessity. Regardless of which approach is taken, the end result will be an "automation system" whose two major components are hardware and software.

Both approaches require an analysis of actual or potential applications. In order to accomplish automation of the QA/QC functions a host of applications must be considered:

APPLICATIONS NEEDED FOR QA/QC AUTOMATION

1. Information storage and retrieval. (Database)

2. Data manipulation and reduction. (Spreadsheet/Statistics)

3. Data output.(Graphics)

4. Word processing and text processing. (Word Processing/Desktop Publishing)

Other applications which might be desirable:

5. Direct data acquisition.

6. Prediction/simulation.

The advantages of the "software driven" approach become evident upon examination of the applications needed for QA/QC automation.

The industrial origins of automated quality are reflected in the types of software applications which are central to its implementation: graphics, statistics, spreadsheet, database, and word processing. These applications are virtually generic in the business or engineering office of today. All the applications listed are available as commercial off-the-shelf ("COTS") software for a variety of operating systems and computer hardware.

Typically, Laboratory Information Management Systems (LIMS) software will incorporate most, if not all, of these functions. It is in the area of **integration** of these functions that strategy once again comes into play.

The purpose of software integration is to permit a variety of software programs to share the same data, perform various manipulations of the data, and effect automatic transfer of information between programs with minimum intervention on the part of the user. Software integration can be implemented in a variety of ways:

INTEGRATION IMPLEMENTATION

1. Tight integration- a single memory-resident program which can perform all the tasks required.
   (Example: Lotus Symphony)

2. Managed integration- specially written programs running under a "manager" or "coordinator".
   (Example: Microsoft Windows)

3. Loose integration- completely independent programs running under a coordinator.
   (Example: IBM Topview or Tandy DeskMate)

The next step is to evaluate the integration potential of software/hardware combinations based on the following considerations:

IMPLEMENTATION CONSIDERATIONS

1. Budget.

2. Current Hardware/Software resources - compatibility.

3. Availability.

4. Support.

5. Documentation.

The fundamental concept is "buyer beware!". Even when computer hardware/software is of the "COTS" variety and within your budget it is not always safe to assume that it is compatible, available, well supported, or well documented. The computer marketplace is extremely dynamic. New producers of hardware and software surface almost daily and as they do others drop out of sight. This is particularly true of vendors of specialized software products like LIMS and SPC applications.

The safest course of action is to choose companies with a large client base and a long-standing reputation for quality products and customer support. With the many new and innovative products in the marketplace the temptation to try a fledgling product may be overwhelming. If this is the case, then insist on a demonstration of the products under the actual conditions of use you intend for them. Accept the products only on a trial basis until you have demonstrated satisfactorily that they are free of defects and capable of performing as advertised. It is also desirable to purchase the actual source code for any commercial software products, if possible. This affords some protection against obsolescence if the vendor discontinues support or goes out of business.

A MODEL SYSTEM DEVELOPED BY WMI-EML

The model system developed by WMI-EML has evolved over the past two years from a PC-based test bed(see fig. 1)to a proposed VAX-based platform using the Virtual Memory System (VMS) operating system and Rdb, a relational database(see fig. 2).

The original PC-based model system allowed users to become familiar with typical functions of a tightly integrated industrial SPC package at relatively low costs. The software (/SPC-QIMS, The Crosby Company, Glen Ellyn, IL.)was installed on a VAX computer running Personal Computing Systems Architecture (PCSA), an extension of Digital Equipment Corporation's systems and networking architecture, DECnet. PCSA merges the VMS and PC Disk Operating System (DOS) environments while creating a framework for integrating personal computers into a VAX-based platform.

A DEPCA(DEC Ethernet Personal Computer Adapter) was installed in the personal computers to allow communications with the VAX server via thin wire Ethernet cables.

Two types of VMS services for PCs were used: file service and disk service. VMS file service provides a remote DOS file system that appears as a transparent extension of the PC system's local computing environment. Users can share DOS files stored on a VAX network server's disk through concurrent access. This system allows a DOS application program to reside on the VAX while being invoked and used by a PC. VMS disk service sets aside space on a VMS disk for access by a PC user as a virtual disk, that is a DOS-formatted remote disk. Disk management may be done from the VAX or remotely from the personal computer.

The combination of disk and file services allowed the PC-based SPC quality software to be used by several PC users concurrently and also allowed for a large disk storage area for all data files generated by the program. The data files, stored on a virtual disk, were afforded the same level of security as VMS files on the system and were included in nightly system backup routines.

While the PC-based model system is viable, it is not without limitations. The DOS utility programs that are specific to PC hardware devices cannot be used with file services, such as. CHKDSK, FDISK, DISKCOPY, DISKCOMP and FORMAT. Only one user at a time may have read and write access to the virtual disk using disk service. The DOS files on the virtual disk are not shareable with VMS users operating terminals or VAX workstations. Additionally, the speed of the SPC software operating under PCSA was noticeably slower than the same software operating on a PC in stand alone mode.

These limitations have prompted the initiation of development on a new model system which is entirely VAX-based. This model will exploit the true multitasking/multiuser hardware and software system advantages, processing speed, and memory inherent in the DEC VAX computing platform.

Knowledge gained through two years of experience with a LIMS using a hierarchical database structure has lead to development of improved database applications using a relational structure. These improvements will be incorporated in the VAX-based model through the use of RDB, a relational database product, as the core application. System configuration, data entry, and reporting will be accomplished via VAX workstations and/or terminals. Personal computers equipped with DEPCA, running terminal emulation software, will also have access to the system. Customized ad hoc reporting can be accomplished through the use of tools such as UDMS(User Data Management System, Interactive Software, Denver CO.), DEC Datatrieve, Structured Query Language(SQL), or forth generation languages(4GL).

The architecture of the VAX-based model is designed to allow maximum access and utility while maintaining real time on-line

performance. The computing capacity of the VAX/VMS environment will allow future development of expert systems for laboratory SPC.

The long term goal of the laboratory SPC development program is to produce a system with distributed collection and access to data while sharing the data to avoid "islands" that cannot communicate. The challenge of developing an adaptable system which provides a high level of access while communicating with a variety of instruments in real time and, at the same time, provides graphical representations of trends and data distributions with situation appraisal, problem analysis, and decision analysis will ultimately lead to an artificial intelligence system for laboratory quality applications.

SUMMARY

The diverse nature of the computing environment in the modern laboratory makes for an assortment of viable automation strategies. The possibilities are almost endless: PC vs. mainframe; stand-alone vs. networked; commercial vs. custom.

The starting point for deciding which strategy is appropriate for any new application should be a review of current computing resources. This review should consider all hardware and software currently in use in the laboratory. Particular attention should be given to any LIMS-type databases utilized by the laboratory. If a LIMS system is already in use, a number of important decisions have probably been made regarding database structure, number and type of workstations, and quality of output. These decisions should be reviewed in consideration of "cross-compatibility" with the type of applications necessary for quality automation.

The examples presented in this paper are indicative of only two potential solutions governed by the circumstances existing in the laboratory which produced the model systems.

Acknowledgment: The author gratefully acknowledges the assistance of Jean Holley of the WMI-Environmental Monitoring Laboratories, Inc. Computer Services development staff in providing invaluable information and assistance used in the preparation of this paper.

References

Dessy, Raymond E., The Electronic Laboratory, American Chemical Society, 1985

Ferrill, Paul, 1990. "PC Meets VAX," PC Magazine, pp. 243-267

Hartely, T.F., Computerized Quality Control, Ellis Horwood Limited, 1987. (US distributors: John Wiley & Sons, NY,NY)

Tikkanen, M.W. and Wilson, G. 1988 "Statistical Process Control: A Versatile Tool of Scientific Management," Spectroscopy, VOL. 4, NO. 7, 30-35

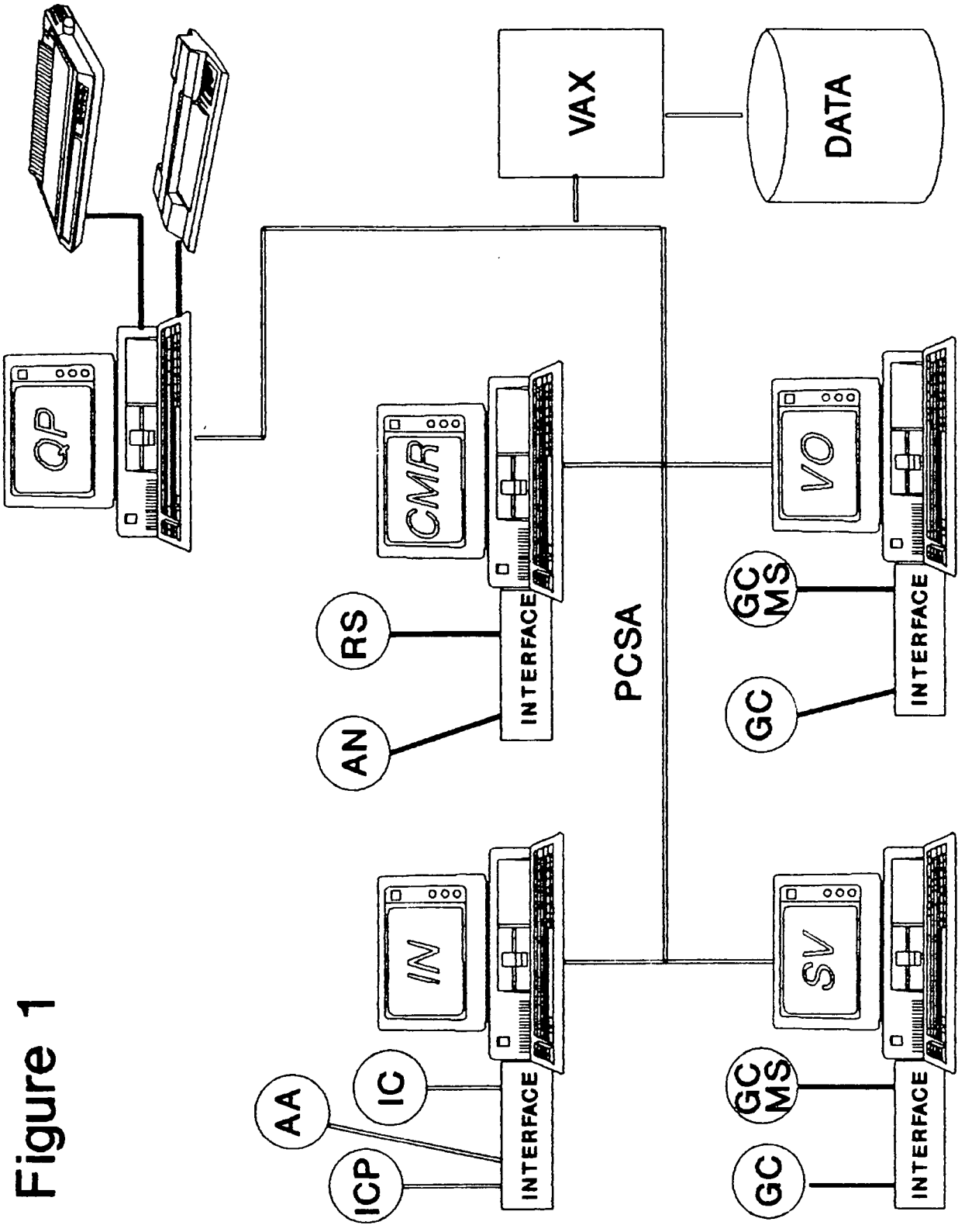
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Figure 1

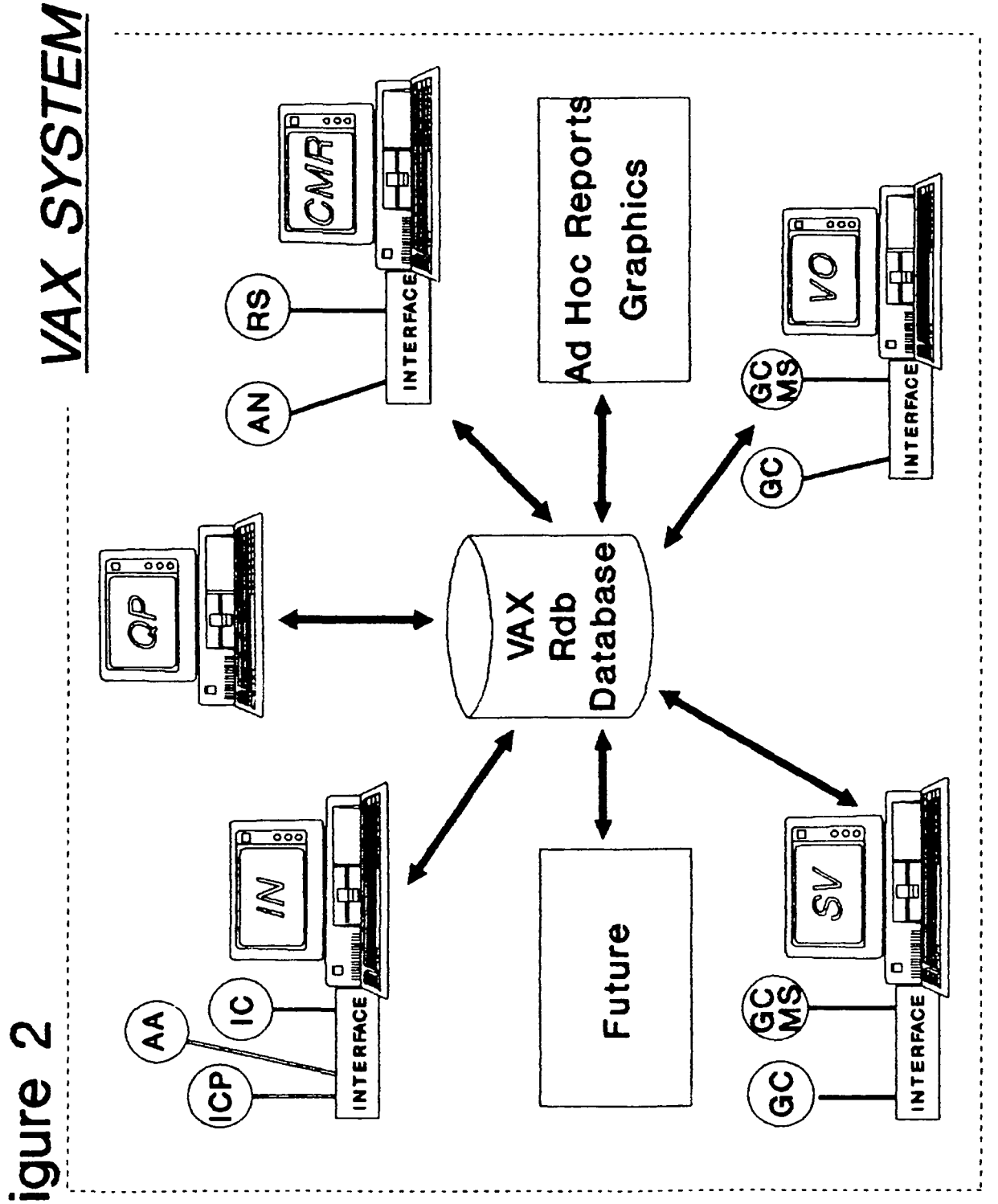
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Figure 2

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PERFORMANCE EVALUATION OF A TRANSPORTABLE GC/MS FOR ENVIRONMENTAL SURVEILLANCE: COMPARISON WITH LABORATORY-BASED METHODS

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The analytical support of environmental field assessment and remediation activities is based upon laboratory-based methods for liquid and solid wastes. Although these methods provide critical information to field support activities, these laboratory-based methods have some shortcomings. Transportation costs, sample holding times, instrumentation costs, sample preparation and analysis time all impact the overall cost and time requirements for these analytical methods.

Some of the advantages of a field transportable instrument over a laboratory-based instrument include:
(1) The problems associated with the shipment of samples to the laboratory and sample holding times are minimized since the analysis of the sample occurs within minutes of sampling. This minimizes the potential loss of volatile materials from the sample between the point of sampling and the point of analysis.
(2) The costs of assessment and remediation activities are significantly reduced. Site activities can be directed in real-time based upon the results of sample analysis without the long time delays usually encountered in waiting for analytical results from remote laboratory-based support.
(3) A field transportable instrument can help field personnel determine the scope of work required for assessment and remediation. The analyses that are performed at the field site can be used in determining the size of the contamination zone as well as the size of the sampling grid to be used. This results in a more selective sampling plan that will save both time and money.

These advantages are based upon the premise that the accuracy and precision of a field transportable instrument is equal to or better than laboratory-based instrumentation.

A transportable gas chromatograph/mass spectrometer (GC/MS) based on the Finnigan Ion Trap has been built at Los Alamos National Laboratory for the analysis of volatile organic compounds. To assess the quality of data obtained with this transportable GC/MS, its performance is compared with that of laboratory-based methodology (EPA method 8260, SW-846[1]) using a GC/quadrupole mass spectrometer system. Evaluation of the performance of the two GC/MS systems is based on precision, accuracy and working concentration range as outlined in SW-846. A comparison is made between the two GC/MS

systems based upon relative retention time of target components, ion abundances, the cost of analysis and method detection limits for water and soil matrices (MDL's)[2].

REFERENCES

1. Test Method for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Update I , Method 8060. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

2. J.A. Glaser, D.L. Foerst, G.D. McKee, S.A. Quave and W.L. Budde. Trace Analyses for Wastewaters, Environ. Sci. and Technol. 15(12): 1426-1435

30 Paper withdrawn.

31

PREPARATION AND CHARACTERIZATION OF QUALITY ASSURANCE MATERIALS FOR XRF MEASUREMENTS OF LEAD IN SOILS

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ABSTRACT

Soils collected from inner-city locations in 3 metropolitan areas were sieved, pulverized, homogenized and split into 20 gram fractions to be introduced as double blind audit samples into analytical sample streams at participating laboratories. Bulk samples with lead concentration ranging from 100 to 19000 parts per million were characterized for homogeneity by X-ray fluorescence analysis. Dust samples were collected from household interiors, homogenized and split into smaller sub-samples, and characterized for similar utility.

Characterization by wet chemistry-ICP analysis and X-ray fluorescence is described. Accuracy, precision, detection, calibration, and acceptance window parameters were determined for each audit sample type. The information is being used in a study program of lead abatement effects in the three cities.

INTRODUCTION

Bulk quantities of soils and dusts were processed to produce gram and sub-gram sized audit samples through a series of sieving, pulverizing and blending operations. They were then characterized for use as double blind audit materials in the Quality Assurance portion of a program designed to measure lead in urban soils and dusts from three large metropolitan areas. The original materials were furnished to the Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) from typical sites in the three areas.

The preparation involved sieving, pulverizing, blending, and testing for homogeneity and concentration levels. Packaged splits to be used as audit samples have been provided to quality assurance officers at participating laboratory in 20 gram quantities for soils and 2 gram quantities for dusts. The Quality Assurance plan calls for the laboratory sample manager or quality assurance manager to introduce the characterized audit samples into the analytical sample streams as regular samples. The QA officer would know the identity of the audit samples but not the concentration values for lead. The audit samples must be double blind to the analyst.

The values for lead in the QA audit samples are to be reported by the laboratory QA officer to a third party QA officer. That person will determine whether the reported values for lead agree well enough with reference values and are within calculated acceptance windows to determine if the data from the related batch samples are suitable for their intended use.

Blind audit samples introduced as regular sample input should resemble the rest of the samples as closely as possible. This is to retain integrity of the blind sample values and to avoid biases caused by any special treatment that might be afforded samples that are identified as audit samples. A compromise must be accepted between having samples that look coarse and natural and between having finely ground materials homogeneous enough to yield a very narrow range for reproducibility. A level of sample sieving to furnish particles with a maximum diameter of 0.25 millimeters was considered acceptable.

One of the methods to be used in the study for which these samples were prepared, is X-ray fluorescence, (XRF). X-ray fluorescence analysis of lead, using L-series emission lines, will record very few signals for fluorescent X-ray photons emanating from beyond 2 millimeters depth in most soil materials. The characteristic XRF signal intensity for a given concentration of lead in a sample as the lead bearing particles are more finely divided and distributed uniformly throughout the sample.
One objective in this study was to determine the degree to which this particle size effect impacted precision and accuracy with respect to these samples, and to determine reasonable limits of acceptance for audit sample data related to analyses of those materials.

The determinations of lead in unknown soil and dust samples are in progress. In order to retain the integrity of the blind and double blind character of the audit samples, relative values for lead concentrations will be used for this paper in place of the true values. Calculated relative standard deviations will be true and calculated acceptance windows will be very close to the ones used in the project. The three cities and participating laboratories will not be identified other than as locations A, B, C, or as laboratories A, B, or C.

Preparation Laboratory Operations

Two bulk soil samples, of different concentrations were supplied to EMSL-LV from each city. From these six samples, EMSL-LV provided three blind audit samples at low, mid, and high concentration ranges and three calibration standards at similar concentrations. The bulk samples were thoroughly dried, sieved and homogenized into 20-gram aliquots. Participating laboratories supplied EMSL-LV with sample containers, labels, and the appropriate labeling techniques for the samples in order to maintain the samples anonymity to the analyzing laboratories.

Sample Receipt

EMSL-LV supplied the field samplers in each city with 30-gallon plastic barrels in which bulk soil samples were collected. When the samples were transported to the preparation laboratory, EMSL-LV identified each soil audit sample by an alpha numeric sample code that uniquely identified each sample. Once audit samples were ready to be sent, the EMSL labels were removed and the city labels were affixed to the sample containers.

Audit Sample Preparation Procedures

Figure 1 describes the soil preparation procedures.

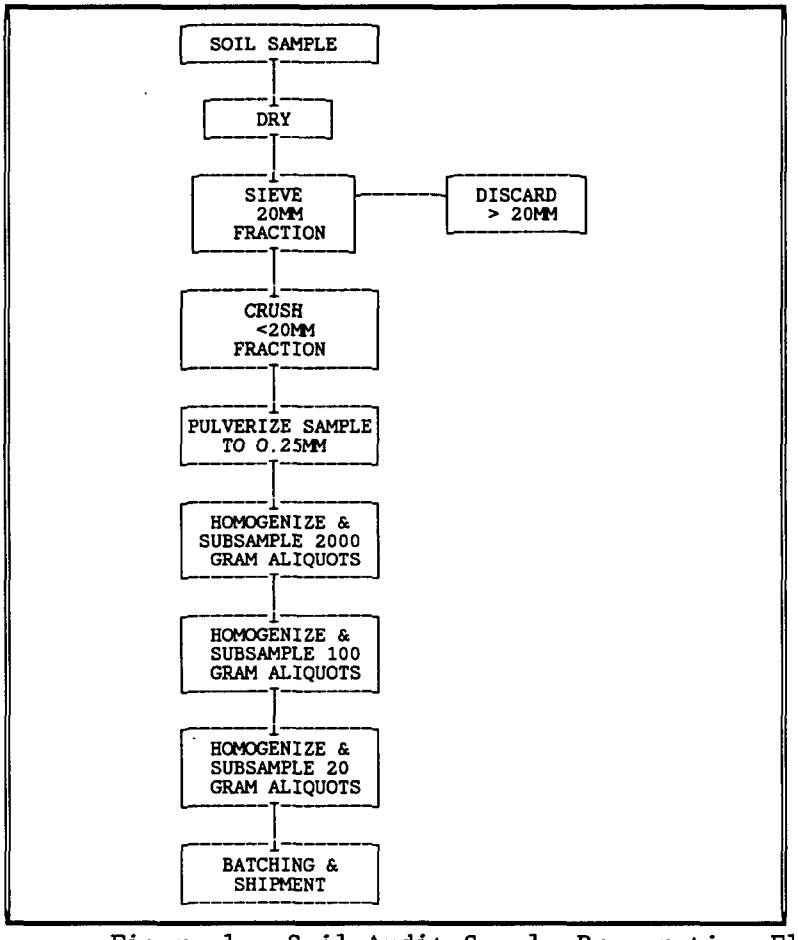


Figure 1. Soil Audit Sample Preparation Flow

Sample drying

Sample drying tables constructed of PVC and heavy mesh were used to air dry the samples. Use of the mesh enhanced air circulation and increased the rate of sample drying. These tables were located in a dust free drying room.

Two sheets of kraft paper, approximately 1 square meter in area, were placed on the drying table. The sample was spread on top of the sheets of paper, taking care not to lose any soil from the paper or contaminate any adjacent samples. Large clods that impeded the spreading of the sample over the entire area of the paper were disaggregated. An additional sheet of kraft paper was placed loosely over the sample. The soil samples were stirred daily with gloved hands to facilitate drying.

Experience in prior surveys established that samples dry to a constant

moisture content of between 1-2.5% within three days at the EMSL-LV preparation laboratory. EMSL-LV allowed the samples to air dry for four days.

Disaggregation and Sieving

After a bulk soil sample was determined to be air dry, it was ready to be disaggregated and sieved to remove large rock fragments and to prepare the sample for crushing, pulverization, homogenization and subsampling. The sieving procedure was accomplished in two steps: (1) disaggregation and sieving through a 20-mm sieve and, (2) disaggregation and sieving through a 0.25-mm sieve after crushing and pulverization.

Crushing

After soils were sieved through the 20-mm sieve, the <20-mm material was passed through a rock crusher. The intention of crushing was to reduce material between 2-20-mm to <2-mm.

Pulverizing

The routine soil samples analyzed by the participating laboratories were prepared and ground to a maximum particle size of less than 0.25mm. Therefore, it was necessary to provide audit materials of the same matrix. The preparation laboratory pulverized the less than 2-mm soil material to a particle size of less than 0.25mm.

With a scoop, a portion of the less than 2-mm soil material was placed into the pulverizer opening. The pulverizer ground the soil and deposited it into a collection bin. After the first scoop was completed, this material was sieved through the 0.25-mm sieve. If all the material passed through the sieve, the grinding plates were sufficiently close enough to continue pulverization; if not, the plates were adjusted and the procedure repeated on the same sample until all the material passed through the 0.25-mm sieve.

Homogenization and Subsampling

Before the soil material could be aliquotted to 20-gram samples it had to be thoroughly homogenized. Due to the large volume of soil for each audit sample, this homogenization was accomplished in three stages: (1) the homogenization of the bulk sample and aliquotting to 2 kg, (2) the homogenization of the 2-kg aliquots and aliquotting to 100 grams, and (3) the homogenization of the 100-gram aliqouts and final aliquotting to 20-gram samples.

Homogenization and Subsampling of the Bulk Sample to 2-kg Aliquots

Homogenization of the bulk sample was accomplished using a drum homogenizer/ cone-and-quartering technique or by riffle splitting. The drum homogenizer is basically a 55 gallon drum with blades attached inside to mix the soil. The cone-and-quartering and riffle splitting techniques are used to produce soil samples of uniform, particle size distribution.

Drum homogenization/Cone and Quartering

Each bulk sample, as received was placed into the drum homogenizer which was slowly rotated for five minutes. The sample was then placed onto a large piece of kraft in the shape of a cone. Homogenization of the cone was performed by dividing the cone into four equal quarters. Using a shovel, the first quarter was removed to form a new cone. The third, second and fourth quarters were piled sequentially over the first quarter. This procedure was performed seven times in succession. If the riffle splitter was used, the sample was evenly distributed across the baffles of the riffle splitter. The procedure was repeated five times in succession.

Subsampling

Once the homogenization operation was completed, 2-kg subsamples were taken. If the cone and quartering technique was used, a clean 2-L sample bottle was placed at the bottom of the cone and, with an upward movement, a sample weighing approximately 2000 grams (+/- 20 grams) was collected. If the riffle splitting technique was used, a clean 2-L sample bottle was placed at one end of the collecting bin and moved to the other end to fill the bottle. The sample was labeled using the procedure described earlier.

Each 2 kg sample was then homogenized and split in a medium sized Jones-type riffle splitter to 100-gram samples and then homogenized in a small riffle splitter and aliquoted to 20 grams. These two procedures were done sequentially in order to avoid the use of intermediate sample containers and the possibility of mislabeling.

Once a set of samples of a given concentration had been prepared, 50 samples were chosen in such a way that an equal number of samples were selected from each of the original 2 kg bottles but were randomly selected within each of the bottles. These samples were sent to the EMSL-LV analytical laboratory where they were characterized. As samples were characterized, precision estimates for each audit sample type were developed. If the pooled precision estimate for an audit sample whose concentration was above 10 times the detection limit (~10 ppm) was greater than ten percent relative standard deviation, the preparation laboratory rehomogenized the sample.

Sample Shipment

The 20-g soil samples were shipped to the laboratories in the sample containers provided by the particular laboratory. As samples were shipped, certain forms were sent to the laboratories and QA managers. The forms sent to each laboratory contained information as to the types and numbers of samples sent, and the city sample code information on each sample. The QA manager also received a copy of this form, and was also be made aware of the EMSL sample code which identified the concentrations of each sample.

Characterization of soil and dust audit samples for lead

Samples were analyzed by XRF to determine lead concentrations and homogeneity. ICP or GFAAS was used to verify XRF concentrations.

Calibration

The XRF is calibrated by acquiring spectra from a series of urban soil standards with known lead concentrations. Acquisition conditions are given in the sample analysis section. The lead Lß peak and silver compton peak intensities are measured from the spectra and the ratio of these intensities are calculated. A calibration line is calculated using linear regression of the ratio vs. lead concentration. A sample calibration curve is pictured in Figure 2. Table 1 lists the recoveries for the standards when plugged back into the regression line. Recoveries ranged from 91.9 % to 104.1 %.

Table 1. Comparison of True Concentration vs. Interpolated concentration for the XRF Calibration Standards.

TRUE CONC (ppm)	INTERPOLATED CONC (ppm)	PERCENT RECOVERY
443.2	407.33	91.9
848.7	883.70	104.1
995.0	981.20	98.6
1068.9	1053.36	98.5
2455.1	2378.96	96.9
3772.2	3892.46	103.2
17993.0	17979.10	99.9

X-ray Fluorescence Sample Analysis

Five gram powdered soil audit samples or 400 mg dust audit samples were poured into a 31mm diameter X-ray sample cup and analyzed by Energy Dispersive X-ray Fluorescence (XRF). A Kevex Delta 770 XRF was used for all measurements. The analysis conditions are: Ag secondary target, primary X-ray tube (Rh) voltage = 35 KeV, X-ray tube current = 3 mA, atmosphere = air, counting time = 200 seconds. Sample spectra were aquired and the lead Lß and Ag compton peak intensities were measured. The lead Lß peak/Ag compton peak ratio was calculated. The lead concentration is determined from the calibration curve of ratio vs concentration.An XRF spectrum for soil sample C is shown in figure 3 illustrating the peak intensity information used for the analyses.

Fifty aliquots from each of 4 soil and 6 dust samples were analyzed by XRF. Both concentration and homogeneity were critical for the intended use of the audit samples. therefore as samples were characterized, precision estimates for each audit sample type were developed. If the pooled relative standard deviation (RSD) for an audit sample whose

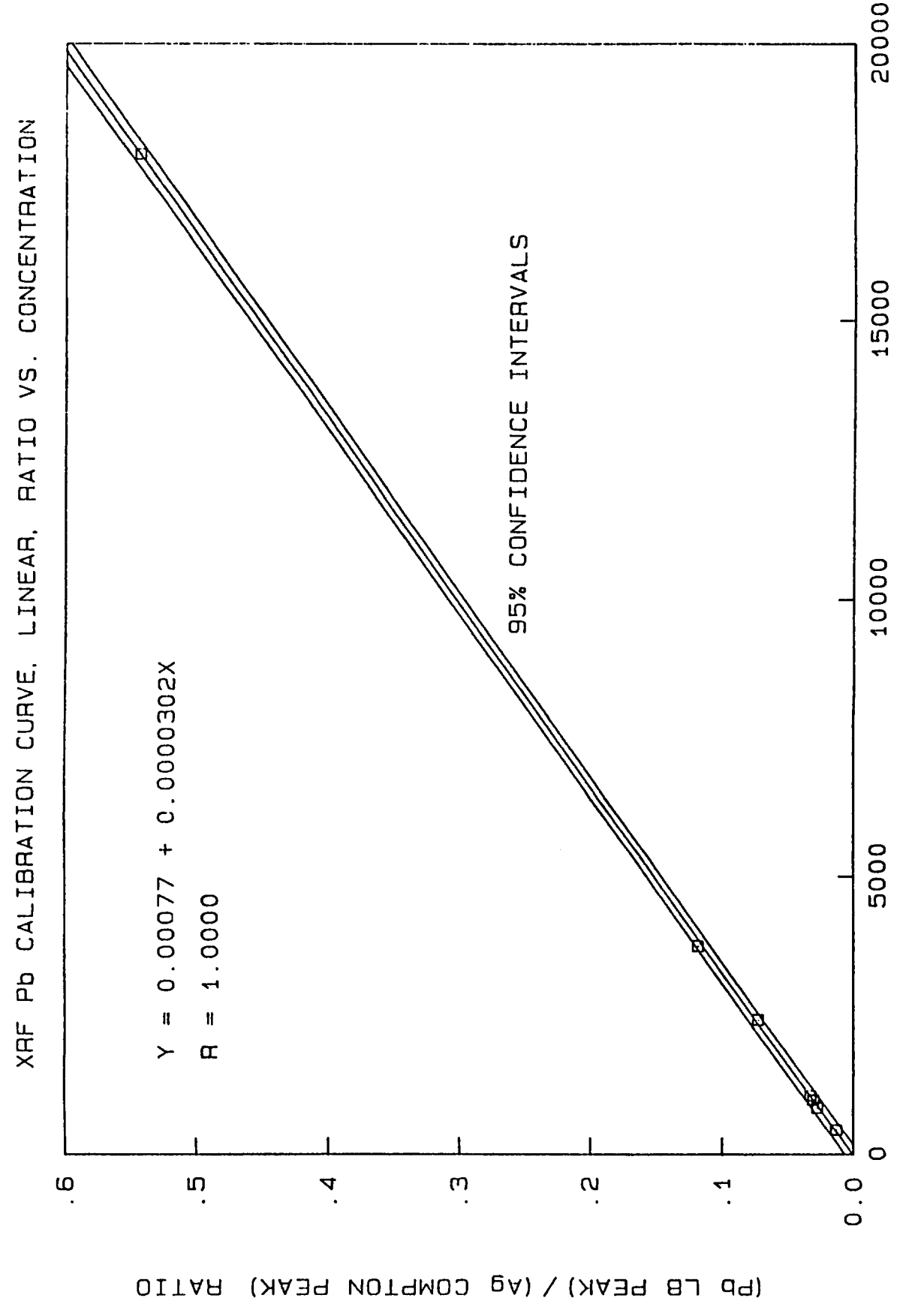


Figure 2 XRF calibration for Pb in soils.

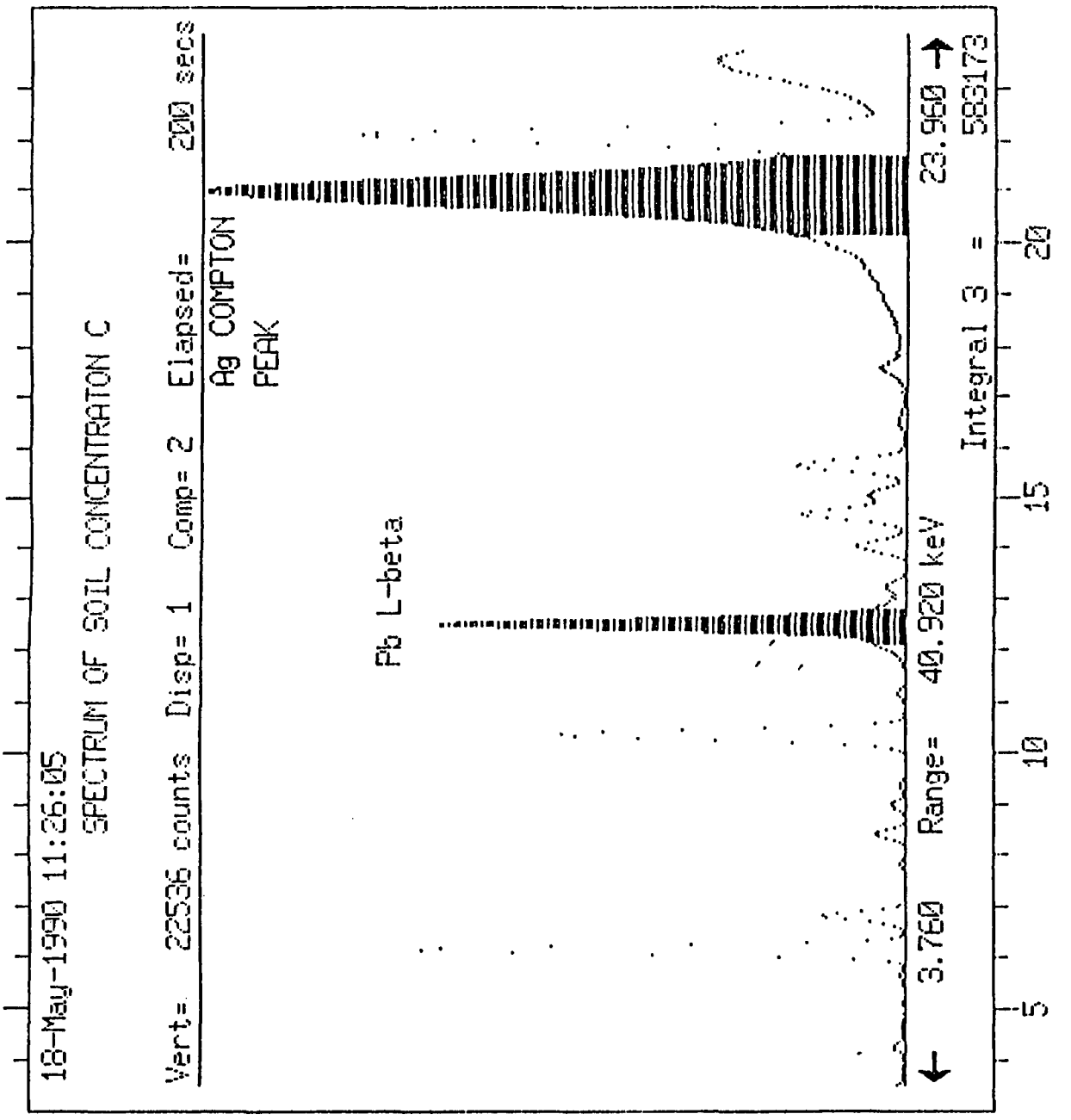


Figure 3 X-ray Fluorescence spectrum.

concentration is above 10 times the detection limit (~10 ppm)) was greater than ten percent, the preparation laboratory combined all 20 gram aliquots, rehomogenized, then resplit into new 20 gram aliquots.

Verification Analysis

The XRF soil audit concentrations were verified by ICP or GFAAS. From the fifty aliquots of each soil analyzed by XRF, a subset of 7 aliquots was analyzed by ICP or .

Prior to ICP or analysis the samples were digested as follows: approximately one gram of a homogenized audit sample was weighed (to the nearest 0.1 mg) into a 250 mL beaker, 50 mL of 7N HNO_3 was added, the sample was then heated on a hot plate for two hours at 90 degrees centigrade, removed from the hot plate and cooled, then filtered through Whatman No. 1 filter paper, and diluted to 200 mL in a volumetric flask with reagent water.

After digestion the samples were initially analyzed by ICP. If the digestate concentrations were less than 100 ppb, the sample digestates were analyzed by . The ICP() values are compared to the XRF. The ICP values are not considered significantly different if they lie within the concentration windows determined by XRF. If the ICP values are significantly different, the cause must be determined and appropriate action taken.

RESULTS

The XRF and ICP results for four soil audit samples are listed in Tables 2 and 3. Table 4 lists the mean XRF and ICP soil results along with relative difference between values. The ICP results are slightly higher than the XRF results indicating a slight bias in the methods. The reason for the bias is being investigated. The XRF results for six dust audit samples are listed in Table 5. Verification analyses by ICP are not yet complete.

A two way analysis of variance is illustrated in Figure 4 with the relative standard deviations for sample splits(within 2 Kg bottles) compared to relative standard deviation between bottles for soil samples B and C.

A statistical scatter plot showing XRF-measured concentration versus 2 Kg. bottle number splits is shown in Figure 5 for soil sample "C." The heavy vertical lines in the diagram indicate a calculated acceptance window of acceptance based a data originateing from a single laboratory. A similar plot for dust sample "I" is shown in Figure 6.

XRF measurement precisions for soil and dust samples are shown graphically in figures 7 & 8 respectively. RSD deteriorates below 100 ppm for the dust samples.

Table 2. Soil Confidence Windows for XRF Analyses

SAMPLE	SAMPLE MEAN	SAMPLE STD DEV	95% INTERVAL* LOWER	95% INTERVAL* UPPER	99% INTERVAL* LOWER	99% INTERVAL* UPPER
A	242.91	8.88	224.54	261.27	218.22	267.59
B	738.74	34.50	668.70	808.77	645.27	832.20
C	4872.10	162.20	4544.88	5199.31	4436.49	5307.71
D	10868.06	336.19	10184.71	11551.39	9955.61	11780.50

* Windows generated using a Bi-weight procedure.

Table 3. Soil Confidence Windows for ICP () Analyses

SAMPLE	SAMPLE MEAN	SAMPLE STD DEV	95% INTERVAL* LOWER	95% INTERVAL* UPPER	99% INTERVAL* LOWER	99% INTERVAL* UPPER
A	260.73	11.58	228.69	292.76	210.29	311.1
B	797.05	22.15	719.11	874.98	674.35	919.7
C	5120.05	99.19	4849.78	5391.26	4694.28	5546.7
D	11656.91	287.30	10931.02	12382.81	10580.90	12732.9

* Windows generated using a Bi-weight procedure.

Table 4. Comparison of XRF vs. ICP/ for Soil Concentration

SAMPLE	XRF SAMPLE MEAN (ppm)	ICP/GFAA SAMPLE MEAN (ppm)	RELATIVE DIFFERENCE%
A	242.91	260.73	7.08
B	738.74	797.05	7.59
C	4872.10	5120.05	4.96
D	10868.06	11656.91	7.00

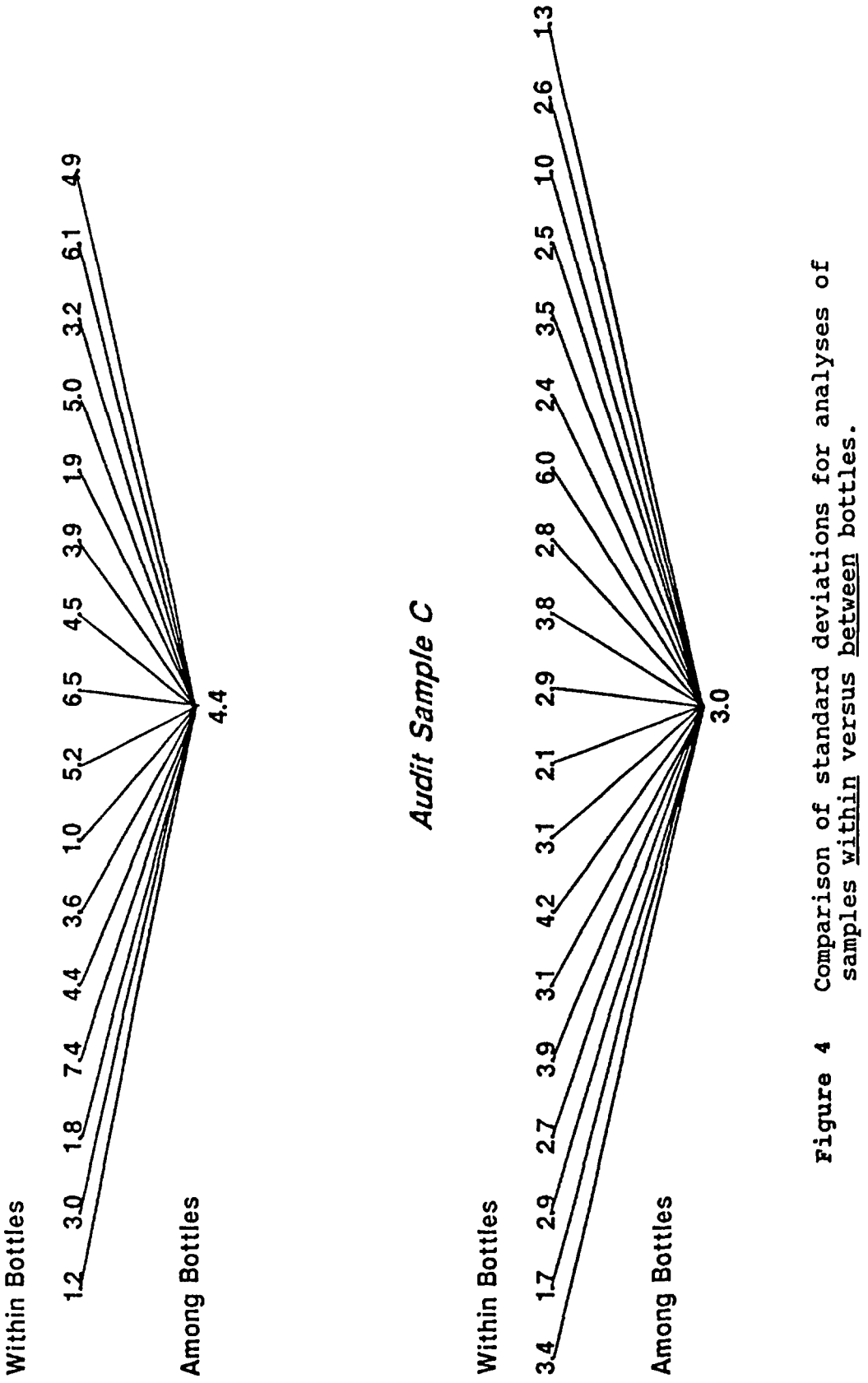
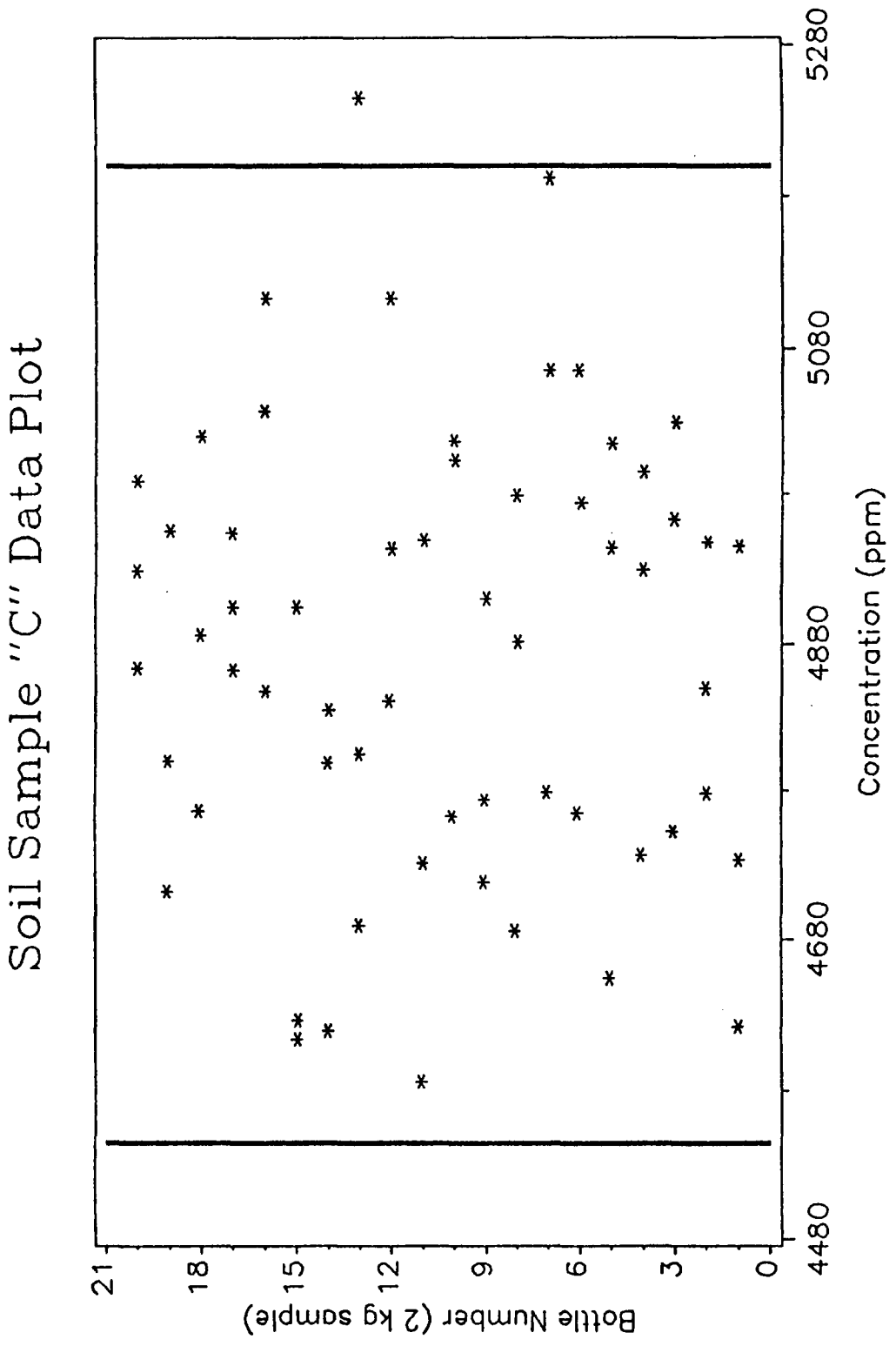
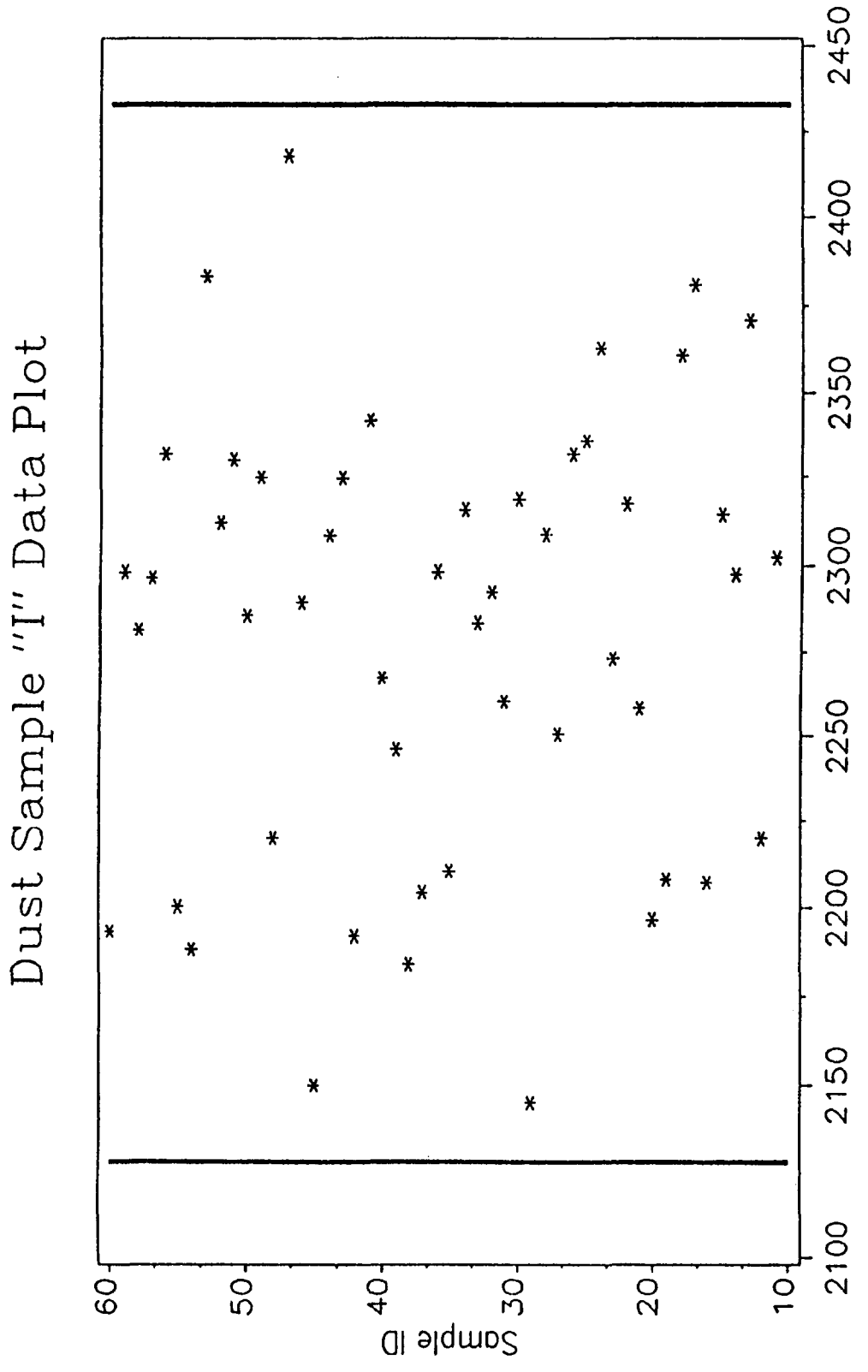


Figure 4 Comparison of standard deviations for analyses of samples within versus between bottles.



Scatter plot of sample "C" concentration audit samples from EMSL-LV characterization associated with the 95% confidence interval Biweight audit windows.

Figure 5 Data plot for soil sample "C".



Scatter plot of sample "I" concentration audit samples from EMSL-LV characterization associated with the 95% confidence interval Biweight audit windows.

Figure 6 Data plot for dust sample "I".

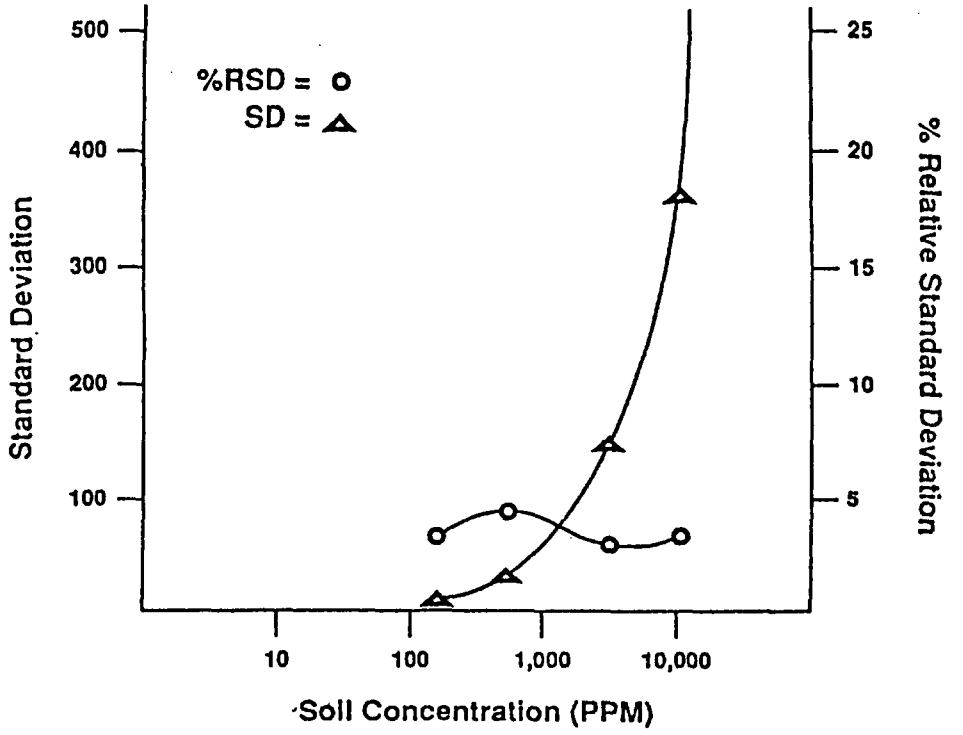


Figure 7 Precision estimates for XRF measurement of lead in soils.

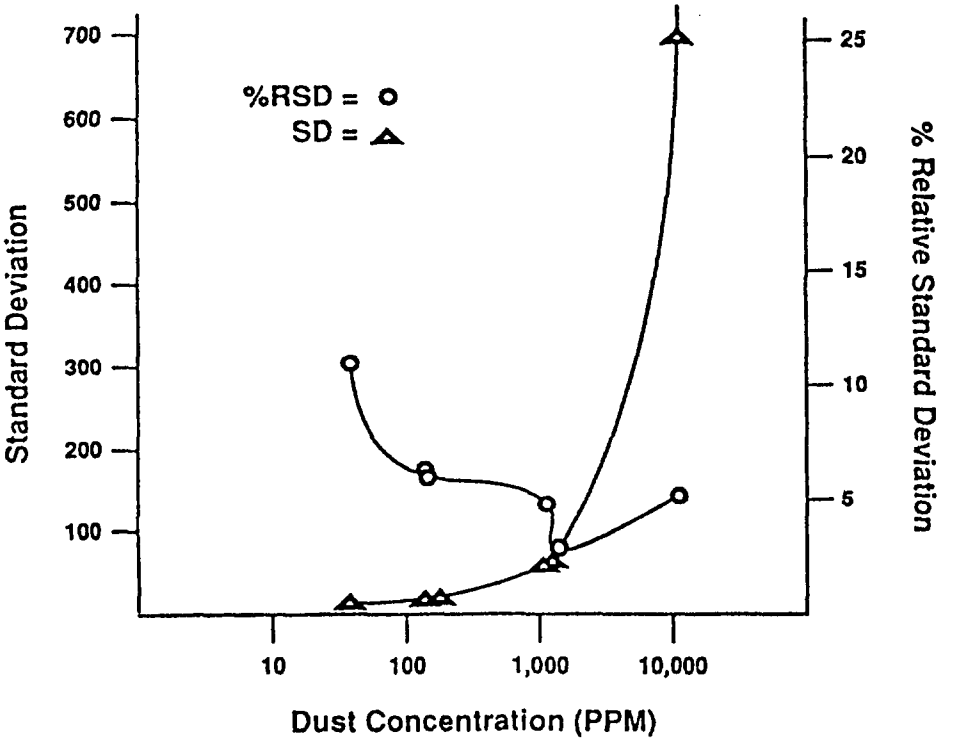


Figure 8 Precision estimates for XRF measurement of lead in dusts.

Table 5. Dust Confidence Windows for XRF Analyses

SAMPLE	SAMPLE MEAN	SAMPLE STD DEV	95% INTERVAL* LOWER	95% INTERVAL* UPPER	99% INTERVAL* LOWER	99% INTERVAL* UPPER
E	62.74	8.04	46.45	79.02	41.00	84.47
F	201.84	14.14	173.17	230.51	163.58	240.10
G	264.44	16.87	230.21	298.66	218.77	310.11
H	1183.87	52.61	1077.07	1290.68	1041.35	1326.40
I	2281.38	75.44	2128.52	2434.24	2077.39	2485.37
J	13612.02	651.14	12289.76	14934.26	11846.98	15377.04

* Windows generated using a Bi-weight procedure.

SUMMARY

Audit samples covering a lead concentration from 100 to 20000 parts per million were prepared from real-world inner-city soils and dusts. 20 gram splits for soils and 2 gram splits for dusts were made available. Characterization for content and homogeniety showed these samples to be adequate to monitor quality assurance for lead analyses and allow the assignment of quality figures of merit for analytical lead values in unknown soils and dusts. Use of soil samples with maximum diameters of 0.25 mm proved acceptable for the confidence levels appropriate to this study. Additional materials of this type are being prepared and will be characterized and made available.

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SINGLE BLIND VERSUS DOUBLE BLIND PERFORMANCE EVALUATION

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ABSTRACT

Laboratories, as a part of their a complete QA program, should analyze proficiency samples to assure that routine sample analyses meet certain criteria and standards. Single blind proficiency sample programs have been established by the EPA, the Army Corps of Engineers, various state agencies and industry to ensure that a laboratory can provide accurate results. Single blind performance evaluations may be handled by a laboratory staff differently and/or more conscientiously than a routine sample. The non-routine handling of performance test samples is due to the critical importance of passing the evaluation for a laboratory's certifications and contract awards. A single blind can help to eliminate laboratories that are bad performers, but unfortunately it does not establish the quality of a Laboratory's routine performance.

A laboratory's performance on a double blind sample is much more effective in establishing its true performance. However, double blind samples tend to be difficult to submit to a laboratory without the laboratory's knowledge. Double blinds are most effective as part of an ongoing contract program, or as an internal Quality Assurance program.

Examples of data from single blind and double blind performance evaluations of a single laboratory are described. The significance of internally prepared double blind performance samples is evaluated.

INTRODUCTION

A performance test is conducted to establish that a laboratory can produce data of a specified quality. The criteria used for a "passing" mark are determined from the results of a round robin or collaborative test of many laboratories. The pooled results of an analytical test are evaluated against a true concentration, the statistical average, and the 95% and 99% confidence intervals. A laboratory has "passed" the evaluation if it has provided a result within the 99% confidence interval.

Environmental chemistry laboratories are required to take part in these collaborative evaluations to achieve and maintain state certifications, establish quality for laboratory contracts, or show continued acceptable performance to established clients. In addition, many laboratories have voluntary intra-laboratory performance testing programs as a part of a Quality Assurance Program.

The increasing number of performance testing programs has become a burdensome but necessary requirement for a commercial laboratory. A commercial environmental laboratory may be a part of a number of different programs. The Environmental Protection Agency (EPA) uses performance tests for pre-contract award selection of laboratories for it's Superfund Laboratory Program. The EPA also provides performance samples for State Certification of Drinking Water and Water Pollution Programs. The United States Navy, Department of Energy and United States Army Corps of Engineers have performance testing programs for laboratories that provide services to their environmental projects. In the commercial arena Chemical Waste Management requires round robin testing of their subcontract laboratories to ensure that the laboratory meets established performance criteria.

These testing programs are a poor means of establishing a quality performance because the testing programs are limited to a selected number of measurements, usually a high and low concentration, and a small number of samples in a single matrix. The results of performance tests identify gross problems that are indicative of the day the test was performed. Acceptable performance on a test should not be construed as representative of a laboratory's ongoing performance. Therefore, most, but not all regulatory agencies or clients who require performance testing, also conduct on-site audits to establish that the laboratory has the personnel, procedures, instruments and Quality Assurance Program to assure a consistent quality performance. A combination of the performance test and site audit are good practices to follow if a regulatory agency or client is to be assured of a laboratory's quality. Site audits may occur quarterly, annually or biannually; while the performance test should be performed more frequently based upon the interval between on-site audits.

Table 1 describes some commonly tested parameters. In addition, the table lists procedures the laboratory is "expected" to use to measure the concentration of analytes. Common acceptance criteria for these analytes is listed to show the wide range of data acceptability. Most performance test samples are laboratory pure water or a characterized soil that is fortified with the analytes of interest. The laboratory receives the sample as a "known" performance sample and is expected to treat this sample as "routine" during handling, preparation and analysis. It is at this point that the greatest degree of bias is encountered in the performance testing of a laboratory or group of laboratories. Because the test samples are known performance samples they are no longer handled routinely.

For all laboratories it is important that the test be "passed". Failure to meet the acceptance criteria for one analyte will result in decertification of the entire laboratory in some states. In other states the laboratory may be de-certified for only those analytes that fail. De-certification may last six months to a year. If the performance test is for a major contract award, then careers and businesses may be on the line should there be a failure to perform ac ceptably. Livelihoods and reputations may be at stake based upon the results of these single blind performance test results.

Table 1. Commonly Requested Performance Tests

Analyte Test	EPA Test Procedures	Example Acceptance Range
Sodium	7770/273.1	17.7-21.8
Silver	7761/272.2	3.98-7.16
Mercury	7470/245.1	0.656-1.32
Nitrate	9200/353.2	4.98-7.37
Vinyl Chloride	8240/624	1.82-4.26
Toxaphene	8080/608	1.26-3.49
Total Cyanide	9012/335.3	0.222-0.364
Oil and Grease	9070/413.2	5.74-16.3
Total Dissolved Solids	160.1	192-485
Fluoride	340.2	1.31-1.61
Ammonia	350.1	0.605-1.03
Alkalinity	310.2	50.4-59.0
Sulfate	9036/375.2	26.3-37.5
Phenol	9066/420.2	0.762-1.79
Potassium	7610/258.1	8.68-11.1
Copper	7210/220.1	18.5-25.8
Lead	7421/239.2	54.9-75.9
Molybdenum	7481/246.2	1.52-7.68
Magnesium	7450/242.1	0.451-0.608
Specific Conductance	9050/120.1	610-714
Herbicides (2,4-D)	8150/509B	34.6-121
PCB's	8080/608	1.34-3.45

As a result, the single blind regulatory performance test sample becomes the most non-routine sample of them all. Even the best, most quality oriented laboratory becomes concerned that the test be acceptably passed. Therefore, the most qualified analyst is delegated to perform the analysis. All glassware is spotless, every reagent and calibration standard is fresh, new calibration standards are prepared, and instruments undergo stringent maintenance protocols. This is all done although the laboratory may already have a stringent QA program in place with numerous verifiable quality control practices. So for a performance evaluation sample, the laboratory goes one step farther in the hope of reducing the potential for failure anywhere in the QA system. Even the reporting of test results is scrutinized more closely than on routine lab reports.

State Certification Programs are most important to a laboratory's continued viability and it is the state certification performance evaluation sample that this paper addresses. Within the laboratory industry there is a certain animosity to the use of performance tests because the test results are for a single day. Despite how stringent a

laboratory's QA Program is, the analytical test conditions will vary from day to day. It is very difficult for a laboratory to be objective about a failed test result. Any analyte missed can be construed as a "gross" laboratory failure and that a serious problem exists. Sometimes this is the case, but more frequently the failure is a correctable error such as a dilution factor error, a transcription error, or use of an inappropriate standard range. Occasionally a failure occurs when all laboratory QC meets criteria and no identifiable reason for failure can be determined.

Due to the lack of objectivity in the handling of state certification samples, an evaluation was begun to determine the impact of this lack of objectivity when compared with the results of double blind tests. A double blind evaluation, unlike the single blind, uses a control sample that cannot be identified as a performance evaluation by the laboratory personnel doing the analyses. The systems used for single blind performance are described and the results of double blind tests are discussed.

SINGLE BLIND PERFORMANCE SYSTEMS

Figure 1 contains the elements used by our laboratory to determine acceptance or rejection of performance evaluation data. An analyst is expected to analyze the test sample using established acceptable procedures without deviation. The test should be performed with the most scrupulous attention to the variables in the procedure that might result in "out of criteria" data. Routine quality control must be performed. This would include laboratory control samples, calibration standards, method and instrument blanks, accuracy and precision checks and calibration verification if required. The raw data produced by an analyst is expected to verify the conditions under which the analysis is performed. In addition to the routine QC, the analyst is expected to analyze an unknown check sample provided by the QA Officer. The QA Officer and Laboratory Director use the form described in Figure 1 to accept or reject the results of the test. Marking the low high concentration bar with the check sample found concentration helps determine whether the test sample should be repeated. The raw data, routine QC, and the extra unknown QC check provided by the QA officer are used in the evaluation.

Should the routine QC data and the QA Officer's check sample meet criteria (95% confidence interval), the results of the performance test sample are reported. Otherwise, the data is checked closely for errors, the analysts interviewed to figure out if there were operating problems, and if necessary, a technical method audit is performed to assure the analytical procedure was correctly performed. The analyst then reprepares and reanalyzes the sample. Laboratories that report more than 100,000 test results a year do not "routinely" place this much attention to any one result. Good laboratory practice does require repreparation and reanalysis of environmental samples should QC samples fail established criteria.

Figure 1. Laboratory Elements for Blind Performance Evaluation Acceptance

PARAMETER: _____
DATE ANALYZED: _____
TECHNICIAN: _____

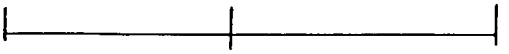
PERFORMANCE EVALUATION RESULTS

RMC ID NUMBER	CONCENTRATION MG/L

FOR QA USE ONLY:

CHECK SAMPLE ID: _____
TRUE VALUE: _____
ACCEPTANCE RANGE: _____

PASS ( ) FAIL ( )



LOW CONC. TRUE VALUE HIGH CONC.

APPROVED: _____
DATE: _____
APPROVED: _____
DATE: _____

ANALYST NOTE:

1. ANALYZE RMC CHECK SAMPLE ON SAME DAY AS PERFORMANCE EVALUATION SAMPLE.
2. ATTACH RUN DATA SHEET TO THIS FORM.
3. DO NOT SUBMIT THESE RESULTS TO DATA ENTRY.
4. DO NOT PROCEED TO SECOND ANALYSIS UNTIL AUTHORIZED BY QA OFFICER.

Table 2 shows the results of EPA performance tests over 4 time periods. The first two columns were prior to and the second two columns were after institution of the above described performance evaluation practices. Of 56 analytes tested, only results of analytes outside acceptance criteria are provided in Table 2. Analysts, prior to the new QA performance program, would frequently analyze a sample multiple times over several days and pool the data for an average value. No statistical outlier tests were used to keep bad data out of the average. Some analytes were failed as a direct result of outlier data being reported. Sometimes the reason for failure could not be identified since the routine QC was acceptable.

In test series 2 all analytes except sodium were failed. Silver, mercury and toxaphene were not required for the next series of tests

Table 2. Results of EPA Proficiency Samples (SINGLE BLIND)

Analyte	1	2	3	4
Sodium	Fail	Pass	Fail	NA
Silver	Pass	Fail	NA	Pass
Mercury	Fail	Fail	NA	Pass
Nitrate	Pass	Fail	Pass	Pass
Vinyl Chloride	Fail	Fail	Pass	Pass
Toxaphene	Pass	Fail	NA	Pass
Total Cyanide	Pass	Fail	Fail	Fail
PCB's	Pass	Fail	Pass	NA

NA = Not Analyzed

listed in Column 3. Column 4 indicates all parameters were passed using the laboratory's QA evaluation system except sodium that was not tested and total cyanide. Evaluation of the cyanide raw data and a complete technical review of the procedure used was unable to find the specific cause for its failure. As a result of the EPA Proficiency Evaluations, the laboratory changed from automated total cyanide analysis to a manual system.

The laboratory, after having found a non-routine system for meeting the State regulatory criteria for performance evaluation samples, then became concerned that a truly effective means of determining routine laboratory performance was needed to assure itself that the data provided to clients was the best that could be produced. A monthly double blind sample was prepared and used to assess the entire analytical, quality assurance and reporting systems within the laboratory.

DOUBLE BLIND PERFORMANCE

Double blind tests quickly reassured management that routine results were of high quality. The double blind results are reported in Table 3. In addition, a system was established to track internal and external data inquiry on results reported to clients. This system in conjunction with the double blind tests helped establish where the "real" problems were within the laboratory. Table 4 lists the results of data inquiries. Table 3 and 4, when compared, shows that "real" world problems do not correlate well with the findings of double or single blind testing. Figure 2 is the Data Inquiry Form.

The first series of double blinds in Table 3 indicated problems with oil and grease, cyanide and potassium. Subsequent double blinds showed that continuing problems existed with both cyanide and alkalinity which were corrected with procedure changes.

Figure 2.

INQUIRY NO.

DATA INQUIRY FORM

DATA INQUIRY

PARAMETER: _____

Purpose of inquiry: _____

_____

_____

Client: _____ Report No: _____

Prompted/Initiated By : Date Initiated: _____

[ ] Analyst: _____

[ ] Internal data review by _____

[ ] Client inquiry to (RMC contact) _____

DATA EVALUATION INITIAL / DATE

1 - Transcription error YES [ ] NO [ ] _____

2 - Calculation error YES [ ] NO [ ] _____

3 - Reanalysis required YES [ ] NO [ ] _____

[ ] Re-prep sample and submit for analysis before: _____ [ ] CLIENT REQUEST [ ] LAB REQUEST

[ ] Re-analyze and re-submit data on or before: _____ [ ] CLIENT REQUEST [ ] LAB REQUEST

RE-PREP

RE-PREP COMPLETED BY: _____ DATE COMPLETED: _____

RE-ANALYSIS

RE-ANALYSIS COMPLETED BY: _____ DATE COMPLETED: _____

RE-ANALYSIS DATA APPROVED BY: _____ DATE APPROVED: _____

INQUIRY OUTCOME

[ ] Transcription error

[ ] Calculation error

RE-ANALYSIS

[ ] Original results confirmed

[ ] Original results not confirmed

[ ] Corrective action required

[ ] Sample narrative required

[ ] NO FURTHER ACTION

COMMENTS/RESOLUTION:

WHITE - QA YELLOW - file PINK - Asst. Lab Mgr

Table 3. Results of Initial Series of Double Blind Tests.

Analyte	1	2	3
Oil and Grease	Fail	Pass	Pass
Cyanide	Fail	Pass	Fail
Total Dissolved Solids	Pass	Pass	Pass
Fluoride	Pass	Fail	Pass
Ammonia	Pass	Pass	Pass
Alkalinity	Pass	Fail	Fail
Sulfate	Pass	Pass	Pass
Phenol	Pass	Pass	Pass
Mercury	Pass	Pass	Pass
Potassium	Fail	Pass	NA
Copper	Pass	Pass	NA
Lead	Pass	Pass	Fail
Silver	Pass	Pass	Pass
Molybdenum	Pass	NA	NA
Magnesium	Pass	NA	NA
Specific Conductance	Pass	Pass	Pass
Herbicides	Pass	Pass	NA
PCB's	Pass	Fail	Pass

NA = Not Analyzed

The results of data inquiries listed in Table 4 show that the biggest concern of clients was chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), total dissolved solids and phenol. None of these tests were found to be problems from double blind or EPA performance test results. The phenol sample container lids were found to contain phenolic compounds that caused false positive values to be reported. Clients were instructed to use sample containers with non-phenolic lids. Total dissolved solids failures were due to inadequate drying procedure. COD results were dilution and calculation errors. TPH was a client perception of expected results based on the physical appearance of the sampling site. The data inquiries from clients never showed a problem with analytes that the double blind and EPA proficiency samples targeted as potential problems. Data inquiries that cannot be corrected from a review of the raw data and associated QC are reprepared and reanalyzed to determine if an analytical error existed.

An evaluation of the double blind results versus "real" world inquiries showed that there is no effective means of assessing the "true" concentration of environmental results or how a laboratory should handle perceived or actual problems. Only an ongoing monitoring program can establish a baseline for comparison of a laboratory's result. Snapshot analyses for site characterization will always be an estimate since the "true" concentration cannot be determined and there is nothing with which to compare the results. Only a laboratory's ongoing QC program can provide the accuracy and precision of the pro-

Table 4. Results of Laboratory Data Inquiries

Analyte	Total Number of Inquiries	Number of Results; Analytical Error	Number of Results; Transcription Error	Number of Results; No Change
Arsenic	3	1	-	2
Zinc	2	-	-	2
Lead	2	-	2	-
Phenol	6	5	-	1
PCB	1	-	-	1
Chemical Oxygen Demand	7	4	2	1
Total Dissolved Solids	7	4	-	3
Total Petroleum Hydrocarbons	5	-	-	5
Semivolatile Organic Analysis	2	-	-	2
Volatile Organic Analysis	1	-	-	1

°Laboratory data inquiries are the result of a perceived problem with results provided to a client.
°The numbers provided cover a seven month time period.
°Total number of tests performed during the seven month span was 43400.
°68% of inquiries were client generated and 32% laboratory generated.

cedure used to make the analytical measurements to assure the results are correct.

Since the double blind samples were prepared from EPA or commercially available check samples, a problem arose in maintaining the integrity of the double blind. The GC/MS group was quick to question the sample as a check because certain compounds were present in concentrations that were not routinely found. For example, all the trihalomethanes were present at a consistent concentration. The metals group was also suspicious of high concentrations of metals that were usually found in trace amounts. The metal results for the Double Blind sample were all from 20 to 50 ppb. In addition, the laboratory staff had been informed that double blind samples were going to start through the laboratory. As a result, the first set of tests was considered biased.

A system was then established for preparing and submitting double blind samples such that the samples at login, through analyses and reporting appeared to be routine monitoring well samples from an established client. Only the individual preparing the double blind samples, the Lab Director and QA Manager were aware of the sample's identity. A client submitted the samples to login. To ensure the

samples were handled like routine environmental samples the results and report were required ten days from date of receipt. Samples prepared and submitted for analysis in this fashion have not been compromised.

The critical factor in a double blind analysis is that the concentrations of analytes must be at concentrations routinely found by that laboratory. Before preparing a double blind a laboratory should determine the best mix of analytes and analyte concentrations before submitting a sample to the laboratory. Commercially available or EPA QC check samples can be used but individual analysts are very quick to recognize these types of samples. Therefore, great care must be taken in preparing the double blind from off the shelf QC samples. It has been noted by this writer that even samples submitted by EPA as double blind to Superfund laboratories are quickly found out by the analysts because of unusual concentrations of analytes or mixes of analytes not routinely found by the laboratory.

Double Blind Versus Single Blind Results

To determine the impact of the loss of objectivity in handling a single blind versus a double blind sample, the laboratory prepared two batches of evaluation samples. Both batches contained the same 24 analytes at the same concentrations. The second set was submitted two days after the first set and was recorded as a QA check sample. Both sets of results were required within 10 calendar days that is the routine reporting period for the laboratory. Column 2 of Table 5 lists only the tests failed and shows that the single blind samples were analyzed within criteria. Whereas, the double blind showed some results were outside criteria. Evaluation of the double blind results found that the PCB result was missed because of a technical defect that was quickly corrected. The other results, however, prove that greater consideration was given by the analysts to the single blind evaluation samples. This double blind/single blind was repeated for only those analytes that were outside criteria for the double blind excluding PCB. The results are found in Table 6 and confirm analyst bias for known check samples.

The follow-up analyses of the double blind and single blind sample showed the double blind results met criteria for all analytes except alkalinity. The alkalinity failure on the double blind resulted in a corrective action in the laboratory. Without the double blind analyses, the problem with alkalinity would not have been found. Because fluoride failed the double blind on the initial evaluation and the single blind on the follow up evaluation, a fundamental measurement error was assumed. Review of the fluoride method and raw data indicated that a longer period of time was required for instrument stabilization following analysis of high concentration samples.

Table 5. Results of double blind versus single blind. First pass through the laboratory.

Analyte	Double Blind	Single Blind
Sodium	Fail	Pass
Alkalinity	Fail	Pass
Fluoride	Fail	Pass
PCB	Fail	Pass
Total Dissolved Solids	Fail	Pass

Table 6. Results of double blind versus single blind. Second pass through the laboratory.

Analyte	Double Blind	Single Blind
Alkalinity	Fail	Pass
Total Dissolved Solids	Pass	Pass
Sodium	Pass	Pass
Fluoride	Pass	Fail

CONCLUSIONS

Single blind performance samples whether submitted by regulatory agencies or as part of an internal QA program, are very frequently biased non-objective tests of a laboratory's performance. The importance of "passing" these regulatory or contract required evaluations lead to non-objectivity and the handling of the test samples as non-routine, special cases. Double blind performance tests when carefully planned to ensure the integrity of the test can prove routine laboratory quality. Care must be taken in preparing the analyte fortifications to ensure that both the analyte concentrations and analytes present do not disclose the identity of the double blind.

In combination with single blind testing, and data inquiry tracking, a double blind program can establish that all laboratory QA and management systems are working effectively.

TO HERE

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QUICK-TURNAROUND CONTRACTS: A SUMMARY OF NEW PROTOCOLS

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ABSTRACT

The EPA Analytical Operations Branch has developed new protocols in response to the need for quick-turnaround data at sites, many of which will be in the process of remediation and clean-up. These protocols will present a two-fold challenge to the laboratory community.

First, laboratories will need to ensure that their quality assurance program is responsive enough to provide data of high quality consistently, and that any problems encountered get immediate corrective action.

Second, direct electronic data transfer and FAX capabilities will need to be developed and monitored by the quality assurance officer to ensure that only data of sound quality is transmitted to the field team. These procedures could include detailed documentation of computer operations and new methods of archiving both computer-resident data and hard copies of laboratory data.

Good data is necessary for decisions affecting not only cost, but the health of field personnel and the public. The authors will present an overview of the new protocols and a discussion of ways in which laboratories can meet these challenges.

SAMPLING/FIELD

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CHEMICAL MUTAGENICITY TEST FOR USE IN WASTE SAMPLE EVALUATION

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The principal objective of this study is to develop a rapid chemical test for identifying potentially mutagenic/carcinogenic compounds in waste samples. The test will be based upon the reaction of the mutagenic/carcinogenic chemical with a nucleophilic reagent that has been designed to mimic the interaction of mutagens/carcinogens with DNA. This is designed to be a laboratory test to assist in prioritizing samples and sample fractions for both chemical analysis and bioassays.

The test uses strong nucleophiles as substrates for reaction with the potential mutagen/carcinogen. Indirect acting mutagens/carcinogens are metabolically activated using liver microsomal enzymes (S_9 mix). The altered reagent is then detected as additional peaks resolved from the original reagent peak using high performance liquid chromatography (HPLC). HPLC with mass spectrometry is used to identify the reacting species. Several reagents have been tested with known mutagens/carcinogens and hazardous waste samples. Results will be presented and compared with results with various bioassay systems.

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Immunobased Personal Exposure Monitors (PEMs)

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Recent advances in antibody based analytical methodologies as well improved antibody production methods, has led to an increase in the applications of immunologically based analytical techniques to environmental problems. Antibody based methodologies possess many advantages including sensitivities in the picogram range, rapid response times, inherent specificity to the antigen (target pollutant), and low cost per analysis. In addition, more recent work in antibody techniques has resulted in improved detection systems involving optical detection which allows for the development of field transportable systems. Immunologically based test kits are available for a variety of pollutants in water such

as atrazine and pentachlorophenol. The limitations to the current immunologically based systems is that they are not applicable to air sampling because antibodies are generally only active in aqueous solution.

This paper will discuss a new immunologicaly based sampling and analysis system for personal exposure monitoring. This lightweight device is designed to be worn by the user and sampling vapors directly as a passive sampler. The antibody is immobilized in a membrane sampling device containing an appropriate buffer system. Air containing the target pollutant can diffuse through this membrane and the target compound is then bound by the antibody. Detection is by standard ELISA or EMIT methods which can be carried out in the field at the end of the use period. Systems under development include pentachlorophenol, atrazine, and BTX. Data to be reported includes diffusion rates, detection limits, precision and accuracy, and final design considerations and limitations. A discussion of the implications and impact of immunologically based exposure monitors will be included.

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36 MONOCLONAL ANTIBODY-BASED IMMUNOASSAY OF CYCLODIENES

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ABSTRACT

Immunoassay is a potentially efficient and cost-effective method for detecting cyclodiene insecticides and their metabolites. We have prepared monoclonal antibodies (MAbs) and developed an enzyme immunoassay (EIA) for these compounds. The immunizing and screening antigens were prepared from an endo ether analog of aldrin which was conjugated to various protein carriers. The four most sensitive MAbs reacted to different extents with aldrin, dieldrin, endrin, isodrin, chlordane α and γ isomers, endosulfan isomers and sulfate, heptachlor, heptachlor epoxide, and toxaphene, between 20 and 200 ppb. They also recognized kepone, but not mirex. Two MAbs were weakly reactive with isomers of lindane, but none reacted with DDT. Hexane extracts of uncontaminated soil contain material that interferes with the EIA. We are attempting to eliminate this interfering material and recover chlordane, heptachlor, toxaphene, and endosulfan by extraction on C_8 and Florisil solid-phase columns.

INTRODUCTION

The polychlorinated cyclodienes ("CDs") are a large family of persistent, stable organochlorine compounds with broad, potent insecticidal activities. CDs are also very toxic to birds, fish, and mammals (Brooks, 1974b). They bioaccumulate in adipose tissue, liver, and brain, and some are carcinogenic (Biddinger and Gloss, 1984; Gupta and Gupta, 1979). Most uses of CDs were discontinued in developed countries between 1975 and 1980 (Brooks, 1974a). However, the large amounts that were manufactured and applied still pose major problems for residue detection and waste disposal. CDs are very hydrophobic, difficult to recover from environmental matrices, and instrumental analysis is costly and time-consuming.

Three immunoassays for CDs, which employed rabbit antisera, have been reported. Langone and Van Vunakis (1975) developed a radioimmune assay

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using a conjugate of dieldrin as immunogen. Bushway, et al (1988) described a coated-tube EIA for cyclodiene determination, which is marketed as a kit by Immunosystems, Inc., and Dreher and Podratzky (1988) reported an EIA for endosulfan. Recently, Stanker (1989) prepared MAbs that react with heptachlor and other CDs, and applied them to analyze CDs in meat fat and dairy products. We undertook development of CD-specific MAbs because they are defined reagents of potentially unlimited supply, and superior to whole antisera for formatting sensors and other immunoassays that could be made resistant to solvent and matrix effects.

Substantial amounts of the banned CDs have accumulated in numerous toxic waste sites nationwide. In California, toxaphene is still registered for scabies treatment of cattle and sheep. Endosulfan, which is still registered for use on several crops, is sold in 16 different formulations (Fleck, 1988), and 400,000 to 450,000 lbs are applied to agricultural land in California each year (Pesticide Use Reports, 1984-1988). Residues from endosulfan applied to artichokes in the Monterey-Salinas valley have been found in the sediment of the Elkhorn Slough, an estuary that drains into the Monterey Bay, and in mussels and fish in the slough and the bay (M. Martin, personal communication). The California Regional Water Quality Board has identified at least 7 sites — mostly surface impoundments at crop dust airfields, in which endosulfan and toxaphene are present at levels from 10 to 14,000 ppm (J. Menke, personal communication). Thus, an ongoing need exists for a rapid, potentially field-portable, quantitative screening assay for CDs.

MATERIALS AND METHODS

Details of the hapten and conjugate syntheses, the derivation of the hybridomas, and optimization of the competition EIA will be published elsewhere (Karu, A.E., et al., in preparation).

Pesticide standards Analytical standards of 11 cyclodienes and toxaphene were obtained from the EPA reference materials repository. Samples of >99% pure endosulfan α and β isomers, endosulfan cyclic sulfate, and the α, β, γ, and δ isomers of lindane were generously provided by Dr. J. Casida, U.C. Berkeley. 4,4'-DDT was the Pestanal® standard, obtained from Fisher Scientific Corp. All standards were prepared by weight, and solutions of 1 mg/ml in dimethyl sulfoxide (DMSO, Fisher Spectranalyzed) in tightly sealed teflon vials were used within 2 days of preparation. All other organic solvents were Fisher Spectranalyzed or Optima grade.

Preparation of aldrin-protein conjugates The hapten, an ether analog of aldrin (Figure 1), was prepared in 3 steps from commercially available norbornenol and 5-bromovaleronitrile by a modification of the procedure described by Langone and Van Vunakis (1975). The stereochemistry was confirmed by high-field proton NMR. This product was converted to the N-hydroxysuccinimide ester, and immunizing and screening antigens were prepared by covalently conjugating the hapten to bovine thyroglobulin (BTG), bovine serum albumin (BSA), and keyhole limpet hemocyanin (KLH), using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride.

Immunization Pairs of Swiss Webster, Biozzi, and Balb/c mice were given a total of 4 subcutaneous injections of either the KLH-, BSA-, or BTG-aldrin conjugate (50 μg in each of the first two doses, 25 μg for the last two doses). The conjugate was administered in 0.1 ml of saline containing 50 μg of Ribi adjuvant (MPL + TDM Emulsion, Ribi Imunochem Research, Hamilton, Montana). Sera from the tail veins were screened by EIA on wells coated with aldrin conjugated to a carrier other than that used for immunization. Unconjugated carrier proteins were used as controls. All 18 mice developed responses to the aldrin-linker combination, but sera taken from only 5 mice — 3 Swiss Websters, one Balb/c, and one Biozzi — gave competitive inhibition by aldrin in solution. The spleen of the Biozzi mouse, which had been immunized with aldrin-BTG, was taken to derive the MAbs.

Hybridoma production Approximately 6 x 10^7 splenocytes were fused with P3X63AG8.653 myelomas at a ratio of 2.5 myelomas per splenocyte, with polyethylene glycol 4000 (50% w/v in water containing 5% DMSO) as the fusing agent, essentially as described by Fazekas de St. Groth and Scheidegger (1980). The remainder (about 4 x 10^7) of the splenocytes was fused electrically, at a ratio of 5 splenocytes per myeloma, in the "03" chamber of an SSH-1 Somatic Hybridizer (Shimadzu Precision Instruments, Inc., Kyoto, Japan).

A total of 4,128 cultures (43 96-well plates) were seeded at 3.5 x 10^4 splenocytes per well, a density at which colonies that developed were better than 95% likely to be monoclonal. Twelve to 21 days later, culture supernates were sampled from colonies and tested for antibodies that bound to aldrin-BSA or aldrin-KLH, but not BSA or KLH. Antibodies from 110 of 991 colonies reacted with aldrin hapten, but only 16 of these antibodies showed competitive binding with aldrin in solution. These hybridomas were expanded to 24-well dishes, and supernates were again screened by direct EIA on wells coated with the aldrin conjugate or the unconjugated carrier protein. Antibodies that did not react with unconjugated carrier were tested for inhibition by free CDs in a

competition EIA. The four cell lines with the lowest I_{50} values for aldrin were subcloned by limiting dilution. Twelve clones of each line were stored frozen, and one clone of each line expanded to produce approximately one liter of culture medium containing sufficient antibody for about 300,000 assays. Immunoglobulin subclass was determined by EIA using a commercial kit (Southern Biotechnology Associates, Birmingham, AL).

Soil extract for matrix and recovery studies The preliminary experiments were conducted with a pesticide-free soil containing 2% organic carbon, originally obtained from Oberlin, Kansas (generously provided by Dr. R. Amundson). This soil is of the type referred to as "argiustoll" in the U.S. Soil Classification (Soil Survey Staff, 1987). Seventy-five grams of soil were ground in a mortar and pestle, dried overnight at 130° in a vacuum oven, and then shaken successively with two portions of 75 ml hexane:acetone :: 1:1 for 1 hr in a glass bottle on a reciprocating shaker. The extracts were pooled, filtered through Na_2SO_4 and Whatman #40 paper into a 500 ml rotary evaporator flask. The filtrates and a rinse of 5 ml of hexane were evaporated to dryness at 55° under 20" vacuum on a Büchi rotary evaporator. The brownish-yellow residue was dissolved in 10 ml of hexane. Half was used for florisil chromatography, and the other half was evaporated to dryness, then recovered in 1 ml of DMSO. Dilutions of this solution were used directly in the EIA.

Sample cleanup with Florisil Florisil columns (1 gram; Fisher Prep-Sep) topped with approx. 500 mg. of Na_2SO_4 were conditioned with 15 ml of hexane. The soil extract in hexane was applied and the column was washed twice with 10 ml of hexane, then eluted into glass tubes with two portions of 5 ml of the eluant being tested. The eluates were evaporated to near-dryness under nitrogen at room temperature, dissolved in 0.04 ml of DMSO, and then 0.01 M KH_2PO_4-K_2HPO_4, pH 7.4 — 0.15 M NaCl— 0.05% Tween 20 ("PBST") was added to dilute the DMSO to 10%. Dilutions of these samples in PBST-10% DMSO were added directly to the EIA.

Sample cleanup with C_8 columns Spikes from a stock solution of 10 ppm of endosulfan in DMSO were added to phosphate-buffered saline containing 10% methanol. C_8 columns (300 mg; Fisher Prep-Sep) were conditioned successively with 30 ml each of hexane:acetone :: 1:1, ethyl acetate, methanol, and PBS-10% methanol. The samples were applied in volumes up to 100 ml. The columns were rinsed with 30 ml of PBS-10% methanol, and endosulfan was eluted into glass tubes with two applications of 2.5 ml of hexane: acetone :: 1:1. The eluates were evaporated to dryness under nitrogen at room temperature, dissolved in 0.04

ml of DMSO, and then PBST was added to dilute the DMSO to 10%. Dilutions of these samples in PBST-10% DMSO were added directly to the EIA.

RESULTS AND DISCUSSION

Properties of the MAbs Only the 4 most sensitive MAbs of the 16 that competitively bound aldrin, were expanded and characterized. These MAbs — designated 8H11, 6A12, 4E3, and 12A9 — were all of the $IgG_1\kappa$ immunoglobulin subclass.

The specificity of the EIA for various CDs was determined in a competition EIA on wells coated with aldrin-BSA. Two different patterns were observed, as exemplified by the results with MAbs 8H11 and 6A12 in Table 1. MAbs 4E3 and 12A9 behaved similarly to 6A12; all 3 bound aldrin and dieldrin better that all of the other CDs tested, except α-chlordane and β-endosulfan. By contrast, MAb 8H11 reacted as well or better with most of the common CDs than it did with aldrin. 8H11 was more than 20-fold more sensitive than the other 3 MAbs to kepone and toxaphene (technical mixture). Differences between these two patterns were particularly evident in the recognition of chlordane isomers. MAbs 6A12, 4E3, and 12A9 were about 9 times more sensitive for α-chlordane (the *cis* isomer) than for γ-chlordane, the *trans* isomer. 8H11 bound γ-chlordane as well, or slightly better, than α-chlordane. Mirex reacted weakly with 8H11 but did not react with the other 3 MAbs, and 4,4'-DDT was not recognized by any of the MAbs.

Enzyme Immunoassay for CDs The EIA we used to select the MAbs and conduct the specificity tests is a "classical" format, in which the analyte in solution competes with the immobilized hapten conjugate for binding a limiting amount of MAb. Wells of standard Dynatech Immulon 2 EIA plates were coated overnight at 4° with 400 ng of aldrin-BSA or aldrin-KLH conjugate. After the competition step, the MAb that remained bound to the plate was quantified by detection with alkaline phosphatase conjugated goat anti-mouse immunoglobulin and p-nitrophenyl phosphate substrate. The color development was monitored on a Flow Multiskan EIA reader and recorded on a Macintosh computer. Dose-response curves (generally 11 dilutions in triplicate from a spectrophotometrically standardized stock solution) were fitted by iterative regression to the 4-parameter logistic equation (Canellas and Karu, 1981) using Passage II (Passage Software, Inc., Fort Collins, CO) on a Macintosh computer. The characteristics of the dose-response curve were expressed as the EIA rate at the limiting low dose (LLD), I_{50} (the concentration that half-

maximally inhibited the EIA), and the slope of the best-fit curve at the I_{50}. This EIA is schematized in Figure 2.

To maximize reproducibility, it was necessary to give the soluble analyte a "head start" at binding the MAb before the mixture was added to the coated wells. We term this the "pre-competition incubation." Figure 3 shows the classical sigmoidal dose-response curves for the EIA using MAb 8H11 to detect technical-grade endosulfan in PBS-Tween containing 10% methanol. The results were essentially identical with pre-competition incubations as short as 1 hr at room temperature. The EIA results were equally reliable with EIA plates that were coated with aldrin-BSA conjugates and stored at 4° and used the next day, or stored at -20° in tightly sealed boxes until needed.

The very low solubility of CDs in aqueous solutions necessitated use of a cosolvent in the EIA. The EIA in its present format was affected differently by various solvents in the diluent used for the pre-competition and competition steps. The best results were obtained when the diluent was PBST with 10% DMSO. MAb 8H11 gave the same results when the diluent was PBST containing up to 30% (v/v) methanol, but the I_{50} values were in the ppm range, because most of the CDs were poorly soluble in these diluents. DMF and acetonitrile were strongly inhibitory, even when present at 10% in the PBST. The sensitivities of MAbs 8H11 and 6A12 to these solvents were similar.

Initial Efforts to Develop Recovery and Cleanup Methods for Soils We have begun to develop methods for concentrating and recovering endosulfan and chlordane residues from soil and sediment. To determine whether a soil extract would interfere with the accurate determination of endosulfan, we prepared hexane-acetone extracts from a defined soil as described in Materials and Methods. These extracts were added in various amounts to samples spiked with 5 or 10 ppb of endosulfan or chlordane. The soil extract had a strong inhibitory effect on the assay. Cleanup on a florisil column greatly reduced this interfering material, but the remaining matrix effect was equal to, or greater than, the value expected for the spike (Figure 4). Thus, although florisil chromatography is potentially an efficient cleanup method, a different solvent system or an additional step will probably be needed to eliminate interference from soil extracts.

We compared three eluting solvents for recovery of endosulfan from Florisil columns. Spikes of 0.3, 0.5, and 1 ppb endosulfan in hexane were applied to 1 gram Florisil columns, and eluted with "eluant C" (methylene chloride: acetonitrile:hexane :: 1:0.03:0.97; Mills, et al., 1972), 2-propanol:diethyl

ether:pentane :: 1:14:35; Archer, 1973), or hexane:methylene chloride :: 40:10 (Lopez-Avila, et al., 1989). None of these eluants gave recoveries better than 70% as measured by the EIA, and the eluants described by Mills, et al., and Archer, strongly interfered with the EIA. Spike recoveries with the eluant described by Lopez-Avila, et al. were between 35% and 70%, the column blank was near the limit of detection, and this eluant was much less inhibitory than the others. We are presently attempting to improve the recovery of endosulfan and chlordane from Florisil by modifying the eluant described by Lopez, Avila, et al.

We also tested the recovery of endosulfan from PBS containing 10% DMSO or 10% methanol from C_8 and C_{18} reverse-phase SPE columns, and recovery from solutions in hexane and hexane:acetone::1:1 by chromatography on Florisil. The best recovery of endosulfan was obtained by SPE on C_8 columns using the procedure charted in Figure C and summarized in Table 1. Only the first set of experiments was complete at the time this manuscript was written, and we are presently attempting to improve this method and evaluate others.

SUMMARY

Monoclonal antibody-based immunoassays are potentially versatile and very cost-effective for quantitative surveys of hazardous materials. MAbs are reagents of defined affinity and specificity, and a MAb can potentially be produced in unlimited quantities. Rapid advances are being made in adapting immunoassays to cards, dipsticks, sensors, and other formats that will be usable of on-site monitoring and rapid decision-making. Our MAbs for CDs appear to be sensitive enough for incorporation into such formats. The major challenge will be to devise and validate protocols for efficiently and reproducibly extracting the CDs from soil and other matrices, and eliminating the matrix effects in the assay.

Most residue recovery and cleanup procedures have been developed for instrumental analysis. Solid-phase extractions are readily adaptable for on-site sample processing. However, substances that interfere with an immunoassay may be very different from those that would interfere with gas chromatography or other instrumental methods. The highly nonpolar nature of the CDs suggests that it will be important to select cosolvents that will not affect the assay. We believe that it will also be important to test ways of protecting the MAb and the competing hapten conjugate from the effects of the solvents and material in the sample matrix. We are presently attempting to

interface the EIA with simplified methods for recovery of cyclodienes and their metabolites from soils, sediments, dusts, and biological matrices.

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REFERENCES

Archer, T.E. Endosulfan Residues on Alfalfa Hay Exposed to Drying by Sunlight, Ultraviolet Light, and Air. Pestic. Sci. 4: 59-68, 1973

Biddinger, G.R., and Gloss, S.P. The Importance of Trophic Transfer in the Bioaccumulation of Chemical Contaminants in Aquatic Ecosystems. Residue Reviews 91:, 103-145, 1984

Brooks, G.T. Insecticides of the Diene-Organochlorine Group. in (G.T. Brooks, ed.) Chlorinated Insecticides, vol. I. CRC Press, Cleveland OH. pp. 85-183, 1974a.

Brooks, G.T. Action of Chlorinated Insecticides. in (G.T. Brooks, ed.) Chlorinated Insecticides, vol. II. CRC Press, Cleveland OH. pp. 63-143, 1974b.

Bushway, R. J., Pask, W. M., King, J., Perkins, B., and Ferguson, B. Determination of Chlordane in Soil by Enzyme Immunoassay. in First International Symposium on Field Screening Methods for Hazardous Waste Site Investigations, Las Vegas, NV, Oct. 1988

Canellas, P., and Karu, A. E. Statistical Package for Analysis of Competition ELISA Results. J. Immunol. Meth. 47: 375-385, 1981

Dreher, R. M., and Podratzki, B. Development of an Enzyme Immunoassay for Endosulfan and its Degradation Products. J. Agric. Food Chem. 36: 1072-1075, 1988

Fazekas de St. Groth, S.; Scheidegger, D. "Production of Monoclonal Antibodies: Strategy and Tactics". *J. Immunol. Meth.* 35: 1-21, 1980

Fleck, J. Endosulfan Use in Monterey County. Internal report, Environmental Monitoring and Pest Mgt. Division, Calif. Dept. of Food & Agriculture, Sacramento CA., Oct. 1988

Gupta, P.K. and Gupta, R.C. Pharmacology, Toxicology and Degradation of Endosulfan. A review. Toxicology 13: 115-130 (1979)

Langone, J. J., and Van Vunakis, H. Radioimmunoassay for Dieldrin and Aldrin. Res. Commun. in Chem. Pathology and Pharmacology 10: 163-171

Lopez-Avila, V., Milanes, J., Dodhiwala, N. S., Beckert, W. F. Cleanup of Environmental Samples using Florisil Solid-Phase Extraction Cartridges. J. Chromatog. Science, 27: 209-215, 1989

Mills, P.A., Bong, B.A., Kamps, L., and Burke, J.A. Elution Solvent Systems for Florisil Column Cleanup in Organochlorine Pesticide Residue Analysis. J. Assoc. Off. Anal. Chem. 55: 1972. Reprinted in: Florisil Pesticide Residue Analysis Procedures, U.S. Silica Co., Berkeley Springs, WV

Pesticide Use Reports, 1984 through 1988, California Dept. of Food and Agriculture, Environmental Monitoring and Pest Management Division, Sacramento CA.

Soil Survey, 1987. Keys to Soil Taxonomy (third printing). SMSS Technical Monograph No. 6, Ithaca, N.Y.

Stanker, L.H., Watkins, B.E., and Vanderlaan, M. Detection of Pesticides in Meats Using Monoclonal Antibody Based Immunoassays. in (M. Vanderlaan, ed.) Immunoassays for Monitoring Human Exposure to Toxic Chemicals in Foods and the Environment. (Symposium held during Meeting of the Pacific Basin Chemical Societies, Honolulu, HI, Dec. 1989. American Chemical Society (1990)

Table 1. Specificity of Cyclodiene MAbs. I_{50} values were determined from competition EIA on wells coated with aldrin-BSA. Stocks of 1 mg/ml of the indicated compound were made in DMSO. Dilutions were made into PBST-10% DMSO to generate the dose-response curves.

Compound		I_{50} (ppb) MAb 6A12	MAb 8H11
aldrin		286	218
chlordane	α isomer	210	129
	tech. mix	779	143
	γ isomer	1,880	82
dieldrin		56	39
endosulfan	α isomer	~500	~200
	tech. mix	398	58 -75
	β isomer	~150	45
	cyclic SO_4	~800	~75
endrin		352	26
isodrin		468	47
heptachlor		667	196
heptachlor epoxide		585	255
mirex		NR*	5,490
kepone		1,300	48
toxaphene	tech. mix	557	24
lindane	α isomer	>7,500	4,800
	β "	1,900	>5,700
	γ "	721	534
	δ "	2,900	605
lindane (Pestanal std.)		1,300	1,900
DDT (>90% p.p.)		NR	NR

NR = no reaction up to 10 ppm

Values preceded by (>) indicate that the compound showed less than 100% inhibition at 10 ppm. Values preceded by (~) are approximate.

Table 2. Recovery of endosulfan from physiological saline - 10% methanol, using C_8 SPE columns. Results were determined by EIA using technical endosulfan as standard.

		Spike (ppb endosulfan)				
		0	0.5		1	
Dilution of C8 eluate	Column -->	1	1	2	1	2
undiluted		0.02	0.73	0.4	0.83	0.66
1:1		0.06	0.82	0.45	0.71	0.91
1:4		0.06	0.77	0.34	1.41	0.73
	Mean	0.05	0.77	0.40	0.98	0.77
	± S.E.	± 0.02	± 0.04	± 0.05	± 0.31	± 0.11

Figure 1. Structure of aldrin hapten conjugate used for immunization and EIA.

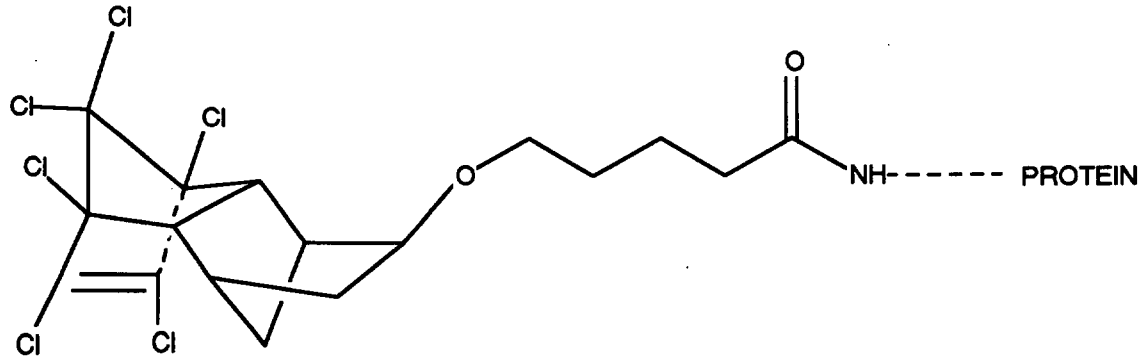


Figure 2. Flow chart of competition EIA for CDs.

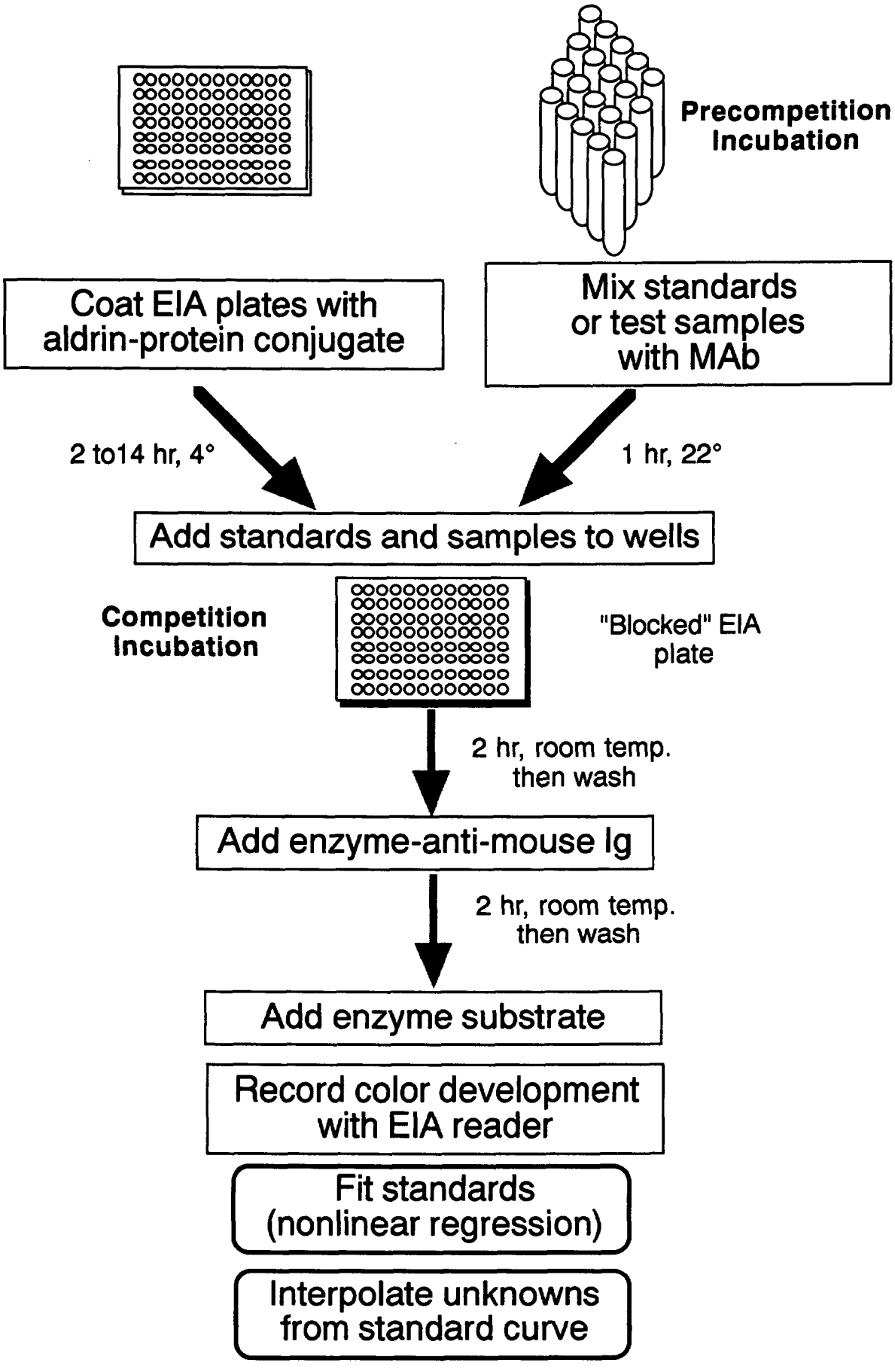


Figure 3. Dose-response of EIA for endosulfan as a function of the length of the "pre-competition incubation at 22°." ○ 1 hr, ● 2 hr, + 4 hr, ▽ 14 hr. The I_{50} values for endosulfan (tech. mixture) obtained after these incubation times were 31, 26, 28, and 29 ppb, respectively.

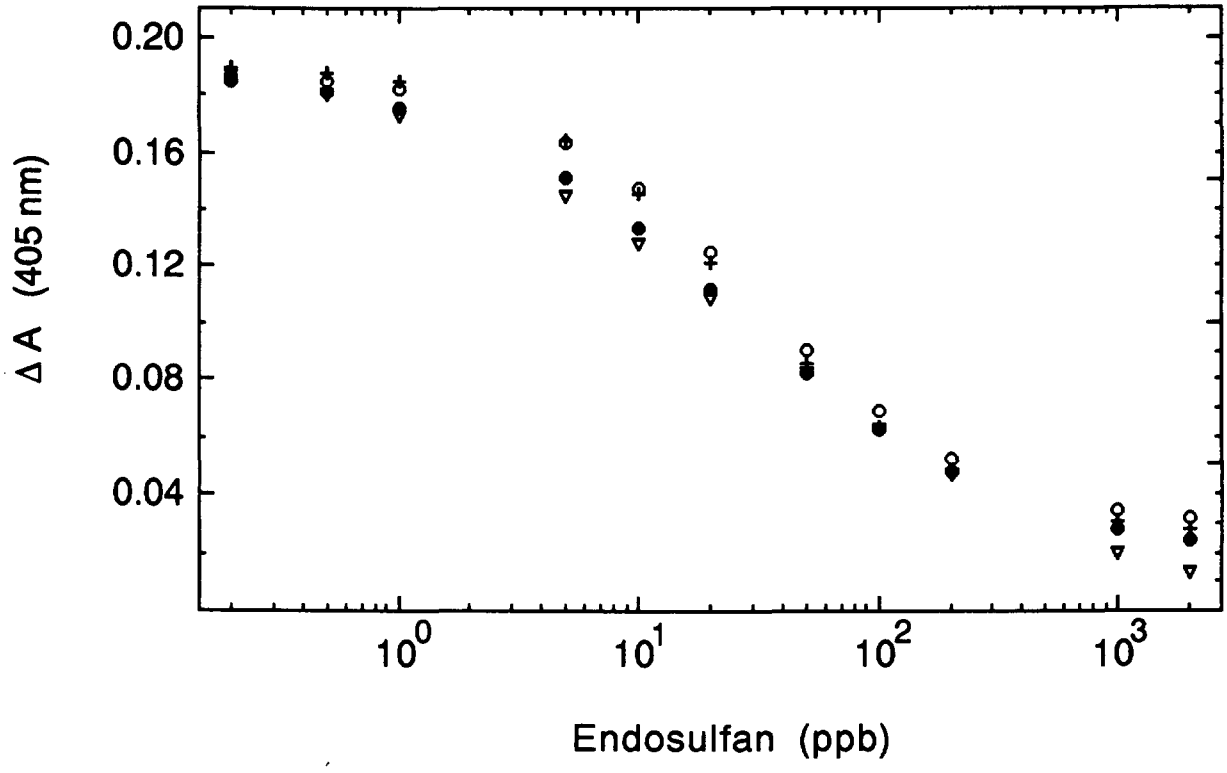
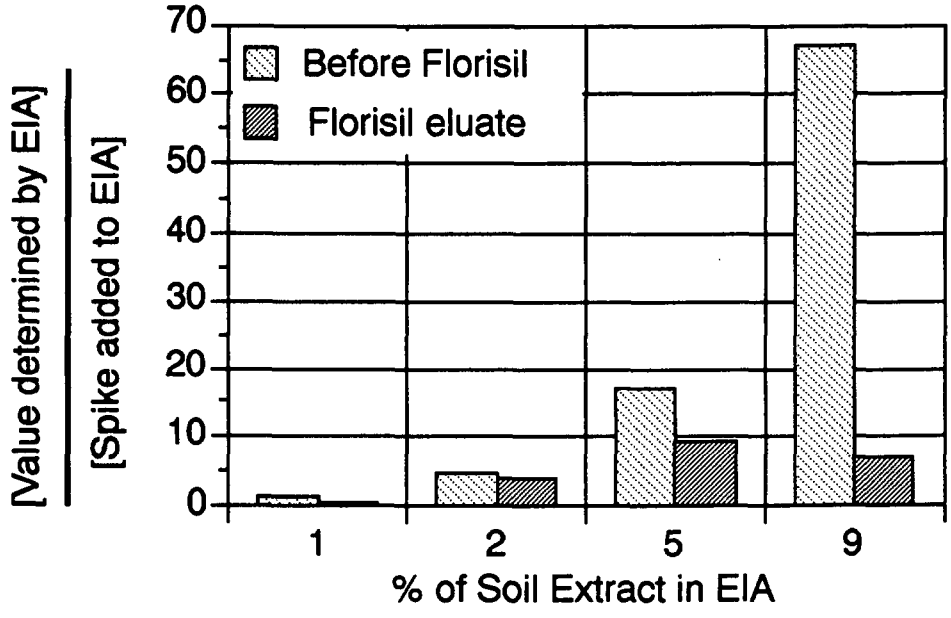


Figure 4. Matrix effect (interference) of soil extract with EIA. A hexane:acetone soil extract prepared as described in Materials and Methods, was added in the indicated amounts to samples containing 10 ppb of endosulfan. A similar experiment was conducted by adding the Florisil eluate of the soil extract to samples containing 5 ppb of endosulfan. The results are expressed as the ratio of the values obtained from the EIA, divided by the actual spike.



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GC/ION TRAP MASS SPECTROMETRY FOR AUTOMATED FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

A transportable gas chromatograph/mass spectrometer (GC/MS) has been developed at Los Alamos National Laboratory for the rapid identification and quantification of volatile organic compounds at hazardous waste sites. The instrument is based on the Finnigan MAT Ion Trap Detector (ITD). A custom purge and trap/GC was constructed for volatile organic sampling and is controlled by an ancillary microprocessor. The sampling system and ITD control software is integrated for automated operation. A laptop computer provides complete instrument control.

INTRODUCTION

The application of field transportable analytical instrumentation can significantly reduce the costs associated with environmental restoration activities. Field analytical support improves chances that schedules and monetary constraints associated with remedial activities are met. Field deployed instrumentation can expedite site characterization and remediation by:

- o improving allocation of limited personnel resources by minimizing time spent on sample management.
- o lowering cost-per-analysis, affording higher density sampling for more detailed site characterization.
- o improving initial site characterization which can help delineate the sample grid used for full analytical protocols performed at a remote laboratory.
- o reducing sample backlog at remote laboratory.
- o minimizing analytical data turnaround time, expediting site characterization and providing analytical data to project coordinators for guidance of ongoing work.
- o reducing clean-up cost by providing information to clean-up crews regarding the amount of contaminated material to be removed, packaged, and disposed of.

- o using clean-up personnel more efficiently such that these teams will not have to be released and reassembled weeks later pending receipt of analytical results.

INSTRUMENT DESIGN

A field transportable purge and trap/GC/MS/data system has been constructed at Los Alamos National Laboratory for volatile organic analysis. The instrumentation and associated methods parallel those outlined in method 8260, SW-846[1]. Qualitative and quantitative analysis for the 68 volatile organics targeted in method 8260 and associated internal standards and surrogates is accomplished in an automated sequence executed every 20 minutes. Part-per-trillion detection limits can be attained routinely from 5g of soil or 5mls of water.

The custom purge and trap/gas chromatograph sampling module is attached to the chassis of a Finnigan MAT Model 800A Ion Trap Detector (ITD) to give total instrument dimensions of 16" by 22" by 24" (HxWxD). Two sampling loops, each consisting of an adsorbent trap and a needle sparger, are incorporated in the purge and trap module to minimize dead-time by providing continuous sampling capabilities. All sample transfer lines are either gold plated or deactivated fused silica. Following sample purge, the adsorbent trap is ballistically heated and backflushed with helium to desorb organics onto the cryogenically cooled GC. The forced air GC oven can be temperature programmed with up to 30 temperature ramps. When the separation/analysis is completed, the low thermal mass GC oven is rapidly cooled by forced air and cryogenic cooling.

ITD modifications include elimination of the open split interface and vacuum system redesign. The standard 50 L/sec turbomolecular pump on the ITD is replaced with a 240 L/sec pump to accommodate carrier gas flow rates associated with mega-bore capillary columns.

All heaters and valves associated with the purge and trap/GC sampling module are controlled by an ancillary microprocessor. The sampling module is controlled through the ITD data system. Instrument automation is achieved by adding key-stroke sequences and FORTH subroutines to Finnigan supplied software. Sample purging, analysis, data reduction, and preliminary report generation proceeds automatically. The instrument can be operated in a continuous mode, pausing only for sample loading and data file specification. All data are archived on machine readable media for subsequent review by a skilled analyst.

The instrument is mounted in a vehicle equipped with carrier gas supply, a small liquid nitrogen dewar, and a portable generator for field operation.

1. Test Method for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Update I , Method 8060. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

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USE OF FIELD MOBILE X-RAY FLUORESCENCE SPECTROMETRY FOR ON-SITE SCREENING OF HEAVY METAL CONTAMINATION ON SUPERFUND SITES.

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Abstract

The on-site analyses of priority pollutants contained in the soil is essential to expedite the solution to this nation's hazardous waste problems efficiently and cost effectively. This paper will describe a sampling and on-site analytical technique, utilizing EDXRF technology, to determine the concentration levels at several sampling depths of the most prevalent inorganic soil contaminants (Copper, Lead and Zinc) at Franklin Burn Site I in Gloucester County, New Jersey. One hundred and thirty (130) samples were collected and analyzed by this method. The EDXRF generated results were used to produce toxic-graphical maps for each target contaminant at several depths to visually depict the contamination and off-site migration.

Introduction

Heavy metal contamination is an important environmental problem at many Superfund sites. The usual method for obtaining analytical results is to collect samples, ship them to a laboratory and have them analyzed by the Environmental Protection Agency (EPA) approved Contract Laboratory Program (CLP). This results in a delay of several weeks between shipment of samples and receipt of the analytical results with an additional delay for review by the Quality Assurance (QA) and Quality Control (QC) staff of EPA. Such delays habitually require remobilization of crews to the site for additional sampling in order to delineate the extent and depth of contamination for effective assessment and remediation of Superfund sites.

In order to streamline mapping and clean-up operations, the EPA has instituted the Field Analytical Screening Program (FASP) to facilitate on-site screening[2]. The availability of a field mobile, analytical quality Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer makes it possible for a crew to collect, analyze and map data for samples while on location. Statistical analysis can be applied to determine where additional samples should be selected and analyzed in order to define the extent of contamination. This program minimizes the number of samples sent to CLP and eliminates the need to remobilize crews[1].

Site Background

Franklin Burn Site I is located on a remote 4 acre lot in a rural area of Franklin Township, as shown in Figure 1. The site was used for over twenty years as a copper reclamation operation. Copper wire, capacitors, transformers and other electrical equipment were burned in an open fire to remove the insulation. The charred insulation fell directly on the ground, releasing toxic substances into the soil and atmosphere. PCB laced transformer fluids were also burned, producing dioxin. The burn operation generated approximately 110,000 cubic feet of hard packed ash. A preliminary assessment, performed by the Technical Assistance Team of the U.S. EPA Removal Action Branch, showed that hazardous materials were present at the site in concentrations that endanger public health and the environment. The analytical results obtained during the assessment indicated the presence of chlorinated dioxins/furans, PCBs and heavy metals. This unique mix of pollutants presents significant health and disposal issues. Public access to the site is of primary concern due to the lack of site security and numerous shallow potable wells located in the general vicinity.

Problem Encountered

The first task was to delineate the horizontal extent and depth of contamination for determination of site boundaries and total waste volume. To achieve this goal, a large number of soil samples needed to be collected on a regular grid pattern at various depths. These samples must then be analyzed for heavy metal content. The most widely used approach has been to send all of the samples to a CLP laboratory for analysis. This technique has several inadequacies:

1. Very Expensive
   The cost of CLP analysis for heavy metal content is approximately $200 per sample. When a large number of sample points are required this procedure becomes cost prohibitive. The cost of analyzing 130 samples for TCL Metals by CLP is roughly $26,000.
2. Long Waiting Period
   CLP results are usually obtained four weeks from the time samples are submitted for Routine Analytical Service (RAS).
3. Remobilization
   After the results are reviewed and mapped additional areas of concern are usually identified which require remobilization of crews to obtain further samples. This increases both the cost and waiting period.

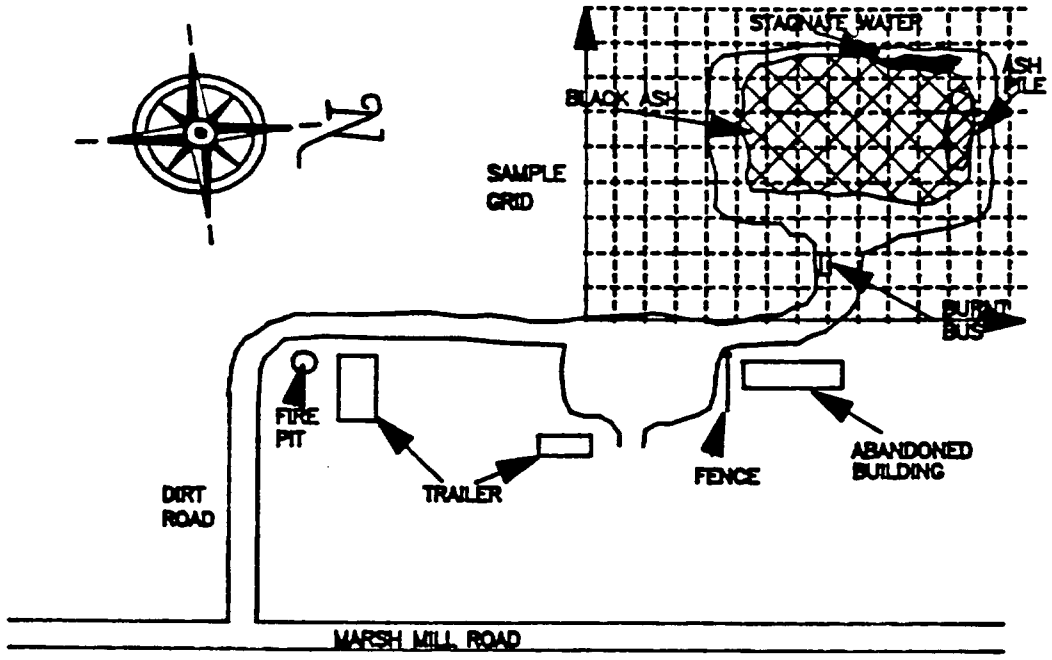


Figure 1. Site Map Franklin Burn Site I

With the increasing number of Superfund Sites involving heavy metal soil contamination, these deficiencies in analytical protocol are becoming intolerable. EPA On-Scene Coordinators (OSC) require more timely information so they can make decisions while on location.

Solution

In order to avoid the inherent delays and expense of using CLP for analyses at Franklin Burn Site I and to establish the feasibility of using on-site analytical methods, a field mobile Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer was rented on a trial basis. This unit provided analytical quality results which could be mapped by the end of the day. OSCs could review mapped data and determine which areas of the site required further sampling. This eliminated the need to remobilize sampling crews back to the site.

Sampling Methodology

The area under investigation was measured off on a regular 10 foot rectangular grid pattern. Samples were obtained from the nodes of this grid pattern in concentric squares around the black ash pile until no contamination was found. Samples were collected at five separate depths: surface, 1 ft, 2 ft, 3 ft and 4 ft. Surface samples were collected using disposable plastic sampling scoops and depth samples were obtained from the core of a stainless steel hand auger. Samples were placed in a stainless steel bucket and completely homogenized. The sample was then placed in a clean plastic zip-lock bag, labeled as to horizontal (x,y) position and depth, and delivered to the sample preparation area. Non-disposable sampling utensils were thoroughly decontaminated using the following procedure:

1. Utensils were scrubbed clean using soap and water to remove the gross contamination.
2. Then a 10 % nitric acid rinse was used to remove residual heavy metal contamination.
3. A distilled water rinse removed the nitric acid.
4. The utensil was then rinsed with both hexane and methanol to remove any residual organic contaminants.
5. A final distilled water rinse to remove any organic solvent.

Data Collection

The sample unknowns from the Franklin Burn Site I were analyzed on-site using the Spectrace 6000, a field mobile Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer from Tracor Xray, Inc. of Mountain View California. The Spectrace 6000 consists of three distinct modules: the spectrometer, the control/pulse electronics and an IBM PC/2 computer. Power can be supplied by a 110 V line or a generator. The modules are completely detachable for ease of mobility and the entire system can be readily installed in an office trailer or van. At Franklin Burn Site I the unit was operated from the inside of a recreational vehicle and power was provided by a 10 kW diesel generator. The Spectrace 6000 uses a state-of-the-art thermoelectrically cooled lithium drifted silicon detector. This detector provides high resolution and eliminates the need for a bulky liquid nitrogen cooling system. The unit is interfaced with a PC computer where the spectral data is analyzed to determine contaminant concentrations and the data is stored in a Lotus spreadsheet. [1]

The Spectrace 6000 has the capability of analyzing unknowns at various excitation conditions. A particular condition is chosen depending on the desired elements to be analyzed, the detection limits required and the time frame of the project.

Table 1
EDXRF Excitation Conditions used at Franklin Burn Site I.

Low Intensity	
Tube Voltage	25 kV
Tube Current	0.17 mA
Filter	0.05 mm Rhodium
Livetime	100 Sec

These excitation conditions were selected to optimize analyses for Cu, Zn and Pb, to provide detection limits below New Jersey Department of Environmental Protection (NJDEP) guidelines and to furnish a high sample through-put.

The NJDEP guidelines for some selected metals are presented in Table 2.

Table 2
NJDEP Soil Action Levels

Cu - 170 PPM	Zn - 350 PPM
Pb - 250 PPM	Ni - 100 PPM
As - 20 PPM	Cd - 3 PPM

The method detection limits using these excitation conditions for the metals analyzed are given in Table 3.

Table 3
EDXRF Method Detection Limits

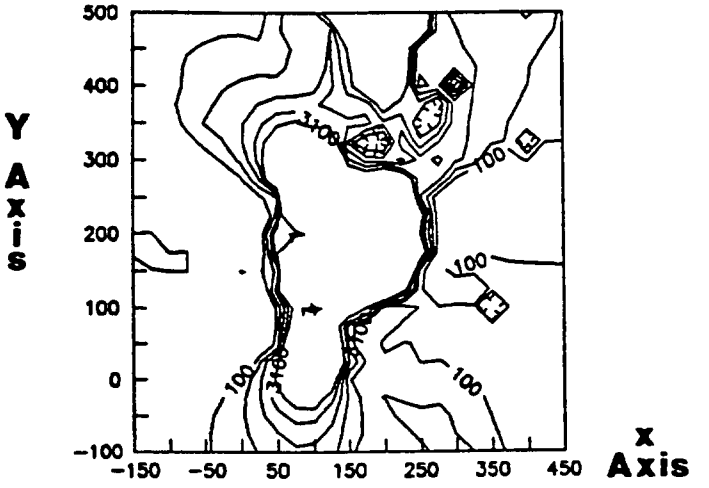
Cu - 15 PPM	Zn - 12 PPM
Pb - 19 PPM	Ni - 25 PPM
As - 20 PPM	Cd - 19 PPM

As can be readily seen, the EDXRF method detection limits are below NJDEP standards. Quantitative analyses of X-ray spectra were performed using a Fundamental Parameters computer program. The program automatically corrects for any matrix enhancement or absorption effects based on stored physical constants. This eliminates the need for any site specific samples previously analysed by the CLP to calibrate the instrument.[1] By removing the need for site specific standards, the presampling preparation time can be deleted, allowing the EPA to mobilize to a totally new site and begin analysing unknowns the same day.

Samples were prepared for EDXRF analysis using the following method:

1. 25 grams of a homogenized sample were placed in a disposable plastic tray and dried in a microwave oven for three minutes.
2. The dried sample was passed through a 10 mesh sieve to remove large objects such as stones and metal fragments.
3. The sieved sample was ground in a clean glass mortar and pestle until it was a fine powder.
4. The ground sample was placed in a disposable plastic sample cup and covered with a .33 mm thick Kapton window film.
5. The sample location and depth were marked on the sample cup.

Fig 2. Toxic–Graphical Map (Cu)



Presentation of Results

Between October 31, 1989 and November 3, 1989 over 130 samples from 37 locations were obtained, prepared and analysed by the Spectrace 6000. The analytical data were used to create toxic-graphical maps using the software package Surfer.[3] A toxic-graphical map is a contour diagram delineating a series of progressive iso-toxic lines representing uniform concentration. Two of these maps are presented in figures 2 & 3. The figures are plotted on a regular X,Y grid. The X axis has an east-west orientation while the y axis has a north-south orientation. The grid scale is in feet. The two figures are described as follows:

Figure 2: This figure shows the Copper (Cu) contamination at the surface of Franklin Burn Site I. The iso-toxic lines range from 100 ppm to 4600 ppm with a 1000 ppm interval between lines. The interior of the 4600 ppm ring contains the highest concentration of contamination. The horizontal extent of contamination can be clearly seen in this figure. Approximately 150,000 square feet of this site is contaminated at the surface above the NJDEP guidelines for copper.

Figure 3

This figure depicts the extent of zinc (Zn) contamination at the surface. The iso-toxic lines range from 100 ppm to 4600 ppm with a 1000 ppm interval. Zinc contamination has not migrated as far away from the black ash pile as has copper. Approximately 80,000 square feet of the surface of the site has zinc contamination levels above the NJDEP guidelines.

Fig 3. Toxic–Graphical Map (Zn)

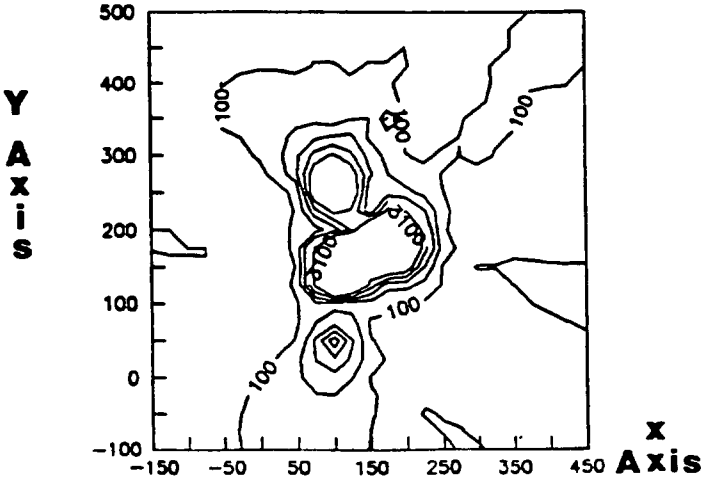


TABLE 4.

Element	Mean	Standard Deviation STD	Relative % Standard Deviation	True Value
Cu	532	24.95	4.69	609
Zn	4551	155.03	3.41	4760
Pb	6159	165.17	2.68	6550

Analytical Precision

To measure the precision of the EDXRF instrument, a known standard was run at the beginning of the day, the end of the day and once every ten unknowns. Over the four day period in which unknowns were analyzed, the National Bureau of Standards (NBS) # 1648 was run a total of 21 times. Statistical analyses of the precision study results are presented in Table 4. The relative percent standard deviations were below 5 %. This indicates that the EDXRF was operating in a precise manner with little error due to machine variability.

Confirmation of Results

In order to ensure the accuracy of the results obtained from the Spectrace 6000, 1 out of every 10 samples was sent to a CLP laboratory for TCL Metals analyses. A total of 13 samples were sent. The metal concentrations ranged from a few ppm upwards to 100,000 ppm. Table 5 presents the comparative data of four samples. The CLP data was plotted against the EDXRF data for all 13 samples. A linear regression was then calculated for these plots. For the two analytical methods to be considered equivalent the regression line must have a slope near unity and the correlation coefficient (R^2) should be greater than 0.90. Table 6 shows the regression data for Cu, Zn and Pb. Figures 4 and 5 show the regression plots for Cu and Zn. There are two lines plotted on each of these figures. The first line is for the ideal case when CLP = EDXRF. The second line is generated using the experimental regression data from Table 6.

Table 6

Element	Slope	Correlation Coefficient	Y Intercept
Cu	0.981	0.968	670.1
Zn	0.936	0.967	204.8
Pb	0.766	0.978	242.1

The slopes for two of the lines are close to unity and all of the correlation coefficients are greater than 0.96. This indicates agreement between the CLP and EDXRF results. Therefore, the Tracor Spectrace 6000 can be used as an on-site screening device to delineate site boundaries and provide information on metal contamination comparable to CLP. The regression analysis could be improved if more sample points and more consistent sample concentration levels were used, however, this was beyond the scope of the project.

Table 5

Sample	Element	CLP	EDXRF
200,200-1 MBBN-09	Cu	100,000	96,691
	Zn	18,600	26,048
	Pb	17,300	20,128
170,190-2 MBBN-07	Cu	51,500	63,766
	Zn	12,600	10,259
	Pb	16,800	19,567
150,230-1 MBBN-08	Cu	1,680	1,185
	Zn	327	386
	Pb	291	343
250,50 MBBN-03	Cu	21	32
	Zn	7	2
	Pb	16	14

VII Conclusions

The primary objective of this sampling project, to define the extent and depth of contamination, has been met. As is clearly shown on the toxic-graphical maps, copper is the most widely spread contaminant and should be used as the criterion for determining site boundaries. The surface contamination is more extended than at depth. The maps also show that the contamination underneath the ash pile extends to a depth of 4 ft.

The secondary goal of this project was to investigate the feasibility of using on-site analytical methods. The analytical precision study demonstrates that the EDXRF was operating in a reliable manner. The relative percent standard deviation for Cu, Pb, and Zn are well within acceptable levels of variance. The regression analyses between the CLP and EDXRF results show that this

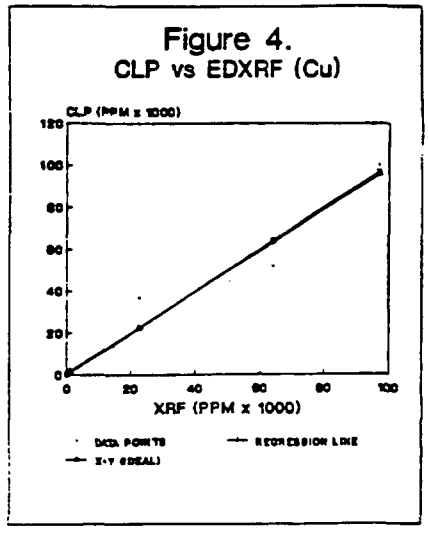
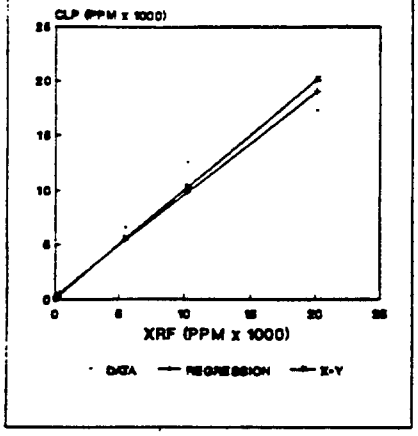


Figure 4.
CLP vs EDXRF (Cu)

Figure 5.
CLP vs EDXRF (Zn)



on-site analytical method is quantitatively comparable to the CLP results. For every sample which EDXRF showed as being above the NJDEP action guidelines, the CLP confirmed. This method also proved to be both cost effective and time saving. Using EDXRF saved the EPA $19,200 on analysis costs. Analytical results were available the same day allowing the OSC to make time critical decisions. Had on-site EDXRF not been used, remobilization definitely would have been required because surface contamination extended further than originally suspected or visually discernable. The EDXRF analyses showed this unexpected contamination and allowed additional samples to be collected and analyzed until the contamination boundaries were found.

This on-site analytical method utilizing this field mobile EDXRF technology is a viable tool available to the EPA for screening soil samples in order to determine heavy metal contamination.

Acknowledgements

The authors would like to thank Stephen Luftig, Richard Salkie and George Zachos of Region II EPA for their support and encouragement during this project. A special thanks to Brenda Glynn and Allson Wiedegreen of Tracor XRay for technical guidance while training the Technical Assistance Team personnel in the operation of the Spectrace 6000. The authors also acknowledge David Belyung and Ali Godhan of the Technical Assistance Team for assisting during sampling operations.

References

[1]. "On-Site X-ray Fluorescence Spectrometry Mapping of Soil Contaminants in Soils at Superfund Sites", Watson, W., Walsh, J.P. and Glynn, B., American Laboratory, July 1989.

[2]. "Field Monitoring Methods in use for Superfund Analysis", Fisk, J. et al., EPA Conference on Field Screening Methods for Hazardous Waste Site Investigations, Las Vegas, 1988

[3]. Surfer™, Golden Software, Inc., Golden, Colorodo

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IN SITU TOXICITY TESTING AND EVALUATION OF WETLANDS IMPACTED BY HAZARDOUS WASTE SITES

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ABSTRACT

The widespread location of hazardous waste sites near aquatic habitats assures their impact upon wetlands in many parts of the country. As a result, ecological assessments for hazardous waste sites located on or near wetlands must consider the likelihood that these wetland habitats receive influxes of complex chemical mixtures from point- and nonpoint-sources, and that adverse biological and ecological effects may be associated with the waste site. Furthermore, the diverse characteristics of hazardous wastes sites in terms of chemical mixtures and their location near aquatic habitats assures frequent exposures to wetlands biota that must be evaluated within the site assessment process. For evaluation of wetlands presumedly impacted by hazardous waste sites, amphibian species common to the transition zones between terrestrial and aquatic systems may be key biological indicators of exposure. As such, these in situ biological indicators may be applicable to integrated laboratory/field studies that evaluate the potential adverse effects associated with mine tailings and spoils, for example. For toxicity assessments related to evaluations of mine tailings and spoils, standardized laboratory test methods such as FETAX (=Frog Embryo Teratogenicity Assay Xenopus) are available and have been applied to hazardous waste site evaluations. Also, as part of an ecological evaluation for a waste site potentially impacting wetlands, in situ toxicity test methods using native amphibian species have been developed to complement the laboratory tests. Together, these laboratory and field toxicity assessment methods improve the site assessment process for wetlands impacted by hazardous waste sites, and contribute to an integrated approach for hazardous waste site assessment which involves field and laboratory methods to gather chemical, ecological, and toxicological information.

INTRODUCTION

Within ecological contexts hazardous waste sites potentially impact various habitats. In part this variety of potentially impacted habitats may be reflected in the site-specific differences which occur within the ecological assessment process for hazardous waste sites. One potential habitat frequently impacted by hazardous waste sites is wetlands. For wetlands an assessment of adverse ecological effects should include toxicity evaluations for species representative of the site, since these species could be exposed to the complex

chemical mixtures characteristic of the nearby waste site. Within a toxicity assessment for wetlands, amphibian species common to these transition zones between terrestrial and aquatic systems may be key biological indicators of exposure. Both laboratory and *in situ* methods are available for toxicity testing with amphibians, and in view of the strengths and weaknesses of both methods, integrated approaches which involve both field and laboratory methods are critical to the site assessment process.

To illustrate the integration of laboratory and *in situ* methods for toxicity evaluations for representative species in wetlands potentially impacted by waste sites, work has been completed evaluating metal toxicity in amphibians. Initially, our work was primarily driven by the ecological assessment requirements for hazardous waste sites associated with mining activities. For example, in the western United States numerous abandoned and active mining sites present tailings or spoils which are frequently considered waste sites and are subject to regulation. Many of these sites directly impact wetlands associated with them, and ecological effects as well as human health effects frequently are considered during the site assessment process. Here, we will consider the laboratory component of a toxicity assessment for metals characteristic of mine tailings, and describe the *in situ* toxicity test methods which are applicable to a wetlands site assessment and are designed to reduce potential "lab to field" extrapolation errors.

METHODS AND MATERIALS

Laboratory Toxicity Testing. Acute and Short-term Chronic Toxicity Testing with *Xenopus laevis*.

For laboratory testing, FETAX (=Frog Embryo Teratogenicity Assay: *Xenopus*) is currently being standardized (ASTM 1990), and a more thorough outline of routine husbandry and culture practices for in-house use is found in Appendix 1. In these preliminary laboratory toxicity tests, selected metals were evaluated in single-compound exposures. All single-compound exposure solutions were prepared as dilutions of acidified stock solutions (except molybdenum which was prepared as an aqueous stock solution) and were analyzed for total metal at 1000 $\pm$ 10 µgm/L (Sigma Chemical); all metal (Al, Cd, Cu, Fe, Mo, Se, and Zn) values in exposure solutions represent nominal concentrations. In order to more closely approximate conditions anticipated for the *in situ* exposures and avoid speciation changes in metals being evaluated through laboratory exposures, no adjustments for pH or hardness were completed for these laboratory toxicity tests. In the laboratory tests, FETAX static-renewal exposures occurred in 60 x 15 mm Petri dishes containing 8-10 ml control (well water was used as diluent) or toxicant solution with renewals occurring every 24-hours during the 96-hour test. Initially,

control and toxicant exposure solutions were dispensed into each Petri dish, then covered and transferred to an environmental chamber (22 +/- 2°C) for the duration of the 96-hour exposure. For each renewal, fresh control and exposure solutions were prepared. Toxicant dilution series were designed to yield exposure concentrations sufficient to yield EC_{50} and LC_{50} data (median effective and median lethal concentrations, respectively). Assays were set up in triplicate with five concentrations plus controls in each of the replicates.

Mortality (LC_{50}) data was gathered at the end of the four-day exposures, and EC_{50} data was collected coincident with acute toxicity (LC_{50}) data. Subacute and chronic response data (EC_{50}) reflected numbers of gross terata (e.g., scoliosis, lordosis, kyphosis and growth reduction) developed in fifty percent of exposed embryos; EC_{50}s were based upon total numbers of animals exposed. LC_{50} and EC_{50} data were analyzed using trimmed Spearman-Karber (Hamilton, et al. 1977). Additionally, lowest observable effect concentration (LOEC) and no observable effect concentration (NOEC) estimates were derived following an analysis of variance, and when indicated, a multiple comparison of means (Weber, et al. 1989) was completed.

In situ toxicity testing. Field Investigations.

While the laboratory test outlined above yields toxicity estimates under controlled experimental conditions, the potential "lab-to-field" extrapolation error should not be understated. Consequently, toxicity test methods applicable to field evaluations have been developed. Unlike the laboratory method (FETAX), the field test requires varying degrees of site-specific application, but each in situ test is completed within the guidelines established under the site-specific data quality objectives which are developed early in the scoping and planning phases of site work. Each wetland or hazardous waste site evaluation is independently designed, thus the in situ methods outlined here reflect a testing framework amenable to site work under existing field conditions. Briefly, the in situ testing method using amphibians is outlined below.

Standard outline for completing amphibian in situ toxicity tests. Initial site scoping activity.

Before any planning can be completed for in situ amphibian testing at hazardous waste sites, site history, toxicity and chemical information presently available must be compiled. Additionally, any comparative toxicity information relevant to the site toxicity assessment should be collected, e.g., fathead minnow (Pimephales promelas) acute toxicity data base or sediment toxicity data base. A thorough scoping activity should also include available maps and climatological or ecoregional information as well as past compilations of site

activities which could benefit site assessment. In particular, information that identifies spatial or temporal variables which should be incorporated into the initial site work plans ought to be identified for these in situ toxicity assessments. Once these scoping activities have been initiated, site-specific considerations should be weighed for developing a plan from the generalized in situ amphibian toxicity test.

In situ exposures are designed with early life stages in mind, since these represent critical life stages for amphibians. While later stages in metamorphosis are clearly critical and could easily be tested in the exposure cages characterized below, the in situ amphibian toxicity test is primarily designed for evaluating the first 4 to 10 days post fertilization. Recognizing the temperature dependency of normal development, the measurement endpoint most clearly used to define test termination is that of developmental stage rather than a strictly defined time period; the significance of a reference exposure cannot be understated since the achievement of stage-specific test termination in the reference locations determines when the test should be considered "finished." While test termination may be determined on the basis of developmental stage, the implicit interspecies variability is unavoidable and must be considered on a site-by-site basis. If Rana spp. are the most frequently tested species, for example, the stage-specific test termination endpoint would ideally range between Stages 20 and 25 (Shumway 1940), if time on-site allowed. And, if time restrictions were unavoidable, then the maximum exposure time would be allowed, and reference site versus contaminated site stage-specific comparisons would be pursued.

In summary order, in situ exposures should be accomplished following the outline below:

(1) Complete a preliminary water quality characterization for the sites to be tested. These measures should include, but not necessarily be restricted to, water temperature, water hardness, alkalinity, dissolved oxygen, ammonia, conductivity, salinity, or other routine water chemistries. Ideally, these should be completed in the field, and if possible, samples should be collected for a more complete laboratory analysis. The extent to which laboratory characterizations of water quality or contaminants concentrations can be completed will be determined in part by the scoping activities and site plan (e.g., site history and contaminants presumed present) and will vary from site to site. If possible, sediment samples should be collected, particularly if the exposure chambers being used will assure exposures to sediments directly as well as via the water column. These routine water chemistries should be done prior to initiation of the actual in situ testing,

since confounding water quality measures may obscure contaminant effects.

(2) If the water quality measurements suggest that the in situ exposures are feasible and do not preclude a successful test, then the field exposures should be initiated. Recognizing the field constraints for in situ testing, these suggested steps should only guide test design; more often than not, site-specific contingencies will require that methods be modified. To assure that site-specific differences in test methods are documented, a complete field notebook must be maintained and all activities completed during the testing process must be recorded in detail.

(2.1) Fertilized eggs or early embryos may be available from either commercial or in-house sources. Alternatively, resident species collections may be gathered, but the problems of quantity and quality of test organisms **must** be considered and addressed **prior** to their use in testing. Regardless of their source, concurrent analytical controls should be run which will determine the quality of test organisms; past experience has used reference toxicants for this quality control/quality assurance measure. Ideally, these QC/QA determinations are completed in laboratory settings, and temperature and water quality measures are controlled according to routine laboratory testing guidelines.

(2.2) Fertilized eggs or early embryos should be sorted on-site or in the laboratory to assure high viability; then, the fertilized eggs and early embryos should be placed into the exposure cage (Figure 1) following their on-site temperature acclimation. On-site temperature acclimation is most easily accomplished by placing the shipping container (e.g., plastic bag, thermos) directly in the water to be tested; then, the fertilized eggs and early embryos should be temperature equilibrated until ambient and shipping container temperatures are within 1-2°C. Temperature equilibration may be expedited by having shipping conditions closely match those of the site, or by using resident species collections which were gathered under ambient conditions. Ideally, water quality conditions in the shipping container should approximate those ambient conditions measured early in site scoping activities.

The transfer of test organisms to the exposure cage is most easily accomplished by pipeting early embryos directly from their shipping container into the cage. Transfer should be as gentle as possible, and may be expedited by using a plastic tissue culture pipet.

When adequate numbers (preferably 25, but no less than 10) of test organisms have been placed into the exposure cage, the lid is secured with a wing nut. The entire exposure cage should be placed into the test matrix (e.g., sediment and water column) at mapped locations on-site. Cages permit exposures to water column only, or they may be constructed to assure concurrent exposure to water column and sediment. The exposure cages are secured with stainless steel stakes or other restraints, then allowed to track environmental conditions without interference. Temperature is monitored with recording or maximum/minimum thermometers and periodic water quality measures are taken. These water quality measures are taken in the field, and are not considered laboratory-dependent unless site work plans so specify. Daily inspections of the exposure cages are recommended, and when possible ancillary field work (e.g., wetland field surveys) should be completed to complement the toxicity assessment while in progress.

(3) Test termination. Depending upon the test species, test termination should be stage-specific and not necessarily limited to a specific exposure period. For example, if Xenopus laevis is used in in situ exposures and the required equipment readily available (e.g., dissecting binocular microscope), Stage 46 could be the stage-specific test termination endpoint; exposure periods of 4 to 6 days would then be anticipated (depending upon exposure temperatures). If resident species or one of the cosmopolitan Rana spp. are tested, however, Stages 20 through 25 (Shumway 1940) may be a more appropriate stage-specific endpoint, and exposure times may range to 10 to 12 days. Regardless of species, adequate definitions of contaminated and reference sites are required, and if time is limited, "stage achieved" following exposure becomes a measurement endpoint recorded in a specified exposure period. To assure adequate sample sizes for comparisons between reference and contaminated sites, 4 to 6 exposure cages at a minimum should be placed on-site in each area (for a minimum of 8 to 12 exposure cages for the site assessment). The number of exposure cages depends upon the spatial characteristics of the site, the heterogeneity presented by the site, and the time and resources available for the effort. At a minimum, the sampling effort should yield an adequate data base to fulfill the data quality objectives developed for the site.

(3.1) At termination, all test organisms should be saved for future reference, and if possible, laboratory work should be completed for full measures of teratogenic endpoints not readily accessible in the field. At a minimum, the field data should yield

mortality data (dead/alive). Embryos can be saved in histological solutions (e.g., formalin, Bouin's) for future reference or work requiring laboratory study. In the field, preparations of MS-222 (tricaine methane sulfonate) may be used as chemical restraint, if nearby facilities are used for reading test endpoints. Endpoints readily measured in mobile facilities or in laboratories include length measures and teratogenic endpoints; field endpoints could also include behavioral observations such as mobility.

The chemical and toxicological data recorded from a routine in situ amphibian toxicity test then may include: water quality measures (minimum: baseline and final measurements) including, for example, water hardness, alkalinity, salinity, conductivity, dissolved oxygen, total dissolved solids, and ammonia; sediment chemistry; water temperature; weather information during the exposure period; acute toxicity data (dead/alive) and subacute/chronic toxicity information, including teratogenic endpoints (e.g., length).

RESULTS AND DISCUSSION

In situ toxicity tests had been previously developed and evaluated in conjunction with laboratory assessments concerned with nonpoint-source impacts of agrichemicals on wetlands (Linder, et al. 1990). Similarly, laboratory tests with amphibians have previously evaluated discharges from acidic mine drainages to early life stages (Dawson, et al. 1985). But, integrated approaches which apply both laboratory and field toxicity test methods have not been completed. From the laboratory toxicity tests reported here, the evaluation of metal toxicity through FETAX presents results consistent with these evaluations, though the interactions between pH and metals cannot be underestimated. As seen in Table 1, in single-compound exposures all the metals or metalloids (except molybdenum) were clearly acutely toxic at water concentrations less than 2-3 ppm. Similar trends were noted for chronic effects as indicated by the LOEC and NOEC estimates for growth. In addition to these laboratory data, a preliminary toxicity evaluation for heavy metal effects on wetland fauna draws from two literature sources, acidic-mine drainage and coal-fly ash work. Historically, amphibians provide a toxicity data base for identifying potential ecological effects for heavy metals impacting wetlands. To a lesser extent, the recent wealth of "acid deposition effects" work presents toxicity information which regards interactions between pH and heavy metals. All these data bases may be beneficial to preliminary evaluations of contaminant bioavailability in wetlands associated with metal mixtures characteristic of mining wastes.

For example, Dawson, et al. (1988) evaluated metal-contaminated sediment extracts associated with acidic-mine

Table 1. Preliminary acute (mortality) and chronic (growth reduction) toxicity estimates for metals generated from 96-hour laboratory toxicity tests using fertilized eggs and early embryos of Xenopus laevis.

METAL[1]	MEDIAN LETHAL EST. (95% C.I.)[2]	NOEC[2]	LOEC[2]
Al	1.6 (1.3 - 1.9) [pH ca 5.50]	nd[3]	nd
Cd	0.8 (NC[4])	0.1	0.2
	0.9 (0.8 - 1.1) [pH ca 6.80]	0.2 [pH ca 7.20 - 7.50]	0.4
Cu	0.11 (0.10 - 0.13) [pH ca 7.50]	0.05 [pH ca 7.50]	0.10
Fe	1.9 (1.6 - 2.3)	0.3	0.6
	1.7 (1.6 - 1.8) [pH ca 6.00]	[pH ca 6.90 - 7.30]	
Mo[5]	23.5 (19.0 - 29.0)	5.0	10.0
	28.4 (24.1 - 33.4) [pH ca 7.60]	[pH ca 7.50]	
Ni	1.8 (1.6 - 2.1)	< 0.3	0.3
	1.7 (NC) [pH ca 6.00]	[pH ca 7.40]	
Se	1.5 (1.2 - 2.0)	0.8	1.6
	2.0 (1.8 - 2.2) [pH ca 6.50]	[pH ca 6.50 - 7.00]	
Zn	1.3 (1.1 - 1.5) [pH ca 6.60]	0.4 [pH ca 5.50 - 6.70]	0.8

[1]nominal concentrations
[2]metal concentration in parts per million [with associated pH]; median lethal concentrations (LC_{50}s) calculated with trimmed Spearman-Karber and NOEC and LOEC derived from analysis of variance and multiple comparison of means test
[3]nd = not determined
[4]NC = not calculable with trimmed Spearman-Karber
[5]no acute toxicity expressed; EC_{50} in parts per million based on failure to attain Stage 46 after 96-hours

drainage using short-term aquatic toxicity tests. Fathead minnow (Pimephales promelas) and African-clawed frog (Xenopus laevis) embryo-larval toxicity test results indicated that acute and subacute effects were expressed following short-term exposures (4 to 6 days) to metal concentrations in sediment extracts; teratogenic endpoints as well as mortality were evaluated in these exposures to sediment elutriates. Zn and Fe were consistently elevated in these extracts, and although no estimates of differences in metal bioavailability were completed in their work, extract heavy metal concentrations were clearly dependent upon the pH of extraction medium. In their experimental design, exposures were stratified to account for pH effects; LC_{50}s and EC_{50}s for fathead minnows and frogs suggested that mortality and expression of terata were consistent with zinc being the most significant toxicant. Analytical concentrations of metals in sediment extracts ranged between 400 and 16,000 parts per billion in these tests. The work reported in Dawson, et al. (1988) was an extension of previous work completed on acidic-mine drainage (Dawson, et al. 1985), and more fully explored the pH-dependent toxicity issues associated with water samples from discharges taken from abandoned lead and zinc mines.

Albers and Prouty (1987) in field studies of salamanders addressed toxicity related problems potentially expressed in surface water impacted by acidic deposition. While results were largely preliminary, correlations between altered water chemistry (e.g., bioavailability of metals), habitat, and salamander survival were analyzed and suggested that the variability in pond characteristics and salamander reproduction could confound contaminant-related interpretations (e.g., acidic deposition and metal bioavailability), particularly in the absence of laboratory or in situ toxicity assessments. Water concentrations for heavy metals in these field studies ranged between 10 and 270 parts per billion, but no sediment characterizations were completed.

Birge, et al. 1985, Francis, et al. 1984, and Birge, et al. 1979 also provide a starting point for interpreting the laboratory toxicity tests reported here. Using the comparative approach, Birge, et al. (1979) summarized the toxicity of numerous heavy metals to traditional aquatic toxicity test species, including a representative amphibian (narrow-mouthed toad, Gastrophryne carolinensis). In support of the current work reported here, the most toxic metals tested with the amphibian were mercury, silver, zinc, chromium, lead, cadmium, copper, and arsenic. Acute LC_{50}s for these heavy metals ranged between 1 and 100 parts per billion for the toad which indicates a greater sensitivity relative to Xenopus laevis, but this trend in sensitivity has consistently been observed for a variety of contaminants (Dawson, et al. 1988; Linder, et al. 1990). The exposures performed by Birge, et al. (1979) involved aqueous heavy metal

concentrations; heavy metal concentrations in sediment which may have been associated with these water concentrations would have to be considered indirectly. Recognizing the potential influence of sediment quality on heavy metal concentrations in water, Frances, et al. (1984) completed work with cadmium-enriched sediments. In a comparative study using goldfish (Carassius auratus), leopard frog (Rana pipiens), and largemouth bass (Micropterus salmoides), exposures were completed with sediment-water column systems, and demonstrated that enriched sediments presenting 1 to 1000 mg Cd/kg yielded water column [Cd] 1.1 to 76.5 µgm/L. While mortality in the test species was variable and did not yield meaningful median effect estimates, tissue residues were measured and strong correlations between water and tissue, sediment and tissue, and water and sediment concentrations of cadmium were apparent. Comparative toxicity assessments were also incorporated into the work of Birge, et al. (1985) which agrees with the present work. By using traditional aquatic test species for evaluating metals as single-compounds and complex mixtures, they suggested that acute endpoints may be achieved at heavy metal concentrations in the water less than 1.0 mg/L.

With these laboratory toxicity estimates from FETAX and the literature data base in mind, the in situ methods outlined above are currently in progress to evaluate the expression of toxicity in field settings where bioavailability, for example, can be more directly assessed. Through in situ exposures to ambient surface waters and sediments in a wetland potentially impacted by mine wastes, estimates of biological effects such as altered growth can then be evaluated relative to these laboratory generated toxicity endpoints (e.g., NOECs) and field reference sites. Together, these complementary sources of toxicity information will yield "lab-to-field" toxicity comparisons which can be evaluated in conjunction with the overall ecological assessment for the site.

SUMMARY

As potential sources of exposure, the complex chemical mixtures characteristic of a hazardous waste site could exert adverse effects on wetlands located on or near the site. As part of an ecological assessment for the site, then, some measure of toxicity may be required. In order to adequately evaluate the role that toxicity plays in mediating any adverse ecological effects, both laboratory and in situ methods may be applied to the process of toxicity assessment. For these wetland evaluations, amphibians may be representative targets in chemical mixture exposures. Thus, standardized laboratory toxicity tests using amphibians may contribute to the site assessment process. To reduce the potential "lab-to-field" extrapolation error, however, complementary in situ toxicity tests should be completed. By performing these complementary tests, the contribution of toxicity to any site-specific

expression of adverse biological or ecological effect may be more adequately described in the site assessment process.

REFERENCES

Albers, P.H. and R.M. Prouty. 1987. Survival of Spotted salamander eggs in temporary woodland ponds of coastal Maryland. Environmental Pollution 46: 45-61.

ASTM. 1990. Draft No. 4, Standard guide for conducting the frog embryo teratogenesis assay-Xenopus (FETAX). American Society for Testing and Materials, ASTM Committee E-47 on Biological Effects and Environmental Fate, Philadelphia, PA.

Birge, W.J., J.A. Black, and A.G. Westerman. 1985. Short-term fish and amphibian embryo-larval tests for determining the effects of toxicant stress on early life stages and estimating chronic values for single compounds and complex effluents. 1985. Environ. Toxicol. Chem. 4: 807-821.

Birge, W.J., J.A. Black, and A.G. Westerman. 1979. Evaluation of aquatic pollutants using fish and amphibian eggs as bioassay organisms. In Animals as Monitors of Environmental Pollutants, National Academy of Sciences, Washington, D.C.

Dawson, D.A., E.F. Stebler, S.L. Burks, and J.A. Bantle. 1988. Evaluation of the developmental toxicity of metal-contaminated sediments using short-term fathead minnow and frog embryo-larval assays. Environ. Toxicol. Chem. 7(1):27-34.

Dawson, D.A., and J.A. Bantle. 1987. Development of a reconstituted water medium and preliminary validation of the frog embryo teratogenesis assay-Xenopus (FETAX). J. Appl. Toxicol. 7(4):237-244.

Dawson, D.A., C.A. McCormick, and J.A. Bantle. 1985. Detection of teratogenic substances in acidic mine water samples using frog embryo teratogenesis assay -- Xenopus (FETAX). J. Appl. Toxicol. 5:234-244.

Deuchar, E.M. 1975. Xenopus, the South African Clawed Frog. John Wiley and Sons, New York, NY.

Francis, P.C., W.J. Birge, and J.A. Black. 1984. Effects of cadmium-enriched sediment on fish and amphibian embryo-larval stages. Ecotoxicol. Environ. Safety 8: 378-387.

Hamilton, M.A., R. Russo, and R.V. Thurston. 1977. Trimmed Spearman-Karber method for estimating median lethal concentrations in toxicity bioassays. Environmental

Science Technology. 11:714-719 (Correction, Environmental Science and Technology. 12: 417).

Linder, Greg, Janet Barbitta, and Ty Kwaiser. 1990. Short-term amphibian toxicity tests and paraquat toxicity assessment. In Aquatic Toxicology and Risk Assessment, Thirteenth Symposium. American Society for Testing and Materials, STP. Philadelphia, PA. In Press.

New, D.A.T. 1966. The Culture of Vertebrate Embryos. Academic Press, New York, NY.

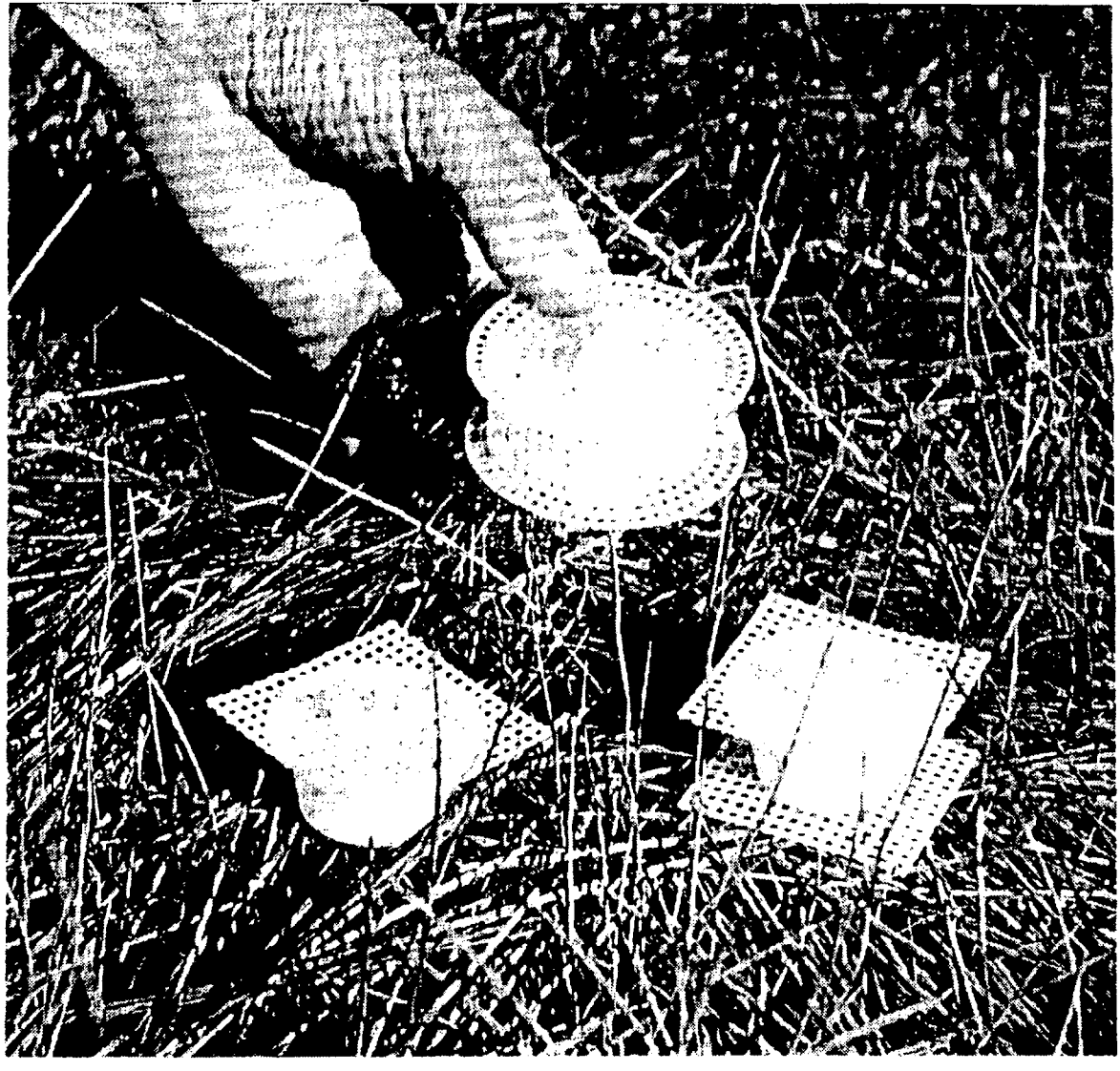
Nieuwkoop, P.D., and J. Faber. 1975. Normal Table of Xenopus laevis (Daubin), North Holland Publishing Company, Amsterdam, Holland.

Rugh, R. 1962. Experimental Embryology. Burgess Publishing Company, Minneapolis, MN.

Shumway, W. 1940. Stages in the normal development of Rana pipiens. Anat. Rec. 78:139-147.

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

Figure 1. Exposure cages used in in situ amphibian toxicity tests. Three cage designs are routinely available for evaluating in situ toxicity with amphibians. Version 4 (held in hand) is a completely open cage which confines the test organisms. When no distinctions are required between sediment and water column borne contaminants, Version 4 is the exposure cage of choice. Versions 2 and 3 (exposure cages in lower left and lower right, respectively) are earlier designs and smaller in physical dimensions. In Version 2, water exchange between inside and outside of the exposure cage occurs only through the 10-count mesh top cover. Design characteristics of Version 2 assure that field exposures approximate the static laboratory conditions characteristic of FETAX, since no direct contact with sediment occurs and passage of water over the developing embryos is minimal. Version 3 is similar to Version 2, but the 10-count mesh is also used on the bottom of the exposure chamber and allows direct contact with sediments. Version 3 allows exposure to both sediment and water column but minimizes the direct passage of water over the developing embryos.



Appendix 1. Laboratory toxicity testing with Xenopus laevis. Routine husbandry and collection of fertilized eggs and embryos for testing.

Routine husbandry. The African-clawed frog (Xenopus laevis) is easily maintained in the laboratory, and husbandry practices are well established (Rugh 1962; New 1966; Deuchar 1975; Nieuwkoop 1975). Owing to its ease of maintenance and responsiveness to hormone-induced ovulation, Xenopus laevis is gaining in its application to subacute toxicity testing (Dawson, et. al. 1988; Dawson and Bantle 1987), and particularly so, in those bioassays which regard teratogenic and mutagenic endpoints. Xenopus breeding pairs, eggs, embryos and tadpoles, as well as post-metamorphic sexually immature individuals should be housed in an environmental chamber (22 +/- 2°C; 16:8 L:D). All animals should be held in glass aquaria as breeding pairs, or two or three post-metamorphic juveniles per aquarium; if raised under static conditions, tadpoles should be cleaned three to four times per week and held in aquaria until metamorphosis, then transferred as age-class cohorts to holding aquaria. All adults and post-metamorphic juveniles should be identified with fingerling tags. Routine husbandry should use reconstituted freshwater or conditioned tap water, and secure covers should be placed over the aquaria housing breeding pairs and post-metamorphic individuals. Feeding and cleaning of adults and post-metamorphic juveniles should be completed twice-weekly (e.g., Tuesday and Friday); adults and post-metamorphic juveniles should be feed beef liver with supplements of commercial chows of appropriate mill. Tadpoles should be fed commercial chow of appropriate mill.

Culture and handling. Breeding pairs should be conditioned by administering hormone injections (HCG, human chorionic gonadotropin) according to routine culturing practices (Rugh 1962; New 1966; Deuchar 1975) which allow harvesting of fertilized eggs and embryos to ensure adequate numbers of Stage 8 through Stage 11 individuals for testing (Dawson, et. al. 1988; Dawson and Bantle 1987). Hormone injections may be required over a three-day period, but egg laying routinely occurs by the end of first day. Fertilized eggs should be collected and held at 22 +/- 2°C until attaining Stages 8 through 11 when they are ready for toxicity testing.

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RAPID SCREENING OF SOIL AND WATER SAMPLES FOR TOTAL PAH CONTENT BY UV FLUORESCENCE SPECTROSCOPY

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ABSTRACT

Methodology has been developed which combines microextraction and UV fluorescence techniques for rapid screening of soil and water samples for total Polynuclear Aromatic Hydrocarbon (PAH) concentration.

Method accuracy and precision were determined by analyzing a series of spikes prepared with background soil and water for each site requiring method use. This method validation step has been conducted using naphthalene, acenapthene and phenanthrene as target compounds. These compounds are representative of PAH compounds in general.

A calibration mixture of seven PAH compounds, containing from two to six rings, was prepared to estimate total PAH content of on-site and background soil and water samples. The resulting data was compared with GC/MS results.

INTRODUCTION

This report describes method development and validation of field screening techniques for rapid determination of the total PAH concentration in soils and waters found at wood treating sites. Available GC/MS PAH data provided the necessary information to proceed with method development.

This methodology arose out of the need to provide field lab capability in support of Remedial Investigation activities at wood treating sites. The intent of this method was to provide a Total PAH concentration comparable to more conventional methods (e.g., EPA-CLP protocol and or 8270). Target detection limits were in the range of 1-10 µg/g in soil and 1-10 µg/L in water samples.

SUMMARY

Methodology was developed to screen soil and water samples for total PAH concentration by microextraction and UV fluorescence. Method accuracy and precision were established by performing a series of sample spikes, using background site matrix and selected PAH compounds. The method yielded quantitative and reproducible results. A calibration mix

containing seven PAH compounds was then prepared to allow for quantitation of the total PAH concentration in field samples. These results compared favorably with conventional GC/MS results.

SCREENING METHOD VALIDATION - COMPOUND SELECTION

To demonstrate and document method performance three PAH compounds, naphthalene, acenapthene and phenanthrene were selected to spike sample matrices to determine method precision and accuracy.

Each of the three compounds were prevalent among PAH compounds quantified by GC/MS at the wood treating sites. These compounds would be expected to closely parallel the behavior of all PAH compounds of interest (from two to six rings) in the analysis schemes developed.

Spectral characteristics of the three compounds are given in Table 1. Naphthalene and acenapthene are quantified simultaneously as total naphthalene/acenapthene while phenanthrene is quantified at a different wavelength pair.

Table 1
UV FLUORESCENCE CHARACTERISTICS OF TARGET COMPOUNDS

COMPOUND	EXCITATION (Ex) and EMISSION (Em) MAXIMA		COMPROMISE WAVELENGTHS USED	
	Ex	Em	Ex	Em
Naphthalene	275nm	355nm	280nm	340nm
Acenapthene	280nm	355nm	280nm	340nm
Phenanthrene	250nm	365nm	250nm	370nm

METHOD VALIDATION - SOIL

Method validation for soil was conducted by initial demonstration of accuracy and precision followed by comparison of rapid screening total PAH concentration with conventional GC/MS results.

To determine accuracy and precision, a series of background, or near-site samples were analyzed to select a relatively clean matrix for spiking. The objective was to select a soil similar in composition to those known to be on-site, as well as low enough in background fluorescence to provide validation data at or near the target detection limit.

After selection of a background soil, a series of spikes were performed on the background soil with naphthalene, acenapthene

and phenanthrene. Due to the spectral characteristics of these compounds (Table 1) naphthalene and acenapthene were quantified as total naphthalene/acenapthene concentration. A summary of the method employed follows:

Rapid Screening of Soil for Total PAH Concentration:

1. Weigh 1.0 g wet soil into a 40 mL vial.

2. Add 1.0 g anhydrous sodium sulfate.

3. Add 10 mL UV grade acetonitrile.

4. Shake vigorously for 15 seconds.

5. Let sample settle for 1 minute.

6. Filter sample through 0.2 micron Teflon® filter (with in-line syringe.

7. Calibrate instrument from 0.1 to 1.0 µg/mL for each target compound.

8. Analyze extracts by UV fluorescence, diluting the extract into calibration range as necessary.

9. Standards must be prepared in acetonitrile, which is the same solvent used for extraction.

Acetonitrile was selected as an extraction solvent over hexane and toluene due to its UV fluorescence transparency, and ability to rapidly disperse wet soil. Additionally, PAH standards in acetonitrile exhibited the greatest fluorescence sensitivity.

A summary of soil validation results from a wood treating site is shown below. Results are based on triplicate analysis and are corrected for background fluorescence. The total PAH concentration is the sum of equal fortification levels for all three compounds.

Table 2
METHOD PRECISION AND ACCURACY
FOR TOTAL PAH IN SOIL SAMPLES

Total Concentration µg/g	Average Recovery(%) Naphthalene/ Acenapthene	RSD(%)*	Average Recovery(%) Phenanthrene	RSD(%)*
6	85	2.5	87	2.0
15	63	1.8	77	1.3

Table 2 (con't)
METHOD PRECISION AND ACCURACY
FOR TOTAL PAH IN SOIL SAMPLES

Total Concentration µg/g	Average Recovery(%) Naphthalene/ Acenapthene	RSD(%)*	Average Recovery(%) Phenanthrene	RSD(%)*
30	79	3.3	78	3.0
150	90	0.6	85	0.7
300	92	0.0	89	0.6

*Relative Standard Deviation

METHOD VALIDATION - WATER

An identical scheme to that used for soil samples was used for validation of the developed water protocol. Selection of a background sample, generation of precision and accuracy data and comparison of rapid screening PAH concentration with conventional GC/MS results were performed. Hexane became the extraction solvent of choice due to its ease of use during the microextraction step. Consequently, calibration standards must be prepared in hexane for PAH screening of water samples.

Rapid Screening of Water for Total PAH Concentration:

1. Mix sample. Add 25 mL of sample to a 40 mL Teflon® capped vial.

2. Add 5 mL UV grade hexane. Shake for 1 minute.

3. Let sample settle for 5 minutes.

4. Filter extract through 1 inch column of anhydrous sodium sulfate to remove water.

5. Prepare calibration standards in hexane, which is the same solvent used for sample extraction.

6. Analyze hexane extract by UV fluorescence.

Precision and accuracy data are presented below in Table 3. Precision is based on triplicate analysis. Note that total concentration is the sum of concentrations of the three spiking compounds. At 9 µg/L, each of the those compounds were spiked at 3 µg/L. Results are corrected for background fluorescence.

Table 3
METHOD PRECISION AND ACCURACY
FOR TOTAL PAHs IN WATER SAMPLES

Total Concentration µg/L	Average Recovery(%) Naphthalene/ Acenapthene	RSD(%)*	Average Recovery(%) Phenanthrene	RSD(%)*
9	94	10	100	11
90	98	4.1	97	2.4
1800	101	4.5	101	3.5

*Relative Standard Deviation

COMPARISON OF RAPID SCREENING VS. GC/MS TOTAL PAH RESULTS

After demonstration of method accuracy and precision by spiking of site background matrices, the method was then adapted to provide a total PAH result comparable with conventional methodology.

This adaptation was made by changing the composition of the calibration mix. Examination of available site data (GC/MS) revealed a fairly consistent pattern of relative abundances of quantified PAH compounds. Of the twelve predominant PAH compounds, seven were selected to prepare a calibration cocktail, as shown in Table 4.

Table 4
COMPOSITION OF TOTAL PAH SCREENING STANDARD MIX

Compound	Group No	No. of Rings	Stock Concentration in µg/mL	Compromise Wavelength (nm Pairs)	Wavelength Pair Group Concentration
naphthalene	1	2	100	280/340}	
acenapthene	1	3	100	280/340}	300 µg/mL
fluorene	1	3	100	280/340}	
phenanthrene	2	3	100	250/400}	
fluoranthene	2	4	100	250/400}	400 µg/mL
pyrene	2	4	100	250/400}	
benzo(k)-fluoranthene	2	6	100	250/400}	

As depicted in Table 4, three compounds were calibrated using the 280 nm/340 nm wavelength pair and four compounds were calibrated using the 250 nm/400 nm wavelength pair. Serial dilutions were prepared to calibrate from 0.005 µg/mL to

1 µg/mL for each component. Thus, the calibration range was 0.015 µg/mL to 3 µg/mL for group 1 (3 components) and 0.020 µg/mL to 4 µg/mL for group 2 (4 components). Results from screening water and soil samples for total PAH concentrations are compared with GC/MS results in Table 5 and Table 6 respectively. Sample preparation for these analyses is identical to the procedures outlined in the method validation sections. The calibration cocktail was prepared in acetonitrile and diluted into acetonitrile for soil screening and hexane for water screening.

Table 5
COMPARISON OF UV FLUORESCENCE RAPID SCREENING AND GC/MS DATA FOR TOTAL PAH IN WATER SAMPLES

Sample I.D.	Type	Technique	Total PAH µg/L Rep#1	Rep#2	Rep#3	Average PAH Concentration µg/L
SW-1	On-site	UV	4800	2600	440	2600
SW-1	On-site	GC/MS	1200	---	---	1200
SW-2	On-site	UV	490,000	310,000	390,000	400,000
SW-2	On-site	GC/MS	150,000	---	---	150,000
BW-1	Background	UV	15	17	24	19
BW-1	Background	GC/MS	ND	---	---	ND
BW-2	Background	UV	23	27	143	64
BW-2	Background	GC/MS	ND	---	---	ND

Table 6
COMPARISON OF UV FLUORESCENCE RAPID SCREENING AND GC/MS DATA FOR TOTAL PAHs IN SOIL SAMPLES

Sample I.D.	Type	Technique	Total PAH µg/gm (dry weight) Rep#1	Rep#2	Rep#3	Average PAH Concentration µg/gm
SS-1	On-site	UV	490,000	420,000	370,000	390,000
SS-1	On-site	GC/MS	64,000	---	---	64,000
SS-2	On-site	UV	230,000	230,000	82,000	169,000
SS-2	On-site	GC/MS	19,000	---	---	19,000
BS-1	Background	UV	38	48	51	46
BS-1	Background	GC/MS	35	---	---	35

Table 6 (con't)
COMPARISON OF UV FLUORESCENCE RAPID SCREENING AND GC/MS DATA FOR TOTAL PAHs IN SOIL SAMPLES

Sample I.D.	Type	Technique	Total PAH µg/gm (dry weight) Rep#1	Rep#2	Rep#3	Average PAH Concentration µg/gm
BS-2	Background	UV	4.2	9.5	5.4	6.4
BS-2	Background	GC/MS	19	---	---	19

NOTE: ND=Not Detected
---=Not Analyzed
Rep=Replicate

RESULTS AND DISCUSSION

The rapid screening methodology presented herein for total PAH content in water and soil provides an estimation of PAH content which compares favorably to results obtained by conventional GC/MS techniques (Tables 5 and 6). In all cases UV fluorescence screening gave total PAH concentration within one order of magnitude of total PAH concentration derived from GC/MS analysis.

GC/MS results for total PAHs are the sum of a discrete number of HSL PAH compounds. GC/MS operators have noted that some of these samples contained numerous PAH compounds not included on the HSL list. These compounds differ from HSL PAH compounds in either parent ring structure or degree of substitution (primarily alkyl) on the parent ring structure. In many cases these compounds were present at levels comparable to the HSL compounds used to obtain a sum representing total PAH concentration. Therefore, it is likely that GC/MS total PAH results actually represent a minimum for each sample. This offers at least partial explanation for the higher results obtained by rapid screening for total PAH (Tables 5 and 6).

Results for total PAH in water show a range of concentrations not observed during method validation. Those using this method should consider the option of sample filtration to minimize effects of non-homogenous samples due to suspended particulates.

Also, due to the difference in sample size between conventional soil PAH methodology and the rapid screening techniques presented here, caution should be exercised during interpretation of soil results. The possibility of a non-

homogenous soil sample can be minimized by thorough mixing or replicate analysis or increased sample size for screening.

Additionally, in the case of both soil and water samples analysis of a percentage of field samples by conventional techniques will give greater validity to those results obtained in the field.

Analysis of high level PAH samples revealed the potential for self quenching. It is recommended that a series of dilutions to verify results be analyzed if self-quenching is suspected.

This method has always been thoroughly validated for the sites requiring field lab PAH screening prior to deployment. It is strongly recommended that this practice be followed due to the non-specific nature of UV fluorescence screening.

In summary the PAH screening techniques presented provide a rapid, valid estimate of total PAH concentration in both soil and water. When validated for each site and used within the method capabilities rapid analytical support at field investigation activities is achieved.

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MONITORING AND MEASUREMENT TECHNOLOGY DEMONSTRATIONS UNDER THE SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION (SITE) PROGRAM

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ABSTRACT

The U.S. Environmental Protection Agency SITE Program was established to satisfy a mandate of the Superfund Amendments and Reauthorization Act of 1986 to demonstrate alternative or innovative treatment technologies. This also encompassed monitoring and measurement of contamination occurring at hazardous waste sites. The present paper describes the monitoring and measurement technology demonstration portion of SITE and gives two examples. One is a demonstration of a pentachlorophenol field immunoassay conducted in the summer of 1989 at the MacGillis and Gibbs Superfund Site, New Brighton, Minnesota. The other is a demonstration of ion-mobility spectrometry being planned for 1990.

INTRODUCTION

The Superfund Amendments and Reauthorization Act of 1986 (SARA) charged the U.S. Environmental Protection Agency (U.S. EPA) with effecting more timely and cost-effective remedies at the Nation's Superfund sites. The costs incurred for site characterization are a direct result of sampling, analysis, and the associated quality assurance activities. The capabilities of field screening methods to yield immediate or short-turnaround environmental data will result in major cost savings. The cost-effectiveness of clean-up efforts will be improved dramatically. More cost-effective and timely remediation will decrease the human and ecological risks around Superfund sites and enhance the ability to manage such risks.

The U.S. EPA SITE Program was established to satisfy the mandate in Section 311(b) of SARA, which requires U.S. EPA to establish "a program of research, evaluation, testing, development and demonstration of alternative or innovative treatment technologies...which may be utilized in response actions to achieve more permanent protection of human health and welfare and the environment." The two categories of technologies included in the SITE Program are (1) treatment technologies which may serve as alternatives to land disposal of hazardous wastes, and (2) monitoring and measurement technologies for contaminants occurring at hazardous waste sites. The Monitoring and Measurement Technologies Program is that component of SITE established to address the latter.

NOTICE

Although the research described in this article has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

The SITE Program provides the Agency with a good mechanism to identify, and demonstrate innovative or alternative site characterization technologies that exist within and outside the Federal government which may provide cost-effective, better, and faster means to detect and monitor contaminants at uncontrolled hazardous waste sites. It also provides developers with the means to rigorously evaluate the performance of their technologies and have the results and recommendations widely distributed, thereby enhancing the market for those technologies.

Products from the various research, development, and demonstration activities conducted under this Program will enhance the Agency's ability to perform statistically-valid sampling and field analytical programs that yield effective site characterization coupled with immediate or quick-turnaround environmental data acquisition.

The Monitoring and Measurement Technologies Program portion of SITE is also the core of the Advanced Field Monitoring Methods Program which was implemented in fiscal year 1988 to provide a mechanism to identify, test, evaluate, and accelerate the use of innovative and alternative field monitoring and measurement technologies, primarily in support of the Regional Superfund staffs. The Advanced Field Monitoring Methods Program enhances the SITE Program by adding an in-house methods research element and additional technology transfer through the preparation, testing, and promulgation of standard methods, and through the development of protocols for the successful use of technologies by field personnel.

This paper describes the program elements of the Advanced Field Monitoring Methods Program followed by a brief summary of Demonstration Program activities and two examples.

ADVANCED FIELD MONITORING METHODS

There are four important components, Technology Identification and Selection, the Demonstration Program, the Emerging Technologies Program, and Technology Transfer (Figure 1). Each component is briefly discussed below.

TECHNOLOGY IDENTIFICATION AND SELECTION

Candidate technologies come from a variety of sources, including U.S. EPA in-house and extramural research projects, other Federal Agencies, and the private sector. New technologies and modifications of existing technologies applicable to soil, ground water, surface water, sediment, biological tissues, etc., and the collection, preparation, and field analysis for use at or around uncontrolled hazardous waste sites are of interest to the Agency.

Technologies included in either the Demonstration or Emerging Technologies Programs are selected based on criteria such as cost, portability, ease of operation, various performance factors, and regional need.

The most mature field screening devices appear to be gas chromatographs, x-ray fluorescence spectrometers, and sampling and analysis equipment for soil gas and air. Those that have been used but are in various stages of improvement include mass spectrometers and gas chromatographs/mass spectrometers. The newest are fiber-optic sensors, other chemical micro-sensors (e.g., piezoelectric), biomethod devices/ kits, and ion-mobility spectrometers. Various spectroscopic techniques are also emerging either as stand-alone methods or in combination with fiber-optic technology. These include surface-enhanced Raman, laser-induced fluorescence, derivative ultraviolet and spectrochemical emission.

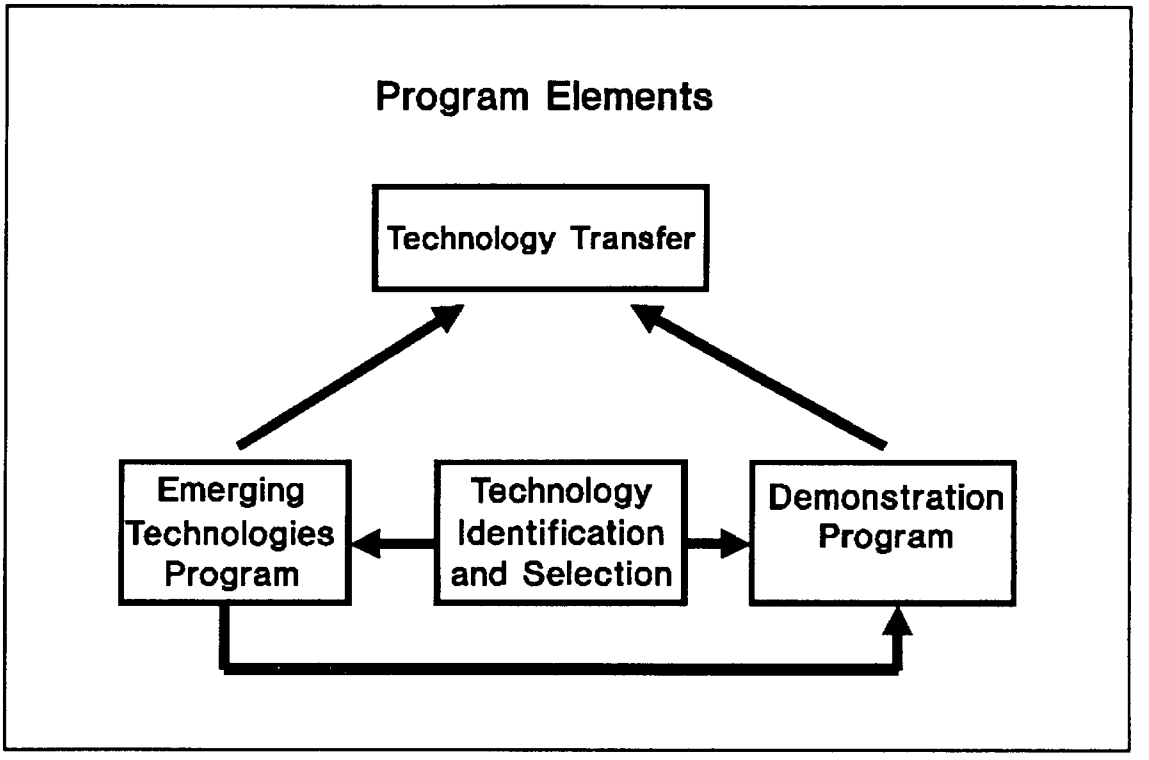

Figure 1. ADVANCED FIELD MONITORING METHODS PROGRAM ELEMENTS

DEMONSTRATION PROGRAM

The major objective of the Demonstration Program is to develop reliable performance and cost information on innovative or alternative technologies. The technologies considered ready for demonstration are those that have had a sufficient amount of pilot testing in the laboratory and are amenable for field use with real-world samples, among other criteria. Evaluation of the data generated in pilot testing determines whether a reasonable likelihood of success in a SITE demonstration can be anticipated or whether additional/testing and technology refinement are required.

The conduct of a demonstration is a collaborative effort between the developer and the Agency. Development of the demonstration plan, selection of QA/QC procedures, selection of a demonstration site, etc., are done jointly and cooperatively. The Agency absorbs the costs of (and has the primary responsibility for) the development of the demonstration plan, collection of confirmatory sampling and analytical data, and other aspects of the demonstration process. The developer will, under most circumstances, be responsible for reviewing plans, the costs of mobilizing the technology on a site, and providing the staff to demonstrate or oversee the demonstration of the technology.

EMERGING TECHNOLOGIES PROGRAM

The Emerging Technologies Program fosters further development of technologies that are not yet ready for demonstration. The goal is to ensure that a steady stream of appropriate technologies are ready to be demonstrated, thereby increasing the number of viable alternatives

available for use in Superfund site characterizations and cleanups. Candidate technologies must show promise at the laboratory scale to be considered for this portion of the program. It enables technology developers to advance from the laboratory toward field demonstration through cooperative funding with the U.S. EPA.

TECHNOLOGY TRANSFER

Efforts in both the Demonstration and Emerging Technologies Programs culminate in technology transfer products. These products may include:

- demonstration reports,
- technology demonstration and evaluation summaries,
- videotapes of the demonstration and/or operation of the technology,
- journal articles,
- technical conferences, workshops, and/or symposia.

SUMMARY OF DEMONSTRATION PROGRAM ACTIVITIES

In FY89 there were three activities that occurred under the Demonstration Program:

- Field demonstration of an immunoassay method for the analysis of pentachlorophenol in water.
- Testing of various air monitoring technologies (pre-demonstration).
- Side-by-side demonstration of five commercially available portable gas chromatographs.

For FY90 and beyond a number of activities are being planned including:

- Demonstration of commercially available field portable x-ray fluorescence spectrometers (tentatively planned for FY91).
- Demonstration of commercially available portable ion mobility spectrometers (being planned for late FY90).
- A demonstration of a field portable mass spectrometer with a thermal desorption probe (being planned for late FY90).
- Testing and demonstration of a global positioning system in combination with various portable field sensors and a bar code reader/generator for labeling and tracking samples. The demonstration is tentatively planned for FY91.

Two of the technologies have been chosen for more detailed discussion in the remainder of this paper. One is a field immunoassay for the analysis of pentachlorophenol in water which was demonstrated in FY89. The other is ion-mobility spectrometry which is planned for demonstration in FY90.

DEMONSTRATION OF PENTACHLOROPHENOL IMMUNOASSAYS AT THE MACGILLIS AND GIBBS SUPERFUND SITE, NEW BRIGHTON, MINNESOTA

The Project Officer for this demonstration was Dr. Jeanette M. Van Emon, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Las Vegas.

Background: Immunochemical methods have traditionally been employed in clinical chemistry applications. This field has been rapidly growing and expanding beyond the traditional borders into problems associated with environmental chemistry. Immunoassay techniques have been applied to the analysis of many hazardous substances, and possess several attributes that make them suitable for field screening methods. In general, immunoassays have proven to be sensitive, selective, precise, rapid, cost-effective, and applicable to a wide range of contaminants. Several different immunoassay formats for environmental analytes are possible. Regardless of the assay design, each is dependent on a highly specific antigen-antibody reaction. A compilation of references addressing the development and utilization of immunoassays has been brought together by Van Emon (1). An excellent tutorial on immunoassay techniques and a summary of applications for pesticide analysis is also available (2).

The immunoassay technology demonstrated was a field analysis kit for the rapid screening of pentachlorophenol in aqueous samples. This technique is a competitive immunoassay method developed by Westinghouse Bio-Analytic Systems (WBAS) of Rockville, Maryland. The method is designed to provide a quick and inexpensive means of detecting pentachlorophenol in water samples under field or mobile laboratory conditions. The method requires about 30 minutes to perform; has a detection limit down to about 2 ppb; has a linear dynamic range from about 2-40 ppb; and can be used with a portable spectrophotometer for standard curve generation and quantification. Eight analyses are performed at one time in a strip of eight polystyrene cuvettes.

An opportunity was available to leverage the WBAS pentachlorophenol field immunoassay demonstration with the field and analytical operations of the BioTrol, Inc. treatment technology demonstration being conducted at the MacGillis and Gibbs Superfund Site. This site demonstration was conducted by the staff of the Risk Reduction Engineering Laboratory in Cincinnati, Ohio. The MacGillis and Gibbs Site is a wood-preserving treatment facility that had historically used pentachlorophenol. As a result of this former wood-preservation practice, the ground water is contaminated with pentachlorophenol at an average concentration of 50 ppm. The contaminated ground water was treated with nutrients and processed through the BioTrol bioreactor for degradation. The resulting treated effluent for the MacGillis and Gibbs demonstration averaged a pentachlorophenol concentration of 1 ppm. The WBAS and BioTrol demonstrations, although conducted at the same site, were separate. Even though the immunoassay results were obtained on-site, the data were not to be used to make conclusions regarding the performance of the bioreactor.

The purpose of the immunoassay demonstration was to evaluate the field technique for the detection of pentachlorophenol in aqueous samples. Preliminary performance data from tests conducted in a controlled laboratory environment was generated by using specified concentrations of pentachlorophenol spiked into laboratory-grade water. In addition, other tests were conducted using bioreactor influent and effluent water samples and raw ground water from the site. The results from these preliminary analyses suggested that the WBAS field method was ready for a demonstration under the SITE Program.

Demonstration Approach: As part of the BioTrol demonstration, composite samples were collected once every 24 hours for a period of six weeks at critical points in the bioreactor system to verify the performance of the technology. The samples were processed and analyzed for a variety of organic, inorganic, and physical characteristics. Analysis of the samples for pentachlorophenol, in support of the bioreactor demonstration, was accomplished using EPA Method 8270 (gas chromatography/mass spectrometry,

GC/MS) after a Method 3510 extraction. Splits of some of the samples were analyzed with the immunoassay field method at three locations (on-site, WBAS, and EMSL-LV), and confirmed with a laboratory-based immunoassay plate assay which was also developed by WBAS. The GC/MS analysis from the BioTrol study was also used to verify the performance of the field kit.

Summary of Results: Based on the information collected from this site demonstration, it was concluded that technologies such as the pentachlorophenol field immunoassay can be useful in monitoring site remediation activities. Data that are collected in real time and on-site can be used to direct remediation activities in a timely and cost-effective manner.

The pentachlorophenol immunoassay was easy to perform on-site by personnel relatively untrained in the methodology. The immunoassay could always distinguish between effluent and influent samples providing a quick check on the performance of the bioreactor. This is a significant attribute of a rapid turn-around method such as the immunoassay. Problems encountered with a remediation technology can, therefore, be corrected in a timely manner.

The immunoassay gave slightly inflated results over the GC/MS analyses. This could be due to cross-reaction with tetra- and trichlorophenol. However, for these compounds, a field screening method with "class" specificity is more appropriate. Also, when the GC/MS data are reported, there are no corrections made for the efficiency of the method, thus the difference seen between the two data sets is actually smaller. The immunoassay samples did not need to be extracted but were simply diluted and analyzed. Thus, losses of analyte were minimized and procedural efficiency was increased. The on-site immunoassay data compared favorably with data obtained when the method was performed under laboratory conditions. Field data also compared well with a parallel laboratory-based immunoassay format.

The pentachlorophenol immunoassay was a good example of how the technology can be used for field screening. The method was easy to perform, rugged, cost-effective, generated only minor amounts of aqueous waste. It compared favorably to GC/MS data in terms of precision and accuracy which was impressive considering the immunoassay is a semi-quantitative method.

The sample throughput of the immunoassay, already much greater than for GC analysis, can be further increased by employing either twelve or sixteen cuvettes instead of eight. This is a simple matter as these cuvettes are commercially available. For field screening, it may be useful to raise the detection limits of the immunoassay. Thus, the number of dilutions that are needed could be reduced, thereby saving time and minimizing procedural error.

Future Perspectives: The pentachlorophenol immunoassay could be used for environmental screening of aqueous samples and for monitoring remediation technologies which generate aqueous samples. The data obtained could be used to make decisions regarding the performance of a remediation technology. A certain percentage of the samples, both negative and positive, should be confirmed by a detailed GC analysis. As with any analytical method, representative samples should be analyzed before employing the method in a monitoring study. The pentachlorophenol immunoassay is a semi-quantitative analytical method that has significant applications to monitoring studies.

A PLANNED DEMONSTRATION OF ION-MOBILITY SPECTROMETRY

Principles: The challenge of choosing monitoring and measurement methods for use at Superfund sites is a major one because of the many different compounds that could be encountered. An emerging technology for vapor monitoring such as the detection of volatile organic compounds in ambient air and/or for quick screening of soil - gas samples is ion-mobility spectrometry (IMS). It is a promising candidate for the monitoring and measurement technologies demonstration portion of the SITE Program. Ion-mobility spectrometers, ranging from hand-held to laboratory bench models, are beginning to appear on the commercial market. This has been facilitated through a long-standing research and development investment by the United States and British Armies in the field use of portable IMS units for chemical defense applications. An appreciation of some of the applications can be obtained from articles by Carrico (3) and Eiceman (4).

Ambient air is usually pumped into the spectrometer through a semipermeable membrane. (One model also uses an adjunct carrier gas.) Ions are formed from air or carrier gas molecules by using an ionization source such as Nickel-63 (beta emitter). These ions then react with analyte molecules to form ion clusters which are subject to atmospheric pressure "time of flight" measurements. The ions are allowed to enter a drift region where they move under the influence of an applied field to a collector electrode. The electrode current is monitored continuously thus allowing a mobility spectrum to be measured. Ionization preferences of analytes and mobility differences of the ion clusters impart specificity. Separations are a function of ion size.

Characteristics: A self-contained instrument is available which weighs under six pounds and can be readily used outdoors. Weight and number of components in other available units increase with degree of sophistication. For example a package is being marketed which contains two basic parts, a controller and a recirculating gas supply, weighing about 27 pounds. A 12-volt battery pack and a portable computer are also required. Another unit weighs about 18 pounds and also needs a peripheral battery pack and a computer but not a carrier-gas module. These latter packages are indeed portable but their design seems to have been optimized for indoor rather than outdoor use. There are other units under development which are claimed to be either portable or field transportable, however, they are not presently available.

The Technology is Still Emerging: The IMS units are intended to be used in a pre-programmed fashion such that they are capable of monitoring one of a number of chemicals in a defined situation. They operate in either negative or positive ion modes. In the hand-held version, specific analytes may be pre-programmed into these modes (e.g., maximum 5 in the positive mode and 3 in the negative mode). The more sophisticated packages allow the operator to reprogram. They also allow more capability in terms of quantitative measurements, and numbers of compounds that can be identified. The hand-held version uses a liquid crystal display of bars which relate to concentration levels.

The IMS data available in the literature deal primarily with chemicals on an individual basis. A large number of compounds can be measured but not simultaneously. The response of a particular analyte may be influenced by the presence of other chemicals. The many ions that might form in a complicated mixture of compounds could interact with each other. Such interactions need to be understood to take full advantage of IMS capability. Since the performance of IMS under hazardous waste site conditions has not been determined a demonstration under the SITE program is logical and attractive.

Selectivity of IMS for different analytes is based on the atmospheric pressure ionization events themselves (which relate to the proton and electron affinities of the analytes), the polarity of the products (i.e., positive versus negative ions) and the mobility of the ions. Target analytes with higher electron or proton affinities than other chemicals in the ambient environment can be differentiated and detected readily. Analytes with low affinities can be measured as long as chemicals with strong affinities are absent.

Compounds likely to be found at hazardous wastes sites and detectable using IMS include phenols, anilines, dialkylphthalates (and other esters), ethers and organophosphorus insecticides, among others. Specificity and sensitivity improve with increasing molecular weight.

Hydrocarbons such as hexane and benzene would not be expected to exhibit high selectivity and sensitivity. However, polychlorinated aromatics should be detected more readily. Compounds such as the PCBs should be very easily detected but their low vapor pressures may provide sampling difficulties in field applications. Some development work has been done on sampling of non-volatiles in conjunction with the use of IMS but the technology has not emerged. Chloroalkanes such as chloroform and methylene chloride may not be easily differentiated, but class detection may be possible which would be attractive.

In general, the sensitivity is in the low ppm to low ppb range with the possibility of ppt depending on the analyte and conditions.

The output is in real time in the order of 5 seconds or less.

The hand-held version is designed for use by unskilled operators. A basic knowledge of chemistry would be helpful with the more sophisticated units. Any servicing of the hand-held unit would require a trained technician. The various IMS packages differ in maintenance requirements but these appear minimal.

Comparison of Technologies Based on Hand-Held Units: Available hand-held units which are applicable to field screening scenarios include a small (less than 1 pound) gas/vapor detector based on catalytic oxidation using tin oxide (SnO_2), self-contained photoionization (PI) devices, and the IMS system.

Judgements relative to cost, sensitivity, selectivity and simplicity follow:

Cost	IMS > PI > SnO_2
Sensitivity	IMS > PI > SnO_2
Selectivity	IMS > PI > SnO_2
Simplicity	SnO_2 > PI > IMS

The major advantage of IMS over the other technologies is the potential for selectivity. If selectivity is not of concern then other options may be more appropriate.

The hand held IMS which is currently available has mobility windows which can be pre-programmed for eight specific analytes. The photoionization instruments detect most organic compounds but not methane or the major components of air. A degree of selectivity is achievable with the photoionization devices by changing lamps. The tin oxide based device represents the most general technology and will detect molecules that can be oxidized including carbon monoxide, methane and most other organics. With the ion-mobility device, if one of the eight analytes is present it

can be readily and specifically detected. Other compounds that have similar proton or electron affinities may cause false positives.

OPPORTUNITY FOR INTERFACE AND TECHNOLOGY TRANSFER

One of the important facets of the Advanced Monitoring Methods Program is to stimulate interface and technology transfer in the various areas discussed in this paper. A major tool to accomplish this has been to stimulate interaction between the research and development and the user communities. An International Symposium for Field Screening Methods for Hazardous Waste Site Investigations was held in 1988 to discuss new and emerging methods for reducing costs and data turnaround time and increasing confidence in scientific decisions based on site investigation data. Over 400 attendees, including representatives from a number of Federal and State Agencies and other countries, became involved in presentations and discussions ranging from field deployable instrumentation to ion mobility spectrometry. An exhibition of new, emerging and established technologies for the rapid, low-cost detection and monitoring of on-site toxicants was also conducted. A convenient summary of the conference proceedings in terms of technology trends and barriers is available (5).

Plans are in progress for another symposium (Second International Symposium: Field Screening Methods for Hazardous Wastes and Toxic Chemicals) to be held in February 1991 in Las Vegas. This will be cosponsored by several government agencies. The objective is to bring an international view to the problems involved in characterizing and monitoring hazardous wastes and toxic chemicals.

Information will continue to be compiled through the Advanced Field Monitoring Methods Program on existing and new technologies. Field screening methods for hazardous waste site investigations need to be rapid and low in cost to support on-site monitoring and characterization activities. The output from research and development on field screening methods may also relate to ambient and indoor air measurements, stationary source measurements and total human exposure monitoring.

SUMMARY

The Monitoring and Measurement Technologies Program portion of SITE provides the U.S. EPA with a good mechanism to identify and demonstrate innovative or alternative site characterization technologies. These may provide a faster and more cost-effective means to detect and monitor contaminants at hazardous waste sites. Developers are provided an opportunity to evaluate performance of their technologies and have the results and recommendations widely disseminated, thus enhancing the market for those technologies. There four key components, Technology Identification and Selection, the Demonstration Program, the Emerging Technologies Program, and Technology Transfer.

The major objective of the Demonstration Program is to develop reliable performance and cost information on innovative or alternative technologies. In fiscal year 1989 there were three activities: demonstration of an immunoassay method for pentachlorophenol, pre-demonstration testing of various air monitoring techniques, and a side-by-side demonstration of five portable gas chromatographs. For fiscal year 1990 and beyond, a number of activities are being planned including demonstrations of field-portable x-ray fluorescence spectrometers, ion-mobility spectrometers, a field portable mass spectrometer, and a global positioning system in combination with various portable field sensors. Details on the immunoassay demonstration for pentachlorophenol and a

description of ion-mobility spectrometry are given in the main text. Results from the immunoassay (pentachlorophenol) demonstration showed that such technologies can be useful for field screening and in monitoring site remediation activities.

REFERENCES

(1)Van Emon, J. M. Selected References Addressing the Development and Utilization of Immunoassay. In: Aquatic Toxicology and Hazard Assessment. 12th Volume, ASTM STP 1027, U. M. Cowgill and L. R. Williams, Eds., American Society for Testing and Materials, Philadelphia, 1989; pp. 427-431.

(2)Van Emon, J. M., J. N. Seiber, and B. D. Hammock, Immunoassay Techniques for Pesticide Analysis. In: Analytical Methods for Pesticides and Plant Growth Regulators. Volume XVII. Academic Press, Inc., New York, 1989; pp. 217-263.

(3)Carrico, J. P., A. W. Davis, D. N. Campbell, J. E. Roehl, G. R. Sima, G. E. Spangler, K. N. Vora, and R. J. White. Chemical Detection and Alarm for Hazardous Chemicals. American Laboratory 18:152 (February 1986).

(4)Eiceman, G. A., A. P. Snyder, and D. A. Blyth. Monitoring of Airborne Organic Vapors Using Ion Mobility Spectrometry. Intern. J. Environ. Anal. Chem. 38:415 (1990).

(5)Poziomek, E. J. Detection and Analysis of Emissions at Hazardous Waste Sites. Part 1. Emerging Technologies in Field Screening Methods for Hazardous Waste Site Investigations. AAAS Science and Engineering Environmental Fellowship Report. American Association for the Advancement of Science. Washington, D.C., 1989; 48 pp.

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A MULTI-LABORATORY DETERMINATION OF METHOD DETECTION LIMITS FOR EPA REGULATED SEMIVOLATILE ORGANIC COMPOUNDS IN INCINERATOR ASH

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ABSTRACT

Under the USEPA Land Disposal Restriction Rules (Landban) Best Demonstrated Available Technology (BDAT) standards are specified for treatment residues. This study was undertaken, under the guidance of the Hazardous Waste Treatment Council (HWTC) Analytical Chemistry Committee, to determine if these BDAT standards were analytically achievable in the residues from a rapidly growing treatment technology, namely, incineration.

Due to differences in composition, surface morphology and activity, it was felt that incinerator ash would behave in a manner dissimilar to other solid matrices like soils and sludges. Method detection limits and practical quantification limits for incinerator residues were generated by carrying out a replicate spike recovery study. In order to minimize analytical and incinerator specific matrix problems, this study was expanded to include six independent laboratories and the use of a homogenized, multi-incinerator composite ash.

INTRODUCTION

In the Hazardous and Solid Waste Amendments (HSWA) of 1984, Congress directed the USEPA to establish treatment standards for all hazardous wastes. The USEPA landban restrictions for the listed hazardous waste codes were promulgated over a period of several years [2,3,4] and are commonly known as the First, Second, and Third Third landban rules. The final third was signed into law on May 8, 1990 [5] with a ninety day implementation period. The purpose of these restrictions was to prohibit the land disposal of untreated hazardous waste and to specify treatment standards that must be attained prior to final disposal.

In order to meet the treatment standards for organic wastes, destruction of the organics is generally required. Additionally, the landban regulations specify that many of the waste codes must be treated by incineration, regardless of the levels of organics in the original waste material. Of the total of 436 listed hazardous wastes that fall under the landban restrictions, 215, or 49%, specify incineration as the Best Demonstrated Available Technology (BDAT), meaning that incineration is the

Note: This paper is also referenced as paper number 83.

technology upon which the treatment standards are based. Another 161 waste codes, or 37%, specify incineration as the only legal method of treatment. Thus, incineration emerges as the treatment method for a total of 86% of the listed hazardous wastes [1].

While the landban restrictions present commercial opportunities to incineration facilities, they also present significant problems. The three major problems are exhaustive tracking of waste codes required by the "derived from rule," the rigorous control of operational parameters to meet stringent treatment standards, and the analysis of all treatment residues to verify that treatment standards have been successfully met.

With respect to the last problem, EPA stated in the preamble to the Third Thirds proposed rule [4] that practical quantification limits (PQLs) for treatment residues, such as incinerator ash, are significantly lower than the PQLs for untreated waste. While this statement may be true for the incineration of pure compounds, the incineration industry felt that this was contradictory to their first hand experience with ash derived from mixed hazardous waste streams.

This study [8] was undertaken as a collaborative effort by six major commercial incineration companies to evaluate the validity of the BDAT standards for incinerator ash. The objective was to determine the method detection limits (MDLs) and associated practical quantification limits (PQLs) for incinerator residues, for use in setting alternative BDAT standards in the First and Second Third restricted waste and for finalizing treatment standards in Third Thirds and future land disposal restrictions.

EXPERIMENTAL

This study was designed to comply with EPA's BDAT Quality Assurance Project plan and to demonstrate that the treatment processes were well designed and well operated BDAT processes.

A representative sample of incinerator ash was obtained from each of the six participating companies. The samples were taken in accordance with each facility's waste analysis and sampling plans, ground, mixed well and passed through a 50 mesh screen. These sieved samples were sent to a single facility for compositing with other ash samples to generate an industry-wide ash matrix.

Standards and spike solutions were obtained from the Pesticides and Industrial Chemical Repository at USEPA EMSL-RTP and commercial sources. Ninety-one compounds were provided in eleven spiking mixes by EPA-RTP. The remaining eight spike compounds were obtained from Accustandard. CERCLA target compound list (TCL) mixes were provided by EPA for calibration purposes. Non-TCL compounds were quantitated against standard solutions provided by Accustandard.

Ninety-nine semivolatile organic compounds were evaluated. Ten grams of the composite ash were spiked and then extracted utilizing the soxhlet procedure described in Third Edition SW-846 Method 3540 with methylene chloride as the solvent. Instrumentation at the six labs represented a wide sampling of commercial GC/MS instruments from a variety of manufacturers. A 30 m x 0.25 mm ID DB-5 capillary column was used by all labs. The final extract was analyzed according to Third Edition SW-846 Method 8270. DFTPP tuning requirements were met, and internal standards and surrogates listed in method were utilized. Five-point calibration curves were generated and evaluated against Method 8270 criteria. Continuing calibrations were accepted if they met all method criteria.

The first phase was the Rangefinder study which was conducted to select appropriate spiking levels for the MDL/PQL study. The multi-incinerator composite ash was spiked in triplicate at levels of [0.2 X BDAT], [BDAT], and [5 X BDAT]. Due to the large number of analytes this phase was broken into high and low response GC/MS response compounds and divided among three laboratories. The spike levels are given in Table I. High responding base/neutral compounds were analyzed by AnalytiKEM, low responding base/neutrals by Chemical Waste Management, and all acid extractables by PEI Associates, Inc.

TABLE I

Spike Levels for Rangefinder Study

	Low Responders	High Responders
Base/Neutral Extractables	4 ppm	0.4 ppm
	20 ppm	2 ppm
	100 ppm	10 ppm
Acid Extractables	1 ppm	0.2 ppm
	5 ppm	1 ppm
	25 ppm	5 ppm

Evaluation of the results of the rangefinder study yielded the spike levels listed in Table II. Seven replicates of the composite ash were spiked at the given levels, extracted, and analyzed by GC/MS using SW-846 method 8270. Due to the fact that a dozen separate solutions were spiked into the ash, the samples were stirred intermittently for five minutes after each addition to enhance evaporation of the solvent. The total contact time between the ash and the spike compounds, prior to soxhlet extraction, was approximately 2.5 hours.

RESULTS AND DISCUSSION

A. Rangefinder Study

Results of this set of analyses were evaluated to establish spiking levels to be used in the set of seven replicate analyses of the MDL study. The spiking level chosen was the lowest concentration level for which:

- all three replicates gave a response;
- the RSD for the three replicates were no greater than 30%; and
- the average spike recovery was no less than 25%.

For some compounds, no recovery was obtained even at the highest spiking level, or the above criteria were not satisfied. In these cases, the highest spiking level in the rangefinder study was multiplied by four for use in the MDL study, or a recommended maximum spiking level of 500 ppm for an individual component was used. Due to the large number of organic compounds that were to be spiked into the ash matrix, it was felt by the participating laboratories that higher concentrations of the target constituents would saturate the active sites and substantially alter the ash matrix.

In addition, the spikes at the BDAT level indicated that for 73% of the acid extractables and for 23% of the base/neutral extractables not enough analyte was recovered from the composite ash to obtain a significant response.

B. MDL/PQL Study

The Method Detection Limit (MDL) was defined as the minimum concentration at which an analyte can be reported, with 99% confidence, that it's true value is greater than zero. The methodology specified in 40 CFR Part 136 Appendix B was followed.

The Practical Quantitation Limit (PQL) was defined as the lowest concentration at which the target analytes can be quantitated with known precision and accuracy while following a laboratory's standard operational procedures. For the purposes of this study, the PQLs were calculated using the following formula:

$$PQL = 5 \times MDL \times \text{Accuracy Adjustment Factor}$$

The accuracy adjustment factor is equal to the reciprocal of the percent recovery. This factor compensates for the unreliability in qualitatively identifying low intensity fragmentation ions of those compounds that have low recoveries.

The spike levels, MDLs, and calculated PQLs are given in Table II. The compounds that have PQLs greater than the original BDAT standards and the analytes with PQLs greater than the final BDAT standards are indicated.

CONCLUSIONS

The results of this study substantiate the concerns, of the incineration industry and of the analytical community that deal with ash matrices, regarding the quantification of semivolatile components at the treatment standard concentrations. As indicated in Table II, out of 99 compounds, 56 have PQLs greater than the BDAT levels promulgated in the Third Thirds Final Rule.

Overall it can be concluded that incinerator ash cannot be reliably analyzed by the same methods, or quantitated accurately to as low a concentration, as soils or wastewater. Ash matrices are different from soil matrices in that they contain a substantial percentage of activated carbon. The composite ash used for this study was found to contain 12% carbon, 34% silicon dioxide, and 50% various metal oxides. This suggests the presence of numerous active sites for binding organic constituents, making methylene chloride extraction difficult and driving down recoveries.

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REFERENCES

[1] "The Effect of Landban Restrictions on the Waste Approval Process for a Commercial Incinerator," John Krecisz, Incineration Technical Manager, Chemical Waste Management, Inc., 150 West 137th Street, Riverdale, IL 60627.

[2] "Land Disposal Restrictions for First Third Scheduled Wastes, Final Rule," Federal Register, Vol. 53, No. 159, 8/17/88.

[3] "Land Disposal Restrictions for Second Third Scheduled Wastes, Final Rule," Federal Register, Vol. 54, No. 120, 6/23/89.

[4] "Land Disposal Restrictions for Third Third Scheduled Wastes, Proposed Rule," Federal Register, Vol. 54, No. 224, 11/22/89.

[5] "Land Disposal Restrictions for Third Third Scheduled Wastes, Final Rule," RCRA Docket No. F-90-LD13-FFFFF, May 1990.

[6] "Methods of Organic Chemical Analysis of Municipal and Industrial Wastewater," James E. Longbottom and James J. Lichtenberg, Ed., USEPA-Environmental Systems Monitoring and Support Laboratory, EPA 600-4-82-057, Cincinnati, OH, July 1982.

[7] "Test Methods for Evaluating Solid Waste," USEPA - Office of Solid Waste and Emergency Response, SW-846, Third Edition, November 1986.

[8] "Method Detection Limits and Practical Quantitation Limits for Incinerator Ash Matrices-Interlaboratory Study," Analytical Chemistry Committee, Hazardous Waste Treatment Council, 1440 New York Avenue, N.W., Suite 310, Washington, DC 20005, January 1990.

TABLE II
Incinerator Ash
Semivolatiles PQL Data Summary

Compound Name	Spike Level (ppm)	% Average Recovery	MDL	PQL	Original BDAT Standard, ppm	Out of Compliance	Revised BDAT Standard, ppm	Out of Compliance
Haloethers								
4-Bromophenyl Phenyl Ether	0.40	95.7	0.224	0.860	15.000		15.000	
Bis(2-chloroethoxy)methane	8.00	47.8	2.457	38.552	7.200	*	7.200	*
Bis(2-chloroethyl)ether	4.00	NR	4.412	28.297	0.037	*	7.200	*
Bis(2-chloroisopropyl)ether	4.00	90.8	2.008	16.329	7.200	*	7.200	*
Phthalates								
Bis(2-ethylhexyl)phthalate	2.00	248.6	8.195	34.506	1.800	*	7.300	*
Butyl benzyl phthalate	0.40	298.2	2.024	7.842	15.000		7.900	
Diethyl phthalate	0.40	162.4	1.168	6.387	28.000		28.000	
Dimethyl phthalate	0.40	75.0	0.396	2.382	28.000		28.000	
Di-n-butyl phthalate	0.40	82.4	0.953	4.861	4.300	*	3.600	*
Di-n-octyl phthalate	0.40	B	0.689	4.316	28.000		28.000	
Phenols								
4-Chloro-3-methylphenol	1.00	292.9	2.650	19.939	14.000	*	14.000	*
2-Chlorophenol	0.20	107.6	0.114	0.625	4.400		4.400	
2,4-Dichlorophenol	0.20	70.4	0.158	0.915	1.000		1.000	
2,4-Dimethylphenol	0.20	87.1	0.140	0.986	14.000		14.000	
4,6-Dinitro-2-methylphenol	100.00	14.9	31.380	871.555	140.000	*	160.000	*
2,4-Dinitrophenol	100.00	8.4	17.056	1145.783	5.600	*	160.000	*
2-Methylphenol (o-Cresol)	1.00	95.8	0.667	3.792	5.600		6.200	
4-Methylphenol (p-Cresol)	1.00	87.8	0.542	2.038	3.200		6.200	
4-Nitrophenol	25.00	47.2	20.024	194.778	2.300	*	29.000	*
Pentachlorophenol	100.00	31.5	37.677	605.212	5.600	*	1.400	*
Phenol	0.20	690.3	1.665	15.610	3.400	*	3.600	*
2-Sec-butyl-4,6-dinitrophenol	100.00	31.6	33.160	1011.025	2.500	*	2.500	*
2,3,4,6-Tetrachlorophenol	100.00	46.4	47.775	582.875	37.000	*	37.000	*
2,4,5-Trichlorophenol	5.00	77.6	2.843	13.371	4.400	*	4.400	*
2,4,6-Trichlorophenol	5.00	80.9	2.104	14.041	0.380	*	0.380	*

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Benzidines								
Benzidine	500.00	NR	----	----	NS		NS	
3,3'-Dichlorobenzidine	100.00	57.5	56.943	786.635	16.000	*	INCIN	
3,3'-Dimethoxybenzidine	500.00	7.6	127.514	10992.460	NS		NS	
3,3'-Dimethylbenzidine	100.00	8.8	10.978	1526.669	NS		NS	
Polynuclear Aromatics								
Acenaphthylene	4.00	88.8	1.430	7.791	3.400	*	3.400	*
Acenaphthene	0.40	102.5	0.198	0.981	3.400		3.400	
4-Aminobiphenyl	100.00	95.5	72.974	1563.294	13.000	*	13.000	*
Anthracene	10.00	80.5	4.742	30.070	1.400	*	28.000	*
Benzo(a)anthracene	100.00	108.5	159.133	794.773	1.400	*	8.200	*
Benzo(b)fluoranthene	100.00	39.9	37.542	567.679	3.400	*	3.400	*
2-Chloronaphthalene	2.00	78.6	0.657	8.519	5.600	*	5.600	*
Chrysene	100.00	132.1	148.430	709.462	0.840	*	8.200	*
Dibenzo(a,h)anthracene	100.00	11.6	11.819	644.495	3.400	*	8.200	*
Dibenzo(a,e)pyrene	40.00	NR	----	----	NS		NS	
Dibenzo(a,i)pyrene	40.00	NR	----	----	NS		NS	
Fluoranthene	10.00	95.6	11.819	48.957	3.400	*	8.200	*
Fluorene	2.00	90.0	0.575	2.830	3.400		3.400	
Naphthalene	0.40	234.5	1.162	6.537	0.840	*	3.100	*
2-Naphthylamine	100.00	28.2	33.873	1441.686	15.000	*	INCIN	
Phenanthrene	20.00	82.6	7.437	43.632	0.840	*	1.500	*
Pyrene	2.00	295.2	6.327	37.829	1.100	*	1.500	*

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Nitrosamines								
N-nitrosodiethylamine	100.00	59.0	34.593	322.286	56.000	*	56.000	*
N-nitrosodimethylamine	4.00	65.0	2.111	27.606	56.000		INCIN	
N-nitrosodi-n-butylamine	4.00	87.4	2.029	13.018	54.000		17.000	
N-nitrosodiphenylamine	0.40	596.4	1.542	41.446	13.000	*	13.000	*
N-nitrosodipropylamine	4.00	32.1	0.801	45.793	14.000	*	14.000	*
N-nitrosomethylethylamine	4.00	84.1	2.027	11.797	2.300	*	2.300	*
N-nitrosomorpholine	4.00	80.6	1.494	18.739	2.300	*	2.300	*
N-nitrosopiperidine	2.00	99.4	1.164	8.582	220.000		35.000	
N-nitrosopyrrolidine	4.00	66.3	2.648	17.232	220.000		35.000	
Chlorinated Hydrocarbons								
3-Chloropropionitrile	100.00	30.7	45.311	959.633	NS		NS	
Chlorobenzilate	4.00	211.1	7.605	42.922	6.600	*	INCIN	
1,2-Dichlorobenzene	2.00	86.5	1.051	5.502	4.400	*	4.400	*
1,3-Dichlorobenzene	2.00	69.2	0.506	3.996	4.400		4.400	
1,4-Dichlorobenzene	4.00	68.5	0.997	9.638	4.400	*	4.400	*
Hexachlorobenzene	0.40	118.4	0.251	1.007	28.000		-----	
Hexachlorobutadiene	2.00	88.1	0.826	5.041	5.600		5.600	
Hexachlorocyclopentadiene	500.00	NR	----	----	2.000	*	2.400	*
Hexachloroethane	4.00	83.4	5.070	34.295	1.800	*	28.000	*
Hexachlorophene	500.00	NR	----	----	1.100	*	INCIN	
Hexachloropropene	500.00	NR	----	----	19.000	*	28.000	*
Pentachlorobenzene	4.00	97.5	1.263	7.359	0.100	*	0.100	*
Pentachloroethane	100.00	51.3	22.314	399.263	28.000	*	INCIN	
Pentachloronitrobenzene	0.40	120.9	0.719	5.808	4.800	*	4.800	*
1,2,4,5-Tetrachlorobenzene	0.40	121.7	0.226	0.964	4.400		4.400	
1,2,4-Trichlorobenzene	0.40	113.7	0.207	1.111	4.400		4.400	

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Anilines								
Aniline	20.00	12.9	2.421	127.117	5.600	*	5.600	*
4-Chloroaniline	20.00	83.8	8.208	231.534	16.000	*	16.000	*
4,4'-Methylene-bis(2-chloroaniline)	20.00	34.5	9.023	114.094	29.000	*	35.000	*
4-Nitroaniline	20.00	54.0	11.208	104.558	28.000	*	28.000	*
Miscellaneous Compounds								
Acetophenone	10.00	74.3	5.614	33.128	9.600	*	9.700	*
Aramite	500.00	102.6	648.602	5481.754	2.500	*	2.500	*
p-Benzoquinone	500.00	3.7	15.709	7357.544	180.000	*	FSUBS or INCIN	
p-Dimethylaminoazobenzene	4.00	169.2	5.937	63.641	29.000	*	INCIN	
1,4-Dinitrobenzene	10.00	60.3	3.912	58.814	2.300	*	2.300	*
2,4-Dinitrotoluene	20.00	69.5	8.636	59.331	2.300	*	2.300	*
2,6-Dinitrotoluene	2.00	90.5	0.706	3.229	28.000		28.000	
1,2-Diphenylhydrazine (Azobenzene)	100.00	40.1	39.438	1004.854	NS		NS	
Ethyl methanesulfonate	5.00	85.3	1.715	11.962	NS		NS	
Isosafrole	0.40	377.8	1.157	15.707	2.600	*	2.600	*
Maleic anhydride	500.00	2.4	8.913	9686.264	NS		NS	
Methapyrilene	4.00	32.3	1.621	39.356	6.900	*	1.500	*
3-Methylcholanthrene	100.00	11.8	11.557	554.927	33.000	*	15.000	*
Methyl methanesulfonate	5.00	53.7	1.450	26.315	NS		NS	
1-Naphthylamine	100.00	124.8	143.166	2367.048	15.000	*	INCIN	
Nitrobenzene	10.00	89.6	5.217	38.568	2.300	*	2.300	*
5-Nitro-o-toluidine	40.00	54.5	25.763	217.207	56.000	*	28.000	*
Phenacetin	2.00	299.7	3.608	92.824	16.000	*	16.000	*
2-Picoline	10.00	36.2	4.961	97.912	NS		NS	
Pronamide	2.00	65.8	2.077	16.780	1.500	*	1.500	*
Pyridine	4.00	37.6	2.364	40.192	14.000	*	14.000	*

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Incinerator Ash
Semivolatiles PQL Data Summary

Compound Name	Spike Level (ppm)	% Average Recovery	MDL	PQL	Original BDAT Standard, ppm	Out of Compliance	Revised BDAT Standard, ppm	Out of Compliance
Resorcinol	500.00	17.8	109.345	3971.317	1.800	*	FSUBS or INCIN	
Safrole	2.00	74.2	0.611	4.433	22.000		22.000	
Tris-(2,3-dibromopropyl)phosphate	100.00	9.9	15.614	1840.990	0.100	*	0.100	*
					TOTAL OUT	65		56

Legend

NR - Spike not recovered
NS - No BDAT standard promulgated
B - Analyte detected in background composite sample. Therefore, results unavailable
INCIN - Incineration as treatment technology
FSUBS - Fuel substitute

Original BDAT Standard - Standard proposed in the second thirds ruling
Revised BDAT Standard - Standard proposed in the third thirds ruling

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A MULTI-LABORATORY DETERMINATION OF METHOD DETECTION LIMITS AND PRACTICAL QUANTITATION LIMITS FOR EPA REGULATED VOLATILE ORGANICS IN INCINERATOR ASH

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ABSTRACT: The current federal regulations established pursuant to the Land Disposal Restrictions (LDR's) specify Treatment Technologies for a significant number of EPA listed waste codes. In addition, most of the remaining non-regulated codes have proposed Treatment Technologies. For the large majority of these wastes, associated Best Demonstrated Available Technology (BDAT) treatment standards have been assigned, in order to confirm effective treatment of the waste. Wastes that fall under these Land Disposal Restrictions must be proven to be treated such that they comply with BDAT treatment standards.

For a significant number of wastes, the preferred Treatment Technology is thermal destruction. However, residues from this process often present the analytical chemist with unique problems when analysis is needed to demonstrate compliance with BDAT treatment standards. In response to these concerns, a group of six independent laboratories participated in a study to define the Method Detection Limits (MDL's), in incinerator ash, and to generate data to define appropriate Practical Quantitation Limits (PQL's) for all volatile treatment standard analytes regulated as a part of the First-, Second- and Third Third listed wastes. It is the purpose of this paper to define study protocols and experimentation, present data, discuss results and to offer interpretation of those results.

INTRODUCTION: Thermal combustion residues represent one of the most unique matrices that a commercial laboratory will be asked to analyze. Without a carefully executed QA/QC program, laboratory staff and the chemists who validate data will not be aware of the significant physical and chemical interactions that occur when analyzing a matrix of this type, and how these interactions can have a dramatic effect on the final data. The composition of these residues are a complex mixture of particle sizes, shapes, and colors. In addition, the distinctive chemical and physical properties are a result of the inhomogeneous chemical composition of these residues, resulting in the unique ability of this matrix to adsorb and bind volatile organic compounds.

The membership of the Hazardous Waste Treatment Council (HWTC), Analytical Committee, expressed concerns with matrix interference problems that had been encountered as a direct result of the chemical composition of incinerator ash matrix when applying standard SW-846 methods 5030 coupled with 8240/8260 for the determination of purgeable volatile organics.

In subsequent meetings held in late August, 1989, the committee prepared an informal list of estimated detection limits that were felt to be

Note: This paper is also referenced as paper number 80.

achievable by each laboratory in the ash matrices that had been received for analysis from a variety of sources. This information indicated that a fair number of First- and Second Third BDAT treatment standards could not be demonstrated in the incinerator ash matrix. This finding, based on the technical expertise from a variety of laboratories, triggered a decision by the membership to conduct a formalized Multi-laboratory study to define the Method Detection Limits for both volatile and semivolatile organics in incinerator ash.

It was decided by the committee that a study of this scope and magnitude (in total when combining all phases of the study, over 10,000 data points were generated) should have input and direction from the USEPA's Methods Branch of OSWER and that the planning and implementation of the study should be such that the data produced would be useable by both the private and governmental sectors. An initial draft study plan was submitted to the EPA on September 15th and was finalized after incorporating applicable comments October 4, 1989.

EXPERIMENTAL SECTION:

DEFINITIONS The Method Detection Limit (MDL) is defined by the USEPA (and for the purpose of this paper) as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the given analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (1) In order to achieve this statistically derived number, several evaluatory mechanisms are offered as suggestions in order to estimate the actual limit of detection. These include instrumental signal to noise, precision data and instrumental sensitivity limitations to the given analyte. By using a combination of these criteria, the committee developed a "rangefinder protocol" to ensure that the spiking levels chosen for each BDAT treatment standard analyte were near the statistically derived "true" MDL.

For the purpose of this study, ash was collected from six permitted and well operated incineration facilities representing a variety of incineration engineering designs. Upon direction from the EPA's Methods Branch, the ash particle size was reduced and screened through a 50 mesh screen. (opening size of 0.0118 inches or 300 microns) The ash was then composited in equal proportions and was distributed to the six laboratories participating in the study. This composite sample is considered, for the purpose of this study, to be representative of incinerator ash.

Spiking solutions for this study were traceable to primary reference standards specially prepared by the EPA Research Triangle Park Laboratory. Dilutions of these spiking standards were used for instrument calibration.

RANGEFINDER PROTOCOL Historical data generated from the analysis of incinerator ash suggests that the matrix appears to effectively adsorb some volatile organics, and the standard purge and trap technique will not permit adequate desorption of these analytes from the matrix. The result is poor recovery of spiked analytes, which appears to be directly proportional to their boiling points. This matrix interference or suppression is theorized to be a result of the ash adsorptive potential, available absorptive surface area per unit weight, temperature, the physical chemistry of the analytes and the amount of time during which the analytes are in contact with the adsorptive matrix. The rangefinder protocol contains several interesting

experiments that were designed to predict possible problems with matrix suppression. In the first of these experiments, the laboratories involved spiked internal/surrogate standard analytes into replicate blank soil matrices (control) and determined the average area count response for the recommended quantitation ion of the Extracted Ion Current Profile (EICP). The average was then used to set the quality control limit intervals, using -50% to +100% of the average area counts, required in SW-846. (2 and 3) Duplicate ash samples were then spiked with the appropriate concentration of internal/surrogate standard analytes, beginning with the normal 5 gram sample size. If outliers were observed, the sample size was decreased by a factor of ten, and the experiment would be repeated until no outliers were observed. If the matrix suppression was observed in the 0.5 gram sample size, a micro-extraction technique would then be employed, as outlined in method 5030. This micro-extraction technique allowed the analyst to purge accurately smaller effective weights (by means of micro-extraction) of a solid sample by varying the amount of supernatant extraction solvent injected into the purge chamber. This technique can produce accurate effective purged sample sizes as low as 0.5 to 0.005 grams.

The time in which the ash sample is in contact with the water media containing the internal/surrogate standard solution was also a factor to consider when exploring the causes of the observed matrix suppression. In response to this variable, a delayed purge time experiment was conducted. In this experiment, seven replicate ash samples (at the final ash sample size established in experiment #1) were spiked and the purge of the sample was delayed starting at 1 minute and at various intervals ending with 2 hours. After data were generated and collected, a simple plot of the time delay until purge, versus the internal standard response would indicate whether the variable of the time in which the ash is in contact with the internal standard analytes is a factor of the matrix suppression for that sample size.

The final experiment was performed to determine the actual concentration of each BDAT treatment standard analyte that should be spiked in the MDL study. All analytes of interest were prepared in methanol, in several cocktail mixes at "base" concentrations of 1, 5, and 10 times the average of all participating laboratories Low Level Soil MDL's. These cocktails were then spiked into the ash samples (at the final ash sample size established in experiment #1) in replicate. As an additional exercise, a cocktail mix was also prepared at the lowest regulatory BDAT treatment standard concentrations that a laboratory potentially could be asked to meet in incinerator ash. After instrument calibration for the analytes of interest, replicate 5 gram ash samples were spiked at the regulatory threshold and percent recovery of the analytes were determined.

Four of the volatile analytes- the simple alcohols: methanol, butanol and isobutanol plus acrylamide- were not analyzed by method 5030 micro-extraction followed by method 8240/8260. The very high to infinite solubility of these analytes in water results in poor purge efficiencies and, hence, high detection limits. The generally accepted approach among the laboratories involved in this study, and unofficially recommended by the EPA, is based on method 8015, GC/FID analysis, by direct aqueous injection.

METHOD DETECTION LIMIT STUDY As regulatory limits approach the limits of detection for a wide variety of analytes covering many chemical classes the importance of the method detection limit becomes paramount. The goal of analyte detection above background in a diverse group of samples subject to environmental regulations, with a known degree of confidence, is the real

world applicability of the MDL. There has in practice been very little agreement between professional and statutory bodies on the exact definition of the limit of detection, based on the suitable interpretation of the phrase "significantly different" response from the blank or background signal. (4) In addition, the synonymous use of "confidence limits" in MDL calculations for classical environmental chemistry applications has been criticized. (5) Although these arguments have excellent technical merit, it was decided by the committee to use the classical approach for the determination of the method detection limit. (1) In this approach, incinerator ash was fortified in replicate (seven) at concentrations specified in the rangefinder study and the Variance and Standard Deviation of these replicates were calculated using the standard statistical formulas for these measurements. (1) The MDL was the calculated using the value for the students' t appropriate for a 99% confidence level, and a standard deviation estimate with n-1 degrees of freedom. This students' t value is then multiplied by the standard deviation of the replicate measurements, resulting in the MDL value. This value is produced by pooling all interlaboratory replicates, resulting in a population as high as n=42.

The Practical Quantitation Limit (PQL) is the lowest level of analyte that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. (3) In addition, this value is highly matrix dependent, and will fluctuate from one matrix to another. In most cases, published PQL's are based only on a general estimate for the method and not on a determination for each individual target analyte. As agreed upon by the committee and representatives from EPA's Methods Branch, the PQL, for the purpose of this study, is estimated to be five times the determined MDL for each target analyte and adjusted for the average percent recovery. (not more than 100%)

RESULTS:

RANGEFINDER In general, the rangefinder study confirmed the historical data gathered by the analytical committee members. The results of Experiment #1 indicate that the matrix interferences or suppression indeed did occur in the 5.0 and 0.5 gram ash sample sizes. (trials #1-4 of graphs 1.0-1.2) However, when the micro-extraction technique was employed, the matrix suppression was not observed. (trails #5-11 of graphs 1.0-1.2) By using the micro-extraction technique, the data collected were within the acceptable Quality Control Limits defined in EPA method 8240/8260. This data indicates quite clearly that the standard purge and trap technique for the low level solid matrices will not produce adequate results when analyzing ash samples. Due to these significant outliers, the committee agreed that the micro-extraction technique would be most feasible for the MDL study, everyday applications, and is in line with the Data Quality Objectives for the study.

The recovery of spiked internal standard analytes from the ash matrix, in the 5.0 and 0.5 gram sample sizes, appears to be indirectly proportional to the compound's boiling point. (see table 1.0) One of four attempts to recover Bromochloromethane (boiling point of 68 degrees celsius at STP) within Quality Control Limits was successful. (trial #3 of graph 1.0) In the 5.0 gram ash sample the average relative percent recovery was 34.6%, a significant outlier, but as the ash sample size was decreased to 0.5 gram, the average recovery was 47.9%, just outside of the Lower Quality Control Limit. However, all attempts to recover D5-Chlorobenzene (boiling point of

132 degrees celsius at STP) were unsuccessful, with both the 5.0 and 0.5 gram ash sample sizes miserably failing the Quality Control Limits. (see table 1.0) In this case the average relative percent recoveries for the 5.0 and 0.5 gram ash sample sizes were 2.4% and 4.9% respectively. Knowledge of a compound's polarity and dipole moment, the presence of absence of specific functional groups, relative solubility in the extraction solvent, and molecular size may also aid in predicting recovery success. Further investigation may lead to correlation with observed recovery data.

Our results indicate that when employing the micro-extraction technique, the amount of time in which the ash is in contact with the internal standards is not a factor in the matrix suppression. The data suggests that over the various purge delay times, precision was quite good for all three internal standards, with Percent Relative Deviations all less than 5. (see table 1.0) It is possible that time is a factor in the adsorption of volatile organics onto the ash when considering the 5.0 or 0.5 gram ash sample sizes, however our protocol did not include the study on each sample size. Further work could be done to confirm the effect of this variable in the adsorptive potential.

The objective of experiment #3 was to determine the actual spiking concentrations for all BDAT Treatment Standard Analytes for use in the calculations of the MDL's and PQL's. Using the results of the previously performed experiments, ash samples were spiked in replicate at three separate levels of "base" concentrations. The end result was three measurements at each of the three respective levels. In addition, the spiking levels were multiplied by the appropriate dilution factor to take into consideration the reduced sample size, due to the micro-extraction technique. The measurements were made and the raw data were compiled, percent recoveries, relative percent deviations (RPD's) were calculated and linear regression curves were prepared. These results were evaluated to ensure that all replicates within a level gave a response, the RPD was no greater than 30% and no recovery was less than 25%. If the results indicated that the lowest spiking level did not conform to these criteria, then the next highest level would be evaluated. This logical procedure was then repeated for all analytes, resulting the concentration for each analyte with a fairly precise measurement and a reasonable recovery value. These results were then tabulated, rounded, and the result is the spiking levels that were used in the MDL study. (table 3.0)

Volatile analytes spiked at the lowest regulatory BDAT treatment standard level into 5.0 gram ash samples recovered poorly. This data (table 2.0) indicates and strongly supports our findings that significant matrix interferences produce a dramatically decreased recovery percentages for most treatment standard analytes. Using external standard quantitation, over 71% of the volatile analytes spiked recovered at less than of equal to 10 percent. This data is by far the most convincing, to indicate that matrix interferences do exist, and that alternative sample preparation techniques are needed, such as micro-extraction.

ALCOHOLS The initial alcohols and acrylamide study involved the fortification of seven 5.0 gram portions of the composite ash with 1 mg/Kg of each of the alcohols and 10 mg/Kg of the amide. An estimated PQL had not been determined for these compounds in the initial rangefinder study and the spiking levels chosen represent a compromise between the existing BDAT treatment standards and the instrument detection limits for these compounds. The method of aqueous micro-extraction, as recommended by the EPA's Methods Branch, was employed for sample preparation prior to analysis by GC/FID. This

method resulted in the composite ash at a 1:1 extraction solvent to ash ratio. Using this approach the analysis resulted in variable recoveries. One laboratory reported approximately 30% recoveries and another laboratory reported no recovery for any of the analytes. Consequently, only in one out of six of the participating laboratories could a MDL be estimated and this data was compromised by the apparent presence of some of the analytes in the associated method blanks.

In a preliminary attempt to improve analyte recoveries, one lab increased the extraction water/ash ratio from 1:1 to 5:1 (5 mls of extraction water to 1 gram of ash) resulting in a trace level of all analytes being recovered. The addition of 7 mg of pure ethylene glycol to a fortified 1 gram ash sample which was then micro-extracted resulted in increased butanol and isobutanol recoveries (20%). The introduction of a second polar solvent which would compete for the active sites on the ash and thereby result in a displacement and resolubilization of some/all of the analytes was hoped for. Results were not significant enough, however, to warrant further investigation and this portion of the study was ended.

METHOD DETECTION LIMITS/PRACTICAL QUANTITATION LIMITS The results of the study are summarized in table 3.0. In general the spiking levels were acceptable for the MDL determination, with the exception of 23 analytes, which had statistically derived MDL's higher than the spiking level. However, the committee considered 19 of these MDL's technically acceptable due the statistically derived MDL's being within a factor of two from the actual spiking level. It is the consensus of the group that by raising the spiking level and performing the experiment over would result in MDL's not statistically different from the data presented. Further work should be performed to determine the actual MDL's for Methylene Chloride, Toluene, 1,1,2-Trichloroethane and 1,1,2-Trichloro-1,2,2-trifluoroethane. All of these compounds had statistically derived MDL's higher than two times the spiking level. One compound, Acrolein, was spiked at a concentration that was in excess of five times the statistically derived MDL. However poor recovery of this analyte will not allow spiking at a lower concentration. Two compounds, Dichlorodifluoromethane and Methylene chloride were present in the background sample, therefore recovery data are not available for these compounds.

Waste management facilities handle a variety of EPA waste codes on a day to day basis. Treatment residues from these codes must meet the lowest BDAT treatment standard for the applicable codes that were incinerated. Column six and eight of table 3.0 represent the lowest BDAT treatment standards for all F, P, K, and U EPA listed waste codes as of the second third and third third respectively.

DISCUSSION:

COMPARISON OF PQL's TO BDAT TREATMENT STANDARDS It is the opinion of the analytical committee regulatory limits should be set at a level that is technically achievable by most laboratories on a routine basis. The PQL meets these criteria with the added advantage of a known degree of confidence with the measurement. When a comparison is made of the PQL's to the lowest BDAT treatment standards (original-as of the first and second third scheduled wastes) one can easily see from table 3.0 that a fair number (over 50%) of compounds had PQL's above the lowest BDAT treatment standard. In these cases the regulated volatile organic had PQL's above one or more of the EPA waste

codes. For instance, Acetone had a PQL higher than the treatment standard for EPA waste codes K086 and U002, Chloroethane similarly for K018. (and so on by using references #6 and #7 presented at the end of this paper)

The third third (8) final rule, which became effective on May 8, 1990, did reduce the number of these "out of compliance" analytes. Just under 16% of the analytes now have PQL's higher than the lowest treatment standard. For one compound, 3-Chloro-1-propene, the treatment standard is 2.4 times lower than the actual MDL, which is direct contradiction of the EPA's goals to set BDAT treatment standards at technically achievable levels. The committee is very uncomfortable with treatment standards set below the PQL and feels that it is not technically defensible to set any treatment standard below the MDL.

INCINERATOR ASH MATRIX INTERFERENCES The preamble to the third third proposed rule (8) states that "... the PQL's are directly related to the amount of interferences that are present in the different waste matrices, and the PQL's listed in SW-846 are not always achievable for constituents as measured in untreated wastes". The EPA further comments that "...most treatment technologies such as incineration, destroy not only the hazardous constituents of the waste, but also other organics that typically interfere with the analysis for constituents in untreated wastes as well. Thus, PQL's typically are significantly lower for treatment residuals such as incinerator ash than for untreated wastes". It is the committee's opinion that while interference from organics present in incinerator ash potentially could exist, the real problem, as presented in this study, is from the adsorption and binding of organics to the ash matrix itself.

Many studies have been conducted throughout the past few years to confirm and postulate, if and why organic compounds adsorb onto combustion residues. (the large majority of these studies have been conducted on fly ash) Most of these studies have been driven by federal air quality regulations. While all studies agree that organic compounds do adsorb and bind onto ash, there has been several theories as to why this occurs, and what causes the adsorptive property. As discussed by Furuya (9) and confirmed by our analysis of the composite ash sample, (table 4.0) the major components of ash consist of metal oxides of silicon, aluminum, iron, calcium and magnesium in relative percent order. In addition, ash contains significant percentages of sulfur and carbon. Dunstan (10) postulates that these elements (carbon and sulfur) vary based on combustion temperature. Based on our experience in testing ash from commercial incineration, and since the combustion temperature is fairly standardized due to permit considerations, the carbon and sulfur content generally does not fluctuate significantly from day to day. Using separation techniques, Dunstan concluded that the adsorption potential (expressed as adsorption isotherms) is directly affected by the following subfractions of the ash:

a) Carbonaceous subfraction
b) "Magnetic" subfraction *
c) "Crystalline/Aluminosilicate Glassy" subfraction **

* Defined as oxides of iron and some oxides of aluminum
** Defined as oxides of silicon and some oxides of aluminum.

All studies that we reviewed, while approaching their conclusions in different ways, agree that the carbonaceous subfraction is the strongest

adsorbent of organic compounds, and has the greatest ability to stabilize those compounds. In some cases in ashes with high carbon content (greater than 5%), the organic compounds were "irreversibly" absorbed. (11) Behymer reports that two ash samples studied which had very large surface areas (63.6 and 53.5 squared meters/gram) and high carbon content (52 and 48%) demonstrated a great affinity for PAH adsorption, "... and it was virtually impossible to extract them back off, even after 24 hours of soxhlet extraction with Methylene chloride".

It is generally agreed by all authors that the magnetic fraction is the weakest adsorbent of organic compounds. It has been suggested by some experts that certain transition metals (mainly iron) and surface pH may play a role in the absorptive properties of ash, however the results are inconclusive. In contrast, while these metal oxides exhibit a very limited ability to adsorb organic compounds, they are very capable of stabilizing organic compounds. (binding of molecules in the "lattice" structure)

The "crystalline"/alluminosilicate glassy subfraction studies have shown an affinity to adsorb and bind organic compounds. While this affinity is much less than that of the carbonaceous subfraction, the unique property of this subfraction is its effect on the overall surface area. Furuya (9) has observed the morphology of several ash types, and has reported some interesting results. He has noticed the presence of crystalline-precipitated particles, on the surface of the ash, producing extremely large surface areas. While the introduction of grinding to the composite ash sample matrix certainly altered the morphology of the particles, we felt it interesting to make a similar observation of the same characteristics. In figure 1, a SEM micrograph of an overview of the ash matrix, on can distinguish the wide variety of particle sizes and shapes. In addition, the "crater like" surface is fairly evident. Figure 2, a SEM micrograph of a single particle of ground glass, shows a fairly smooth surface, with a relatively small amount of surface area. In contrast, figure 3, a SEM micrograph of a single particle of composite ash, shows quite clearly the "crater like" surface, significant surface area and the crystalline-precipitated particles on the surface of the ash. It is the belief that this significant "active" surface area per weight and the "crater like" morphology provides an effective adsorptive surface and binding structure to stabilize organic compounds. It must be considered that the extremely adsorptive nature of the ash matrix is not due solely to any one factor mentioned above, but to each of the factors functioning together. It is the committee's position that the ash matrix is a very different matrix from that of common soils or water samples, the only matrices for which PQLs have previously been established.

CONCLUSIONS: A scientific estimation of the MDL and PQL for all volatile organic BDAT treatment standard analytes was performed on the incinerator ash matrix. The results of these PQL's indicate that for some EPA listed waste codes, the technical abilities of the laboratory community as a whole, using current SW-846 methodologies, may be insufficient to demonstrate compliance with RCRA Land Disposal Regulations. Each individual laboratory which will analyze incinerator ash samples to demonstrate compliance with existing BDAT treatment standards should make evident, as a part of the QA/QC program, the ability to provide MDL's and PQL's which are lower than the published treatment standards. There is need for further work in characterizing the complex nature of the ash matrix and developing methodologies to deal with the problems that this matrix presents.

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ENTEK, Norma James

IT Analytical Services, Tim Sanders

Ross Environmental Services, Inc., Thomas Robertson

LITERATURE CITED:

(1) U.S. EPA. 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule". Federal Register. 40CFR Part 136, Appendix B-Revision 1.11: Friday, October 26, pp.198-199.

(2) U.S. EPA. 1986. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods". Methods 5030 and 8240-Revision 1, Third Edition.

(3) U.S. EPA. 1987. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods-Proposed Update Package". Method 8260-Revision 0, Third Edition.

(4) Miller, J.C., Miller, J.N., 1986. "Statistics for Analytical Chemistry". Halsted Press, Chichester. pp. 96-97.

(5) Gibbons, R.D., 1989. "Method Detection Limits". Proceedings of the Fifth Annual Waste Testing and Quality Assurance Symposium, Volume II, p.II-295.

(6) U.S. EPA. 1988. "Land Disposal Restrictions for First Third Scheduled Wastes; Final Rule". Federal Register. 40CFR Parts 264 etc., Wednesday, August 17.

(7) U.S. EPA. 1989. "Land Disposal Restrictions for Second Third Scheduled Wastes; Final Rule". Federal Register. 40CFR Parts 148 et al., Friday, June 23.

(8) U.S. EPA. 1989. "Land Disposal Restrictions for Third Scheduled Wastes; Proposed Rule". Federal Register. 40CFR Part 148 et al., Wednesday, November 22.

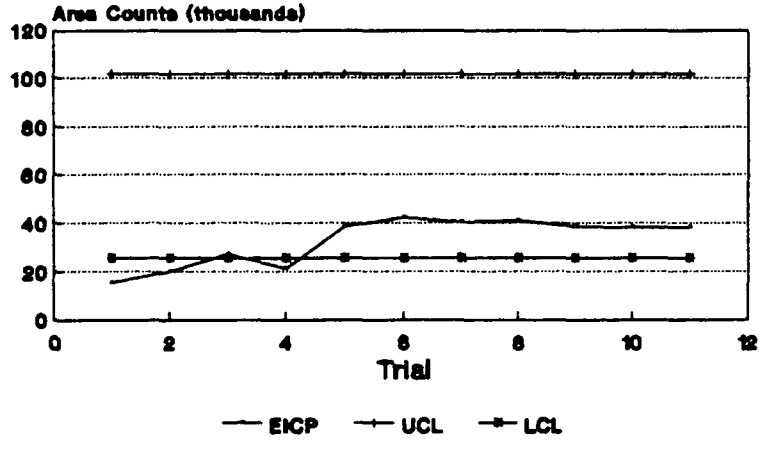
(9) Furuya, K. et al., "Elemental Characterization of Particle Size-Density Separated Coal Fly Ash by Spectrophotometry, Inductively Coupled Plasma Emission Spectrometry, and Scanning Electron Microscopy-Energy Dispersive X-ray Analysis", Environ. Sci. Technol. 1989., Vol 21, No. 9, pp. 898-903.

(10) Dunstan, T.D.J., et al., "Adsorption and Photodegradation of Pyrene on Magnetic, Carbonaceous and Mineral Sub-Fractions of Coal Stack Ash", Environ. Sci. Technol. 1989., Vol. 23, No.3, pp. 303-308.

(11) Behymer, T.D.; Hites, R.A., "Photolysis of Polycyclic Aromatic Hydrocarbons Adsorbed on Fly Ash", Environ. Sci. Technol., 1988., Vol. 22, No. 11, pp. 1311-1318.

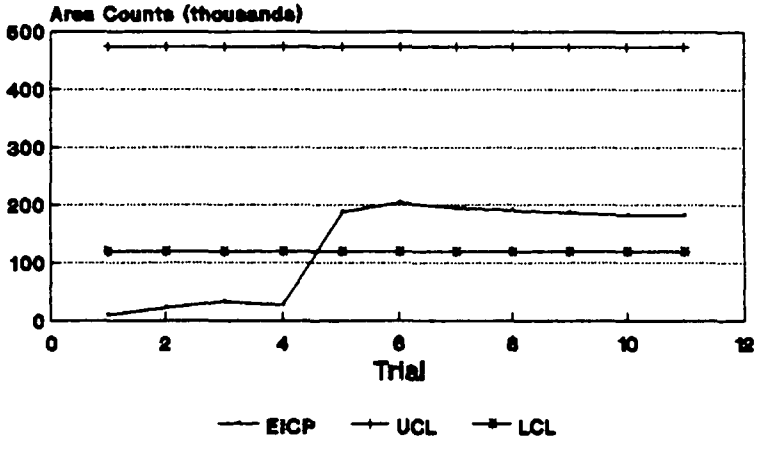
Experiment Results
Rangefinder Study

Extracted Ion Current Profile
Bromochloromethane (m/z 128)



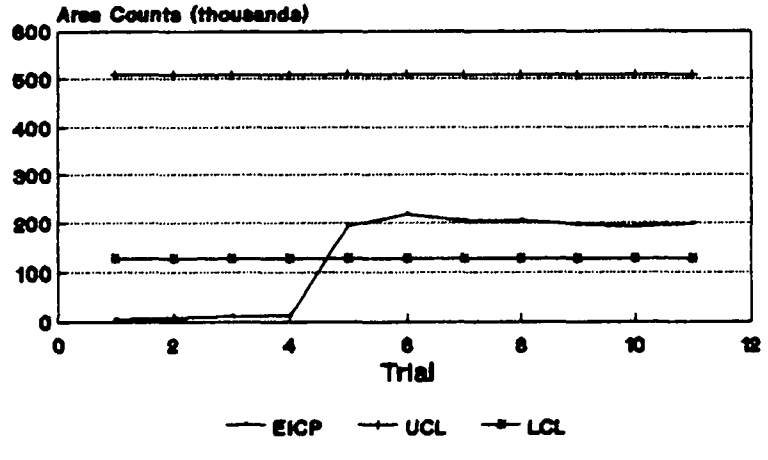
Graph 1.0

Extracted Ion Current Profile
p-Difluorobenzene (m/z 114)



Graph 1.1

Extracted Ion Current Profile
D5-Chlorobenzene (m/z 117)



Graph 1.2

KEY TO GRAPHS 1.0-1.2

X Axis of Graph	Sample Size	Time Delay Prior to Purge
Trial 1	5.0 Grams	1 minute
Trial 2	5.0 Grams (Duplicate)	1 minute
Trial 3	0.5 Grams	1 minute
Trial 4	0.5 Grams (Duplicate)	1 minute
Trial 5	0.05 Grams (Micro-extraction)	1 minute
Trial 6	0.05 Grams (Micro-extraction)	3 minutes
Trial 7	0.05 Grams (Micro-extraction)	5 minutes
Trial 8	0.05 Grams (Micro-extraction)	10 minutes
Trial 9	0.05 Grams (Micro-extraction)	30 minutes
Trial 10	0.05 Grams (Micro-extraction)	1 hour
Trial 11	0.05 Grams (Micro-extraction)	2 hours

UCL= Upper Quality Control Limit based on the average response in the calibration standards.

LCL= Lower Quality Control Limit based on the average response in the calibration standards.

Table 1.0

Recovery of Internal Standard Analytes, Relative to the Calibration Standards in a Variety of Ash Matrix Sample Sizes (Experiment #1, Rangefinder Study)

	Average % Relative Recovery		
Sample Size	Bromochloromethane BP= 68 degrees C	p-Difluorobenzene BP= 89 degrees C	D5-Chlorobenzene BP= 132 degrees C
5.0 Grams	34.6% (24.9% D)	6.3% (82.5% D)	2.4% (79.2% D)
0.5 Grams	47.9% (24.2% D)	12.5% (18.4% D)	4.9% (10.2% D)
0.05 Grams	77.5% (4.4% RSD)	79.9% (4.3% RSD)	79.1% (4.6% RSD)

BP= Boiling Point
% D= Percent Difference
% RSD= Percent Relative Deviation

Table 2.0

Recovery of Analytes Spiked into the 5.0 gram Ash Sample at the Lowest BDAT Treatment Standard Regulatory Threshold (Experiment #3, Rangefinder Study)

% Recovery of BDAT Treatment Standards Analytes	Number of Analytes Recovered
≤ 5%	33
6-10%	17
11-25%	3
25-50%	3
51-100%	1
Total Analytes	57

Incinerator Ash
Volatiles PQL Data Summary

Table 3.0

Compound Name	Spike Level (ppm)	Average Recovery (%)	MDL	PQL	Original BDAT Standard (ppm)	Out of Compliance	Revised BDAT Standard (ppm)	Out of Compliance
Acetone	1.00	12.3	1.762	71.712	0.140	*	160.000	
Acetonitrile	5.00	30.5	3.621	59.335	0.350	*	INCIN	
Acrolein	5.00	0.4	0.070	99.017	2.800	*	2.800	*
Acrylonitrile	5.00	79.8	3.854	24.143	0.280	*	84.000	
Benzene	0.50	83.0	0.287	1.728	0.030	*	14.000	
Bromodichloromethane	0.50	95.6	0.334	1.745	16.000		16.000	
Bromoform	0.50	75.2	0.377	2.508	16.000		15.000	
Bromomethane	1.00	42.2	0.629	7.456	NS		NS	
Carbon Disulfide	0.50	36.7	0.412	5.621	NS		NS	
Carbon Tetrachloride	0.50	97.6	0.690	3.532	6.200		5.600	
3-Chloro-1-propene	0.50	60.2	0.678	5.631	0.280	*	0.280	*
Chlorobenzene	0.50	26.5	0.213	4.014	4.400		4.400	
Chloroethane	1.00	41.3	0.733	8.867	6.000	*	6.000	*
2-Chloroethylvinyl Ether	1.00	29.3	0.568	9.700	NS		NS	
Chloroform	0.50	95.9	0.312	1.626	6.000		5.600	
Chloromethane	1.00	24.4	0.764	15.673	5.600	*	33.000	
cis-1,3-Dichloropropene	1.00	79.7	0.293	1.841	0.014	*	18.000	
Cumene	0.50	67.3	0.245	1.818	NS		NS	
Cyclohexanone	10.00	109.0	16.106	80.528	1.900	*	FSUBS or INCIN	
Dibromochloromethane	0.50	72.8	0.346	2.373	16.000		16.000	
1,2-Dibromoethane (EDB)	0.50	92.8	0.361	1.943	NS		NS	
1,2-Dibromo-3-chloropropane	5.00	89.8	6.868	38.253	15.000	*	15.000	*
Dibromomethane	0.50	93.9	0.352	1.875	16.000		16.000	
Dichlorodifluoromethane	1.00	B	1.390	6.950	10.000		7.200	
1,1-Dichloroethane	0.50	84.6	0.400	2.365	0.014	*	7.200	
1,2-Dichloroethane	0.50	111.7	0.417	2.083	0.014	*	7.200	
1,1-Dichloroethene	0.50	57.5	0.670	5.827	6.200		33.000	
Dichloroethyl Ether	5.00	115.0	8.912	44.560	7.200	*	7.200	*
1,2-Dichloropropane	0.50	100.5	0.320	1.602	0.014	*	18.000	
Diethyl Ether	5.00	71.8	3.563	24.817	140.000		160.000	
1,4-Dioxane	5.00	24.4	1.939	39.662	280.000		170.000	
Ethyl Acetate	5.00	97.2	5.433	27.945	5.600	*	33.000	
Ethyl Benzene	0.50	56.2	0.230	2.044	0.080	*	6.000	
Ethyl Cyanide	5.00	108.3	6.387	31.934	NS		NS	
Ethyl Methacrylate	1.00	100.9	0.645	3.223	160.000		160.000	
Iodomethane	0.50	55.3	0.721	6.520	65.000		65.000	
Methacrylonitrile	5.00	108.1	6.922	34.608	84.000		84.000	
Methyl Ethyl Ketone (MEK)	1.00	187.5	6.030	30.151	200.000		36.000	
Methyl Isobutyl Ketone (MIBK)	1.00	125.5	1.185	5.925	33.000		33.000	
Methyl Methacrylate	1.00	88.5	0.590	3.334	160.000		160.000	
Methylene Chloride	0.50	B	1.348	6.738	31.000		33.000	
2-Nitropropane	1.00	53.3	1.390	13.038	5.600	*	5.600	*
1,1,1,2-Tetrachloroethane	0.50	84.7	0.356	2.098	5.600		42.000	
1,1,2,2-Tetrachloroethane	0.50	84.7	0.451	2.661	5.600		42.000	
Tetrachloroethene	0.50	77.7	0.432	2.778	1.700	*	5.600	
Toluene	0.50	123.6	4.476	22.380	0.034	*	14.000	*
trans-1,2-Dichloroethene	0.50	54.2	0.512	4.728	6.000		33.000	
trans-1,3-Dichloropropene	1.00	86.2	0.308	1.788	0.014	*	18.000	
trans-1,4-Dichloro-2-butene	1.00	60.4	1.220	10.093	30.000		INCIN	
1,1,1-Trichloroethane	0.50	100.2	0.390	1.951	6.000		5.600	
1,1,2-Trichloroethane	0.50	172.9	1.599	7.994	6.000	*	5.600	*
Trichloroethene (TCE)	0.50	125.1	0.497	2.485	5.600		5.600	
Trichlorofluoromethane	0.50	81.7	0.767	4.693	33.000		33.000	
1,2,3-Trichloropropane	0.50	93.4	0.352	1.885	0.014	*	28.000	
1,1,2-Trichlorotrifluoroethane	0.50	25.5	1.060	20.797	28.000		28.000	
Vinyl Chloride	1.00	43.8	0.617	7.044	0.035	*	33.000	
Xylenes (total)	0.50	81.1	0.693	4.271	0.070	*	22.000	
					Number Out	25		8

Legend

B - Analyte was detected in the background composite sample. Therefore results are unavailable.

NS - No BDAT standard has been proposed

INCIN - Incineration as treatment technology

FSUBS - Fuel substitute

Original BDAT Standard = Standard proposed as of second thirds final ruling

Revised BDAT standard = Standard proposed as of third thirds final ruling

TABLE 4.0

MAJOR CHARACTERISTICS AND COMPOSITION OF INCINERATOR ASH

Constituent	Percent
SiO_2	34.13
Al_2O_3	11.09
CaO	10.80
MgO	5.53
MnO	0.25
Cr_2O_3	0.27
P_2O_5	0.95
Fe_2O_3	10.25 *
TiO_2	4.30
Na_2O	2.49
K_2O	0.87
S	3.08
C	12.26
Total	96.3

Characteristics	
pH	11.46 **
Density	1.24 grams/ cubic centimeter
Particle Size	300-20 microns
Estimated Surface Area	5 meters squared/gram
Estimated Intrusion Volume	1 cubic centimeter/gram
Color	Black

* All of the Iron in the sample was calculated as Iron (III) oxide.
** pH of the water extract from 1 gram of ash to 30 mls of distilled water

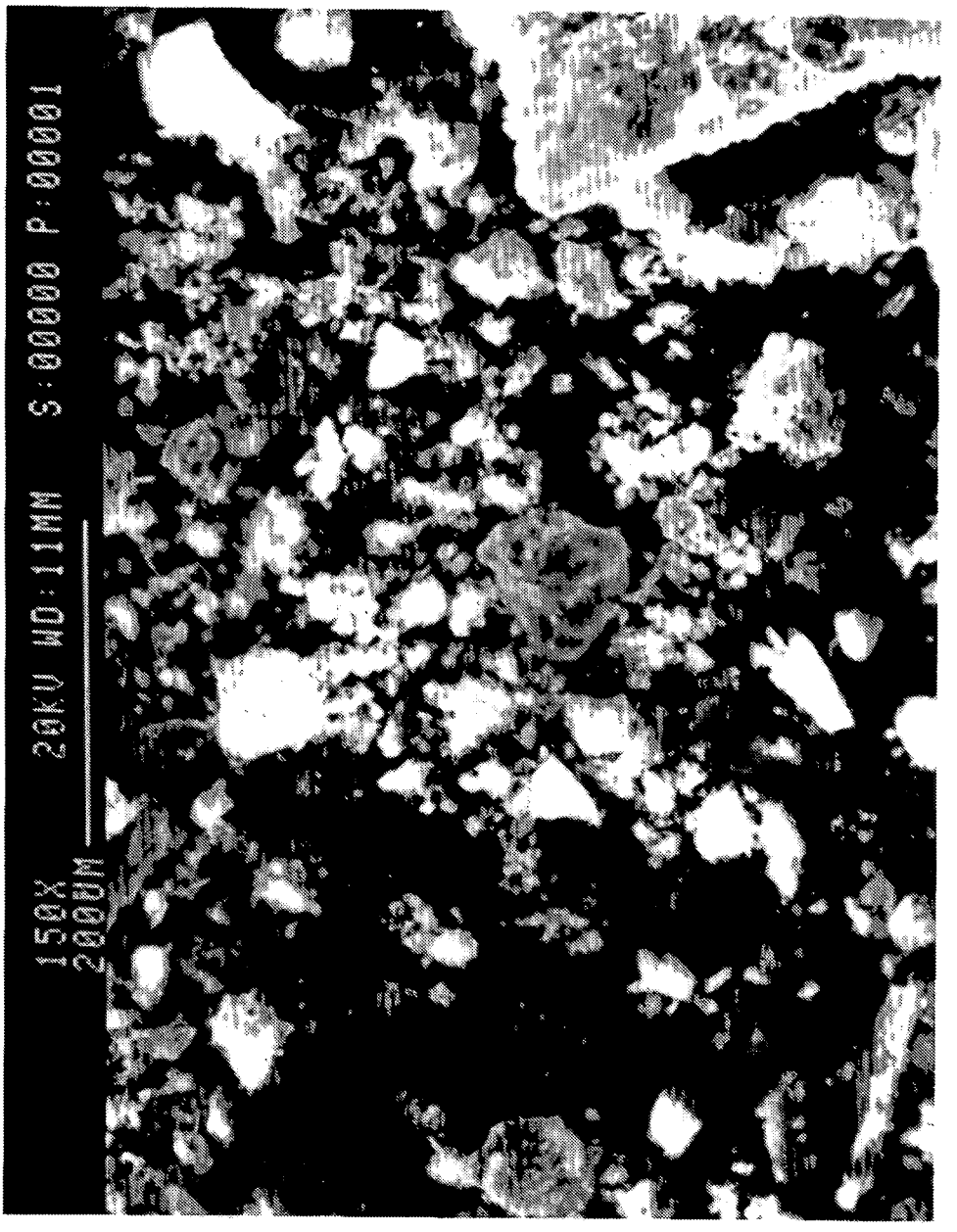


Figure 1 Overview of the composite ash sample

Magnification: 150X

Figure 2 View of single ground glass particle, approximate size 50μm

Magnification: 1230X

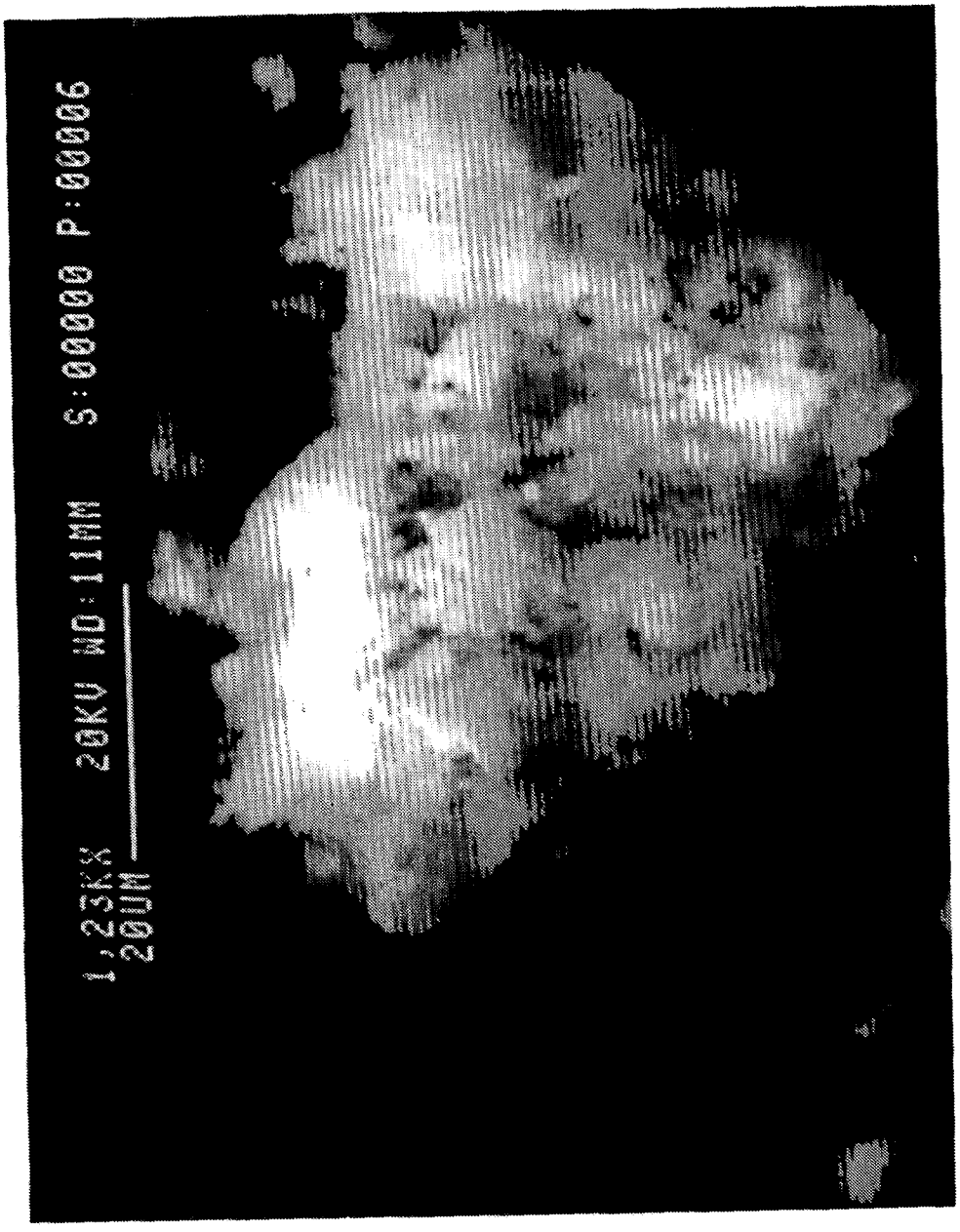


Figure 3 View of single composite ash particle, approximate size 50μm

Magnification: 1230X

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DEVELOPMENT OF A COMPREHENSIVE SAMPLING AND ANALYSIS PLAN FOR A LARGE RCRA FACILITY INVESTIGATION

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ABSTRACT

The National Fertilizer & Environmental Research Center (NFERC) of the Tennessee Valley Authority (TVA) has a RCRA Hazardous and Solid Waste Amendments (HSWA) Permit which requires the investigation of 50 Solid Waste Management Units (SWMUs) to determine the nature and extent of contamination. The type of SWMUs to be investigated include drum-storage areas, pits, storage tanks, abandoned rail cars, ditches, ponds, lagoons, sumps, abandoned buildings, and others.

The investigation phase of the RCRA Facility required the development of a comprehensive sampling and analysis plan. The plan provides for the sampling and analyses of the individual SWMUs to be conducted sequentially or concurrently. A computer program allows for tracking the status of the individual samples through the investigation process.

An individual approach for the investigation of each SWMU was developed to include a sampling and analysis plan. The individual Sampling and Analysis plan addresses the (1) sampling strategy (sampling locations, depths, media, etc.), (2) sampling procedures including sample chain-of-custody, and (3) sample analysis.

INTRODUCTION

The National Fertilizer & Environmental Research Center (NFERC), formerly the National Fertilizer Development Center, was established by Congress in 1933 as a part of the Tennessee Valley Authority (TVA) to research, develop, and improve fertilizer and fertilizer application processes for the fertilizer industry and the agricultural community. The NFERC is composed of approximately 625 acres, housing numerous laboratories, pilot plants, warehouses, and demonstration-scale production units. Many of these production units have been abandoned over the years.

The NFERC applied for a RCRA HSWA Permit to treat, store, or dispose of hazardous waste. A visual site inspection (VSI) of NFERC facilities resulted in the identification of 192 Solid Waste Management Units (SWMUs) in the RCRA Facility Assessment (RFA) Report. The permit requires a RCRA facility investigation (RFI) workplan for 50 of the SWMUs. A list of the 50 SWMUs is shown in Table I.

A task force consisting of six NFERC employees from various backgrounds and disciplines was formed to develop the RFI workplan which includes the Sampling and Analysis Plan. An environmental engineer from NFERC's Environmental Services was appointed as the task force project leader. The Manager of Environmental Services has overall management responsibility for the project. A project organization chart is shown in Figure 1.

In addition to the above task force, the project leader formed a technical support group of seven TVA technical experts in the fields of hydrogeology, soils, biology, air quality, climatology, and water quality. The technical group reports to the RFI project leader and to the task force to advise them about technical matters and to furnish technical data.

For each SWMU requiring a workplan, the task force reviewed the information and recommendations in the RFA report, collected and evaluated any ancillary data, and performed a visual inspection. The sampling and analysis plan was developed from the above information.

An outline for the RFI workplan was developed by the task force. Task force members were then assigned the responsibility to prepare those sections requiring their expertise.

Table I. Solid Waste Management Units, TVA, NFERC, Muscle Shoals, Alabama
List of Solid Waste Management Unit Requiring an RFI

SWMU number	SWMU name	Unit type	Current operational status
5	Outdoor Drum Storage Area No. 1	Drum storage	Active
6	Abandoned Rail Cars	Rail tank cars	Active
7	Furnace Building	Drum storage	Active
8	Dumpster	Dumpster	Active
9	Tank Car Washing Pit	Concrete basin	Active
10	Tank Car Washing Sumps	Concrete sump	Active
42	Phosphate Fertilizer Storage Building	Metal storage building	Active
43	Sulfur Cake Storage Area	Storage pad	Inactive
53	Carpenter Shop Outdoor Storage Area	Drum storage	Active
59	PDW Service Pits (21)	Concrete pits	Inactive
60	PDW Step Zero Clarifier	Concrete pit	Inactive
65	PDW Fuel Oil Storage Tanks (33)	Steel tanks	Active
76	PDW Area 309 Drum Storage Area	Drum storage	Active
83	PDW Area 307 Drum Storage	Drum storage	Active
84	PDW Surface Drainage Ditch	Unlined ditch	Active
85	PDW Storm Water Pond	Holding pond	Active
86	PDW Lagoons (2)	Holding pond	Active
91	ACP Gasifier Blowdown Sump	Concrete sump	Inactive
92	ACP Drum Storage Area No. 2	Drum storage	Active
93	ACP Drum Storage Area No. 3	Drum storage	Active
97	ACP Conditioner Tank	Concrete tank	Inactive
100	ACP Equalization Basin	Lined equalization basin	Inactive
104	Ash Settling Pond	Holding pond	Active
107	NFDC Scrap Yard	Storage area	Active
108	NFDC Landfill	Landfill	Inactive
109	Northeast End Drum Storage Area	Drum storage	Active
110	Coal Pile Run-Off Ditch	Lined ditch	Inactive
112	Precipitator Dust Piles	Waste pile	Inactive
115	Coal Slag Landfill	Landfill	Inactive
117	Old Ammonia Plant	Drum storage	Active
122	Building 321 Outdoor Drum Storage Area	Drum storage	Active
123	Building 321 Storage Area	Storage area	Active
128	Building 404 Outdoor Drum Storage	Drum storage	Active
130	Waste Oil Containment Area	Steel tank/drums	Active
131	Waste Oil Storage Area	Storage area	Active
137	Building 407 Outdoor Drum Storage Area	Drum storage	Active
140	Area 508 Sulfur Storage	Storage area	Inactive
141	Building 509 Drum Storage Area	Drum storage	Active
150	Ammonia Plant Compressor Blowdown Sump	Concrete sump	Active
151	Ammonia Plant Oil/Water Separator	Steel tank	Active
152	Ammonia Plant Oil Accumulation Area	Drum storage	Active
153	Ammonia Plant Compressor Oil Area	Drum storage	Active
164	Urea Plant Waste Oil Accumulation Area No. 1	Drum storage	Active
165	Urea Plant Waste Oil Accumulation Area No. 2	Drum storage	Active
166	Urea Plant Waste Oil Catch Basin	Steel tank	Active
168	Urea Plant Oil and Ammonia Sump	Concrete sump	Active
169	Urea Plant Waste Oil Accumulation Area No. 4	Steel tank	Active
170	Urea Plant Ditch	Unlined ditch	Active
173	Urea Plant Overflow Sump	Concrete sump	Active
189	PDW Chemical Sewer	Underground pipe	Inactive

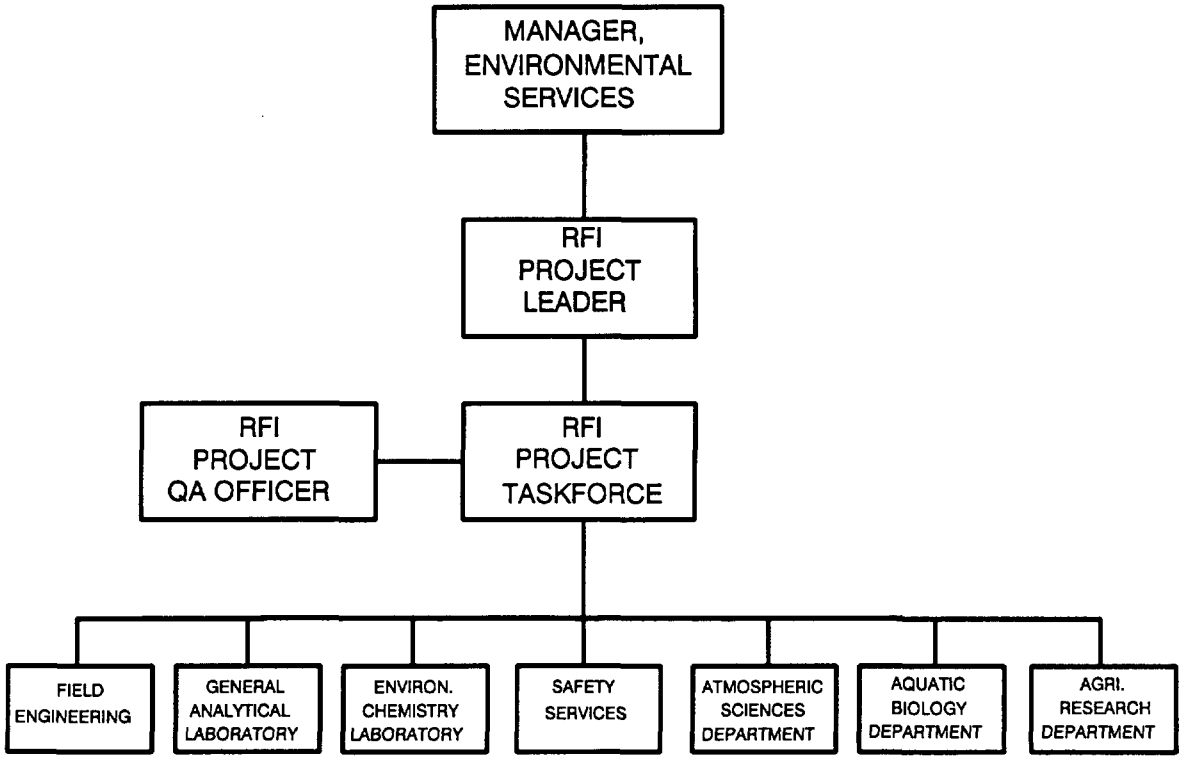

Figure 1: RFI Project Organization Chart

SAMPLING AND ANALYSIS PLAN

The sampling and analysis plan is one of the key elements of the RFI workplan and includes the following sections:

Sampling Strategy

The sampling strategy section includes the following topics:

- Selection of Sampling Sites

  The selection of individual sampling sites is location-and-release dependent. The selection of a particular approach depends on the level of knowledge regarding the release or potential release from a particular SWMU. Authoritative sampling sites are determined based on existing knowledge of the release configuration (e.g., visual evidence such as stressed vegetation). Systematic sampling sites are established by a predetermined line or grid which helps establish the boundaries of a contaminated area.

- Selection of Media To Be Sampled

  The selection of which media to sample (e.g., waste containers, piles, air, soil, sediment, groundwater, etc.) is based on the level of knowledge concerning any release or potential release from a SWMU. A phased approach is outlined. If waste containers are present in a SWMU, they are to be sampled in the first sampling phase to determine the presence of any hazardous constituents. If hazardous constituents are found, then further sampling to include other media is specified to determine the extent of contamination.

- Determination of Parameters To Be Measured

  The determination of parameters to be measured is based on the recommendations in the RFA Report. If the contaminants are not known, then the analysis of all inorganic and organic contaminants are specified in addition to the determination of RCRA hazardous waste characteristics.

- Selection of Sampling Types

  The selection of sampling types (e.g., grabs or composites) is based on nature and type of media sampled. For example, if several drums in the same location contain the same material, then composite sampling is specified. If the waste is determined to be homogeneous, then a grab sample is specified.

Sampling Procedures

The sampling procedures section includes the following topics:

- Preparation of reagents and supplies
- Sample collection
- Documentation of specific sample preservation
- Calibration of field instruments
- Submission of field QC samples
- Construction materials and techniques associated with monitoring wells and piezometers
- Field equipment listing and sampling containers
- Sampling order
- Decontamination procedures

Sample Chain-of-Custody

Field sample chain-of-custody requirements prior to shipment are specified. Preprepared sample labels and custody seals contain all of the information necessary for effective sample tracking.

The Sampling Team

The members and their responsibilities are specified in the sampling and analysis plan as follows:

- The sampling team leader is responsible for coordination of the sampling task.
- TVA's Field Engineering and/or TVA's General Analytical Laboratory team representatives are responsible for the collection and transport of all samples. Field Engineering staff representatives are also responsible for the installation of piezometer wells around SWMUs and conducting groundwater field monitoring tests.
- TVA's Atmospheric Science Department team representatives are responsible for the collection and analysis of air samples associated with the SWMU.
- NFERC's Safety Services team representative is responsible for all health and safety monitoring associated with the sampling task.

Sampling Operations and Sample Transport

Procedures outline the proper transport of samples to the laboratories for analysis. A sampling team member or the Field Engineering courier transports samples to one of two TVA laboratories depending on the analyses required for the investigation. The samples requiring gas chromatography/mass spectroscopy (GC/MS) analysis are sent to the Environmental Chemistry Laboratory, Chattanooga, TN. The samples requiring inorganic and non-GC/MS organic analysis are sent to NFERC's General Analytical Laboratory, Muscle Shoals, AL. Air samples are analyzed at the SWMU by TVA's Atmospheric Science Department. Field tests such as pH, conductivity, alkalinity, etc., are performed in the field by TVA's Field Engineering Staff. A diagram of the RFI Sampling Operations is shown in Figure 2.

Sample Analysis

The Sample Analysis Section includes the following topics:

- Laboratory Sample Chain-of-Custody

  The identification of the laboratory sample custodian, provisions for a laboratory sample custody log, and intra-laboratory sample custody requirements are outlined.

- Sample Storage

  The proper laboratory sample storage requirements and sample security measures are specified.

- Sample Preparation Methods

  Sample preparation procedures from *Test Methods for Evaluating Solid Waste Physical/Chemical Methods,* SW-846, are used in preparing samples for analysis.

- Calibration Procedures and Frequency

  All Field Engineering instruments and equipment are calibrated in accordance with existing Field Engineering calibration procedures. The General Analytical Laboratory instruments and the Environmental Engineering Laboratory instruments are calibrated with the respective laboratories' existing instrument calibration procedures. All Atmospheric Science Department field instruments are calibrated in accordance with *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-84-041.

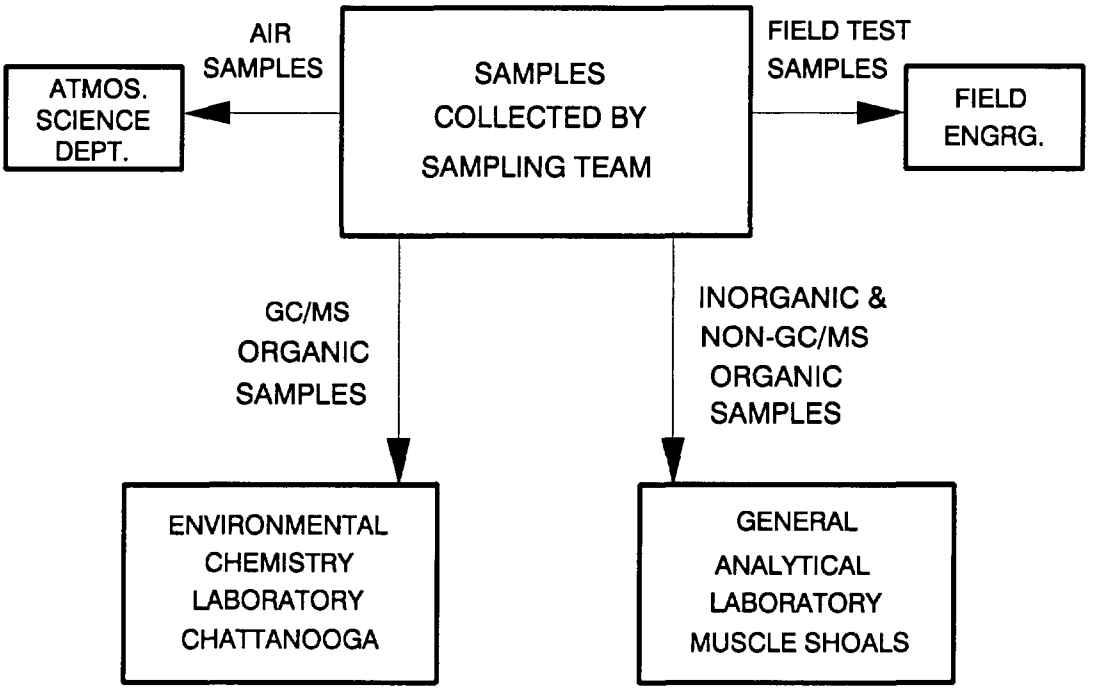

Figure 2: RFI Sampling Operations

- Analytical Procedures

  Where possible, all parameters are determined by the analytical procedures in SW-846. In cases where the SW-846 does not specify a method for a parameter to be measured, methods from the laboratories performing the analysis are used. The measurement parameters and their methods are shown in Table II.

- Data Reduction, Validation, and Reporting

  All results calculations are performed in accordance with the requirements in SW-846. The requirements for data validation and reporting are outlined. A flow chart of the RFI data flow and reporting scheme is shown in Figure 3.

- Laboratory Quality-Control Checks

  Laboratory quality-control checks and their performance frequencies are outlined (Table III).

SAMPLE TRACKING PROGRAM

A computer program is used to track the status of the individual samples through the investigation process. An example of the computer generated data sheet is shown in Figure 4. The RFI task force leader is responsible for entering data into the program. Data is entered into the program when any SWMU sampling task has been completed and when analysis results are received. Comments may be entered reflecting the current status of the sample and if further sampling of the waste is required.

SUMMARY

With the combined effort of many TVA employees with various backgrounds and disciplines, a viable comprehensive sampling and analysis plan was developed to produce quality data for the RFI at NFERC. The plan is being used to investigate 50 SWMUs at NFERC.

The computer tracking program allows quick access to the status of any sample in the investigation process.

For the plan to work successfully, the following is required:

- Effective coordination and communication between the sampling team laboratories and the RFI task force
- Proper training of sampling team members in the Sampling and Analysis Plan requirements
- Adherence to the requirements of the Sampling and Analysis Plan by those involved with the sampling and analysis of RFI samples
- Implementing the required quality-control parameters for the investigation
- Correct evaluation of the data produced by the plan.

Table II. Parameter Precision, Accuracy, and Completeness Objectives

Measurement parameter	Method	Reference	Experimental conditions	Precision std. dev.[a]	Accuracy	Completeness
ICP metals	EPA 6010	SW-846	Duplicate/spikes	±3s	±10%	95%
Mercury in liquid	EPA 7470	SW-846	Duplicate/spikes	±3s	±15%	90%
Mercury in solids	EPA 7471	SW-846	Duplicate/spikes	±3s	±15%	90%
Chloride Fluoride Nitrate Nitrite Orthophosphate Sulfate	EPA 300.0		Duplicate/spikes	±3s	±15%	90%
Total organic carbon	EPA 9060	SW-846	QC sample/duplicate	±3s	±10%	90%
Total organic halogens (TOX)	EPA 9020	SW-846	QC sample/duplicate	±3s	±15%	90%
Total petroleum hydrocarbons (TPH)	GAL AP9080	GAL lab manual	QC sample/duplicate	±4s	±25%	85%
Total & amenable cyanides	EPA 9010	SW-846	QC sample/duplicate	±3s	±20%	90%
Sulfides	EPA 9030	SW-846	Duplicate/spikes	±3s	±20%	90%
Phenols	EPA 9065	SW-846	QC sample/duplicate	±3s	±10%	90%
Volatile organics	EPA 8240	SW-846	Duplicate/spikes	See Table 7 in SW-846	See Table 7 in SW-846	90%
Semi-volatile organics	EPA 8270	SW-846	Duplicate/spikes	See Table 7 in SW-846	See Table 7 in SW-846	90%
Polynuclear aromatic hydrocarbons	EPA 8310	SW-846	Duplicate/spikes	See Table 4 in SW-846	See Table 4 in SW-846	80%
PCBs	GAL AP8080	GAL lab manual	QC sample/duplicate	±5s	±30%	90%
Organochlorine pesticides	GAL AP8081	GAL lab manual	Duplicate/spikes	±3s	±20%	90%
pH	EPA 9040	SW-846	QC sample/duplicate	±0.05 unit	±0.05 unit	95%
Principle organic haz. const. (POHCs)	EPA 0030	SW-846	QC sample/duplicate	±50%	±50%	90%
Corrositivity	EPA 1110	SW-846	QC sample/duplicate	±3s	±10%	90%
Ignitability	EPA 1010	SW-846	QC sample/duplicate	±1.1 C	±1.1 C	95%

[a] s = standard deviation.

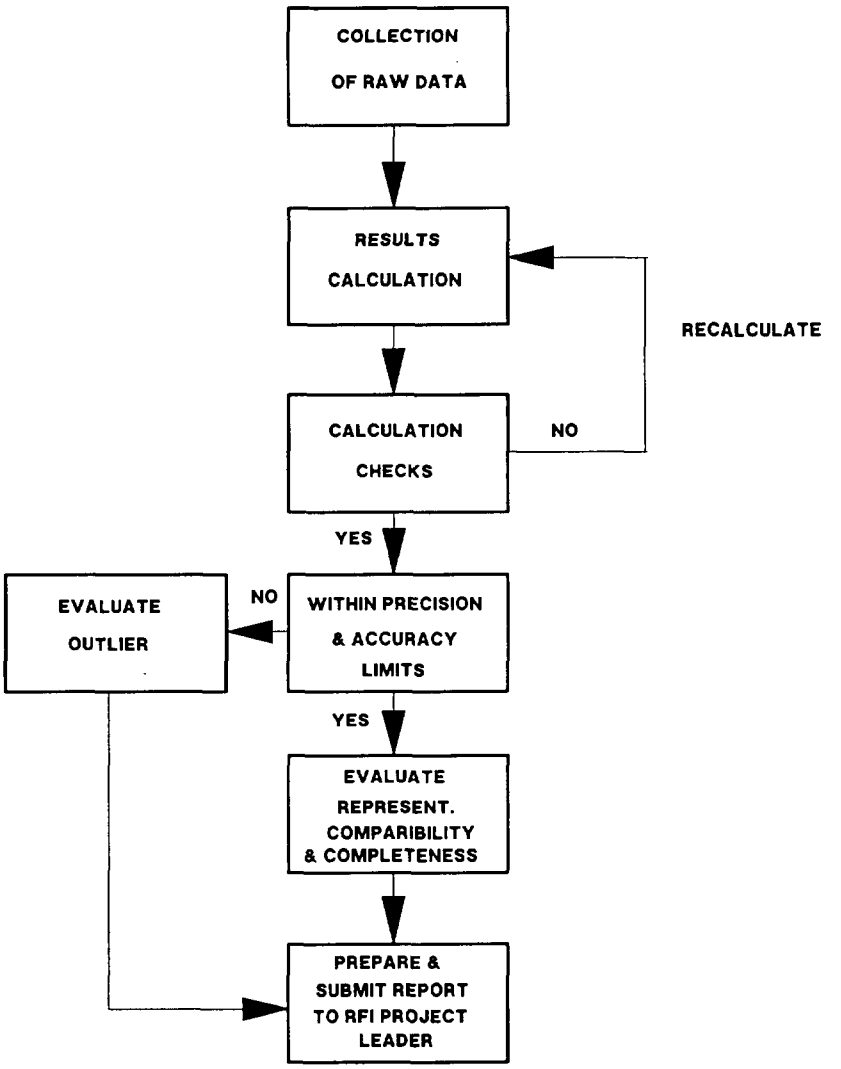

Figure 3: RFI Data Flow and Reporting Scheme

Table III. Performance Frequency of Quality Control (QC) Samples

QC Sample	Frequency
Method Blanks	One per analytical batch per matrix or every 20 samples, whichever is greater
Laboratory QC Samples	One per analytical batch per matrix or every 20 samples, whichever is greater
Calibration Checks	Refer to specific method for necessary calibration checks
Replicate Samples	One per analytical batch per matrix or every 20 samples, whichever is greater
Matrix-Spiked Samples	One per analytical batch per matrix or every 20 samples, whichever is greater
Surrogates	Add prescribed surrogates to every blank, sample, and laboratory QC sample. Surrogates only apply to volatile and semivolatile organics and pesticides
Zero Span Gases	One per new cylinder of gas
"Blind" QC Samples	One per quarter for each parameter
Calibration Standards	Refer to specific method for necessary periodic calibration
Column Check Sample	One per batch of absorbent. Applies only to absorbent chromatography and back extractions of organic compounds
Column Blanks	One per batch of absorbent. Applies only to absorbent chromatography and back extractions of organic compounds
Reagent QC Check Sample	One per batch of new reagent
Reagent Blanks	Refer to specific method for frequency

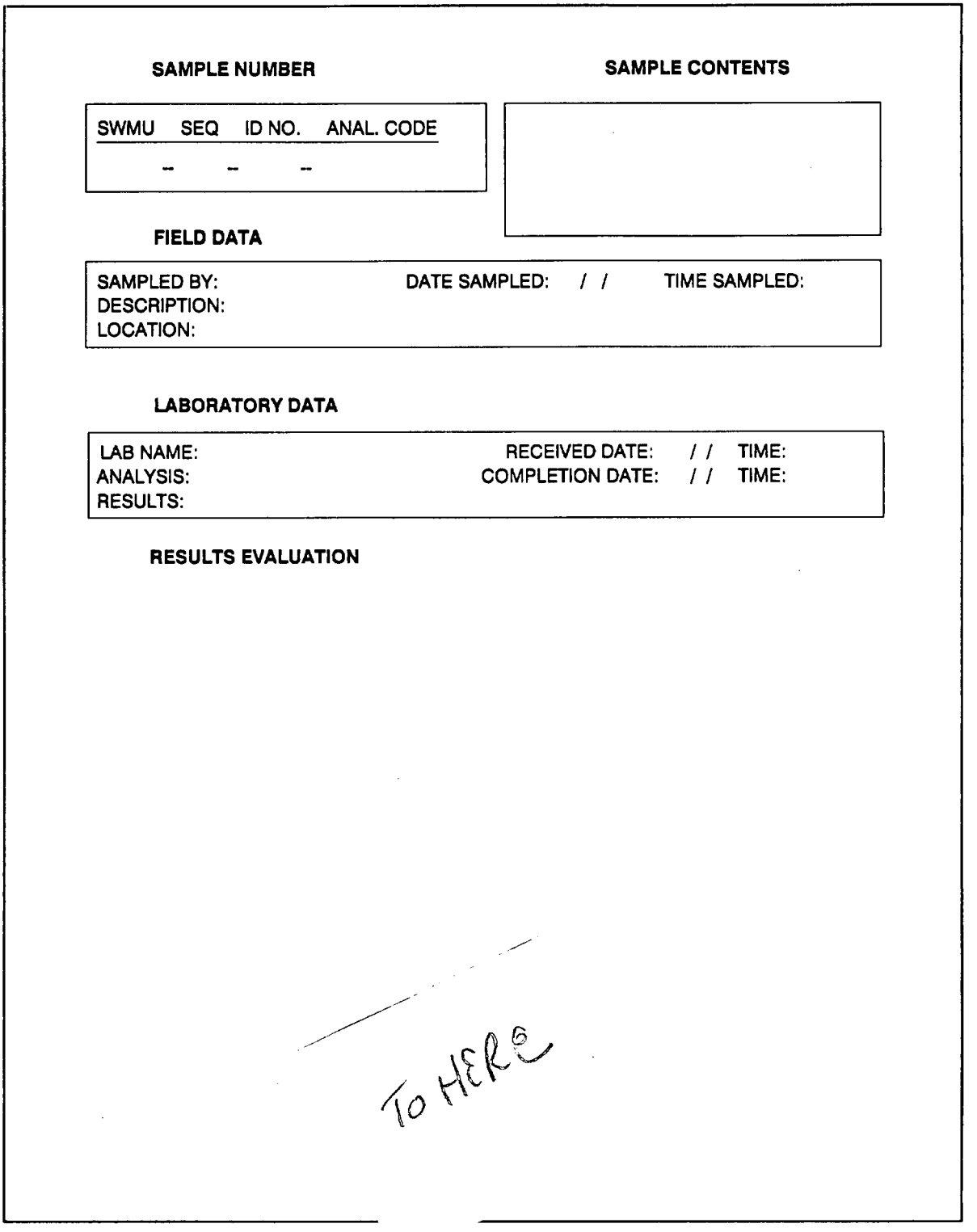

Figure 4: Sample Tracking Data Sheet

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ADVANCES IN SAMPLING UNCONSOLIDATED FORMATIONS

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ABSTRACT

Ground water remediation at hazardous waste sites often fails to meet established goals because the subsurface matrices are not adequately characterized and the processes involved in remediation are not adequately understood. Traditional designs of monitoring and aquifer restoration systems are based on the results of water samples alone. Such information is fundamentally inadequate in describing mass transport limitations, the indigenous microbial ecology, and the dimensional as well as the partitioned distribution of contaminants. In order to obtain the type of information required for the design of most aquifer remediation projects, it is also necessary to collect formation samples, but this can be difficult, especially in cohesionless material. It is of paramount importance that sampling procedures assure the physical, chemical and biological integrity of the samples is maintained and that the information they provide accurately describes conditions at the site. Hollow-stem auger drilling offers one of the best methods for collecting core samples at contaminated sites, however problems are often encountered in cohesionless material. This paper outlines advances made over the past few years in the collection of representative unconsolidated formation samples.

INTRODUCTION

Ground water remediation at hazardous waste sites often fails to meet goals established by state and federal regulators. In a recent study of 19 active pump-and-treat systems, Haley et al. (1989), found that most systems had been in operation longer than planned. Estimates could not be made as to the time remaining for restoration. The failure to properly design and evaluate ground water remedial actions stems from the failure or inability to understand complex processes involved in the transport and transformation of contaminants in the subsurface environment. Paramount to this understanding is an adequate hydrologic, physical, chemical and biological characterization of the subsurface.

Traditional designs of aquifer remediation systems are based on information gained only from ground-water samples. This approach is flawed in many respects. For example, water samples alone provide little insight into governing mass transport limitations, the indigenous microbial ecology, the three dimensional

distribution of contaminants, or the partitioning of contaminants into liquid, solid or vapor phases.

Conventional monitoring wells can accurately define a ground water plume but are inadequate in locating sorbed or entrained contaminants. This is because water collected from wells is usually from the more conductive sands and gravels while contaminants are often associated with less conductive silts and clays. The concentration of contaminants in the more conductive strata is controlled by contaminant diffusion from fine-grained materials. Therefore, water samples tend to underestimate the true contaminant mass.

Core samples can be useful in evaluating the sorption and desorption of contaminants. For example, in a recent study by the Robert S. Kerr Environmental Research Laboratory (RSKERL), a core was taken from a sandy aquifer about 1,000 meters down-gradient from an aviation gasoline spill which occurred in 1969. The concentration of toluene in a nearby monitoring well was 32 mg/l. To determine the number of pore volumes required to displace the mass of toluene, the core material was packed into a column and eluted. The first pore water sampled contained 33 mg/l toluene which remained constant and then decreased slowly with the elution of additional pore volumes. The mass and elution time of toluene in this core was greater than would be expected based on the compound's hydrophobicity and magnitude of humic material in the aquifer formation. Further analyses of the core revealed the presence of residual phase petroleum hydrocarbons which sorbed most of the toluene. If the remediation design had been based on monitoring well information alone, the time and expense required to restore the aquifer would have been substantially underestimated.

When evaluating the feasibility of enhanced biological degradation of ground water contaminants, the collection of aquifer core material is important for a number of reasons. One is that most subsurface bacteria are associated with the solid phase and cannot be characterized by ground-water samples alone. Another is that the use of microcosm studies to determine treatability parameters must be carried out using core material that represents aquifer conditions as accurately as possible. It is also important to describe the vertical distribution of contaminants so that injected water carrying oxygen and nutrients is efficiently utilized.

The use of cores is also necessary to determine the distribution of contaminants in order to assess the applicability of soil vacuum extraction for remediation. If most of the contaminant mass lies a few feet above and below the water table, as is common with underground petroleum tank leaks, it may be possible to lower the water table and apply vacuum extraction which can be faster and less expensive than pump-and-treat systems.

The selection of a sampling method is often based on time, cost, and the availability of drilling equipment rather than being tailored to the sites hydrogeologic conditions (Keely and Boateng, 1987). Cores are greatly affected by the sampling method used, therefore the sampling design should be dictated by the intended used of the core material. Once a subsurface core is removed, physical, chemical and biological changes can begin immediately. These include moisture loss, oxidation, gas exchange, and alterations to the biological community. The cost of sample collection should not play a major role in designing a monitoring system. Often this phase of aquifer remediation is a small percentage of the total project cost and can be justified by the assurance that the information collected leads to an efficient and lasting restoration of the site.

HOLLOW-STEM AUGERS

Since the 1950s hollow-stem augers have been used extensively as a practical method of obtaining soil samples in geotechnical investigations. The widespread availability and use of hollow-stem augers has resulted in the adaptation of this technology to the installation of monitoring wells at hazardous waste sites (Hackett, 1987). Riggs and Hatheway (1986) estimate that over 90 percent of all monitoring wells installed in unconsolidated materials in the United States used hollow-stem auger drilling.

Hollow-stem auger drilling offers one of the best methods available for collecting core samples and constructing monitoring wells in a contaminated unconsolidated environment. However, as Hackett (1987) states, the procedures for their use are neither standardized nor thoroughly documented in the literature. This is due in part to the variable hydrogeologic conditions encountered, the variety of monitoring well construction specifications, and other site specific problems unique to hollow stem augers.

In addition to serving as a temporary casing, the open auger flight allows the collection of formation and water samples at any point of interest, and is particularly useful when using split spoon or thin-walled sampling tubes. One of the primary advantages of hollow-stem augers is that drilling fluids are not required. This alleviates the potential impact of these fluids on subsurface samples and allows the cuttings to be more easily controlled. The latter is most important when the cuttings are contaminated and must be contained for disposal.

HEAVING SANDS

The collection of representative aquifer formation samples can sometimes be impeded by the presence of heaving sands and vertical movement of contaminants during drilling. Heaving occurs when loose sediments and water enter the hollow stem auger due to a sudden release of hydrostatic pressure upon removal of the pilot assembly or central plug. The buildup of sediments in

the hollow auger annulus interferes with the collection of formation samples, the installation of monitoring wells, and even additional drilling.

When heaving sands are present, difficulties in drilling can be overcome by either maintaining a positive pressure within the auger or modifying the drilling procedure. A positive pressure can be maintained by adding clean water or another drilling fluid to the inside of the hollow-stem. Clean water is preferred in order to minimize the potential interference with samples collected from completed wells. In any event, the column of water inside the auger must exceed the hydrostatic pressure of the heaving formation in order to prevent the entrance of formation material.

One method of addressing the problem of heaving sands is by using commercial devices that allow water to enter the column but exclude formation materials. Perry and Hart (1985) present two such devices. The first consists of a slotted coupling attached to a knock-out plate. As the auger moves below the water table, formation water enters through the slotted coupling, and when the auger reaches the correct depth, a ramrod is used to dislodge the knock-out plate. Although the slotted coupling is successful in heaving sands, it tends to plug when clays and silts are encountered. To overcome this problem, a second device was developed which is actually a screened well swab. Once the auger has advanced to the correct depth, the swab is lowered through the column and the knock-out plate removed. The screened swab filters the sand and allows only formation water to enter the column. Once the water rises in the column, the swab is slowly removed so that movement of the sand is not induced.

Other commercial devices that permit only formation water to enter the auger are also available. Some of these are designed to replace the traditional pilot assembly. In one, flexible center plugs are seated inside the auger which allow split-barrel and thin walled tube samplers to pass through to the formation (Hackett, 1987). Since the flexible center plug cannot be retracted, the ability to construct a monitoring well through the auger column is greatly restricted.

Another method for dealing with heaving materials is to modify the drilling rotation. In reverse flight augering the center plug and rod rotates in an opposite direction of the auger column so that sand deposits are pushed outward from the auger head while formation water enters to counter the hydrostatic pressure. Once drilling is completed, the center plug is slowly retracted so that the movement of sand into the hollow stem is not induced.

VERTICAL MOVEMENT Of CONTAMINANTS DURING DRILLING

Another consideration when using hollow-stem drilling is the vertical movement of contaminants during drilling. Vertical movement of contaminants within the borehole during drilling may

significantly bias sampling results (Gillham et al., 1983). This potential is greatest at sites where shallow formations contain sorbed or immisicible phase contaminants.

The vertical movement of contaminants within a borehole may occur from several causes including adherence to drilling and sampling equipment, particularly in cohesive clayey deposits, and the upward or downward movement of cuttings during drilling. This movement can also occur when the borehole is enlarged or through leakage through the auger joints. Augering may also cause clays and silts to smear sand and gravel strata, altering their permeabilities, and therefore their relative flow to the monitoring well (Keely and Boateng, 1987).

Contaminants can also move within a wells because of variations in the hydrostatic head. When the water level in a contaminated strata is higher than the potentiometric surface of lower formations, downward leakage will occur. This downward flow may even occur when the auger is continually rotated in an attempt to maintain an upward movement of cuttings (Gillham et al., 1983). Conversely, upward leakage of contaminants may occur when the potentiometric surface of an underlying zone is higher than the water level in an overlying saturated zone (Hackett, 1987).

The vertical movement of contaminants within a borehole drilled with hollow-stem augers is not well documented in the literature. It is often difficult to determine if an aquifer was contaminated prior, during, or after drilling and installing a monitoring wells (Hackett, 1987). It is possible to lessen the opportunity of vertical contaminant movement during auger drilling by installing a larger diameter surface casing to seal upper contaminated zones before deeper drilling is attempted. According to Keely and Boateng (1987), the auger is advanced a few feet with the subsequent driving of surface casing to the new borehole depth. This sequential augering and casing driving continue until the borehole is protected to below the depth of known contamination.

CONVENTIONAL SAMPLING DEVICES

- Split-Spoon Samplers

Split-spoon samplers are the most common conventional devices for obtaining disturbed samples. It consists of a heavy steel cylinder which can be split to reveal a soil sample. A removable tapered nose piece attaches to the lower end of the tube to facilitate cutting, and a basket sample retainer can be fitted to the lower end to hold loose, dry soils in the tube after the sample is removed from the drill hole. The tube is forced into the soil, typically 45.7 to 61 cm (18 to 24 inches), by dropping a 63.6 kg (140 pound) weight. The diameter of samplers varies between 5.1 and 11.4 cm (2 and 4.5 inches) with the larger diameters being used for gravely soils. Standard practices for

using split-barrel samplers are established under ASTM Standards D1586-84.

- Thin-Walled (Shelby) Tube Samplers

Thin-walled or Shelby tubes enable the collection of minimally disturbed cores. The tube is a metal cylinder with a beveled end for cutting into the soil. They vary from 45.7 to 61 cm (24 to 30 inches) in length and 5.1 and 11.4 cm (2 to 4.5 inches) in diameter, with lesser degree of sample disturbance being associated with the larger sizes. The larger sizes are also necessary in sampling coarse grain materials. Cores obtained from Shelby tubes are frequently used for hydraulic testing, however, since the soil must be extruded from the tube, it is sometimes difficult to remove the core in one piece. Standard practices for using thin-walled tube samplers are established under ASTM Standards D1587-83.

- Continuous Sampling

When formation samples are required at frequent intervals, the sequential removal and insertion of the pilot assembly and center rod use in hollow-stem augers can be time consuming and expensive. Continuous sampling with thin-walled tubes can be used to minimize this time while collecting minimally disturbed formation samples. Continuous sampling tube systems typically use a 1.52 m (five feet) barrel sampler which is inserted through the auger head, replacing the pilot assembly; however, the sampler is held stationary inside the hollow auger. The open end of the sampler extends a short and adjustable distance below the auger head allowing sampling to occur as the column is advanced. After the auger column has advanced 1.52 m (5 feet), the loaded sample tube is either emptied or exchange for another sampler (Hackett, 1987).

NEW TECHNIQUES FOR COLLECTING MINIMALLY DISTURBED COHESIONLESS SEDIMENTS

- Past Efforts

Shelby and continuous thin-walled tube samplers are frequently ineffective when sampling coarser grain or cohesionless samples in the saturated zone as the materials tend to flow from the sampling tubes upon retrieval. As a result, investigators have been attempting to design better sampling methods for the last thirty years.

In 1960, Parsons designed a thin-walled sampling tube containing a gas operated valve which was to seal the core barrel under vacuum to aid in sample retrieval. In 1978, Patterson utilized a modified Livingston piston corer to sample cohesionless soils. In this case a piston within the core barrel was secured to the surface by a wire line and a vacuum was created when the corer was driven past the stationary piston. Although this system

seemed to work fairly well at shallow depths, Munch and Killey (1985) failed to use it successfully at greater depths as material was lost as the core barrel hung in the borehole during retrieval. They modified the fixed piston system by using thin-wall tubing and a series of neoprene discs attached to the piston.

In 1987, Zapico et al., published another modification of the piston core barrel. They found that the sampler described by Munch and Killey (1985) was incapable of coring in pebbly sand and gravel although it performed well in soft sand and silt. The sampler, referred to as the Waterloo Cohesionless-Aquifer Core Barrel, contains an inner sleeve for sample collection and an outer housing to protect the inner sleeve. Four rubber washers and brass spacers were attached to the lower portion of the piston to maintain suction, thereby aiding in the retention of pore fluids and formation materials without the use of a catcher in the drive shoe. The core barrel is pounded into the sediment with a hammer-drive head attached to the end of the drill rod while a wireline holds the piston at its initial position. Zapico utilized a 12.7 cm (5 inch) diameter sampler with an average recovery of 85 percent. They have also used 7.62 and 10.2 cm (3 inch and 4 inch) samplers successfully.

- Sampling Advances by the Robert S. Kerr Environmental Research Laboratory

The special wireline piston sampler described above was originally designed and tested by the Institute of Water Research, University of Waterloo, Ontario, Canada (Zapico et al., 1987). RSKERL has made several modifications to that system in order to collect and seal aseptic samples in sterile containers using a sterile environment in the field.

The aluminum canister used at Waterloo was discarded. A piston was built to fit tightly inside a conventional thin-wall sample tube. A valve was added to the top of the sampler to relieve internal pressure between the top of the piston and the sampler cap when the piston is moved up the interior of the sample tube. Since internal pressure inside the sampler can retard driving and create vibration as fluids are compressed, the ball feature of the conventional cap design was retained. As shown in Figure 1, Teflon and stainless steel plates were added to the bottom of the piston to prevent organics from the neoprene seal contaminating the sample. Additional allen screws were added to provide a more uniform compression of the neoprene seals.

Initially a hardened steel drive shoe, without core catcher, was tested with the piston positioned flush with the cutting edge of the shoe. However, when tested in very fluid heaving sands, the piston would not create a sufficient suction to hold the sample when the barrel was raised. This problem was solved by assembling the original manufacturers core catcher and cutting shoe and positioning the piston on top of the core catcher. An

excess of 95 percent core recovery in saturated, unconsolidated sands has been achieved with these modifications (Leach et al., 1988; Armstrong et al., 1988).

When sampling in heaving materials, it is often necessary to flood the borehole with water or drilling mud to establish hydrostatic equilibrium (Zapico et al., 1987). As discussed earlier, the introduction of fluids, particularly mud, to the borehole is often not desirable. In order to avoid this problem a special clam-shell cap was designed to cover the annulus of the lead auger as shown in Figure 2. The hinged clam-shell door is held in place at the surface until the auger is forced into the soil at the onset of drilling and the constant vertical pressure holds the device in place until the desired sampling depth is reached. During drilling none of the inner tools such as the center head or sample tube are used (Leach et al., 1988). When the borehole is completed, the augers are detached from the spindle assembly, and since the clam-shell remains in place, the integrity of the material below the bit is retained until the piston sampler is in proper position for sample collection.

The sampler is positioned by lowering with the center rods while assuring that the wireline attached to the piston is slack. When the sampler contacts the clam-shell the center rods are decoupled and attached to the rotary spindle to prevent upward movement when the clam shell is opened. The decoupled auger string is then raised 30 to 45 cm (11.8 to 17.7 inches) which opens the clam shell. The auger is then pinned to prevent rotation or vertical movement which could damage the clam-shell door. This procedure traps the soil with the sampler before heaving and the aquifer can be sampled by hydraulic percussion procedures.

Once the clam-shell door has been opened, slack in the wireline is removed and the wireline is held in place by tension on the reel or fixing directly to the rig. The wireline is marked at some reference point, usually the top of the auger, so that its position can be observed during sampling. If the piston moves while the sampler is being lowered, less material will be collected than indicated by the depth of penetration.

The piston and tube is retrieved much like that for conventional sampling. It is slowly removed from the soil by a wireline attached to the center rod. No tension should be applied to the piston wireline during retrieval as upward movement would result in additional material entering the sampler. Otherwise, the sample could become contaminated with water or air if the piston moves during retrieval through the auger annulus.

As the sampler is lifted from the auger, the cutting shoe is immediately covered with plastic wrap to minimize aeration. The drive cap and piston is then removed while assuring that the sampler is held in a vertical position. This keeps the fluid sample intact until a stainless steel plug can be inserted to trap the sample tightly inside.

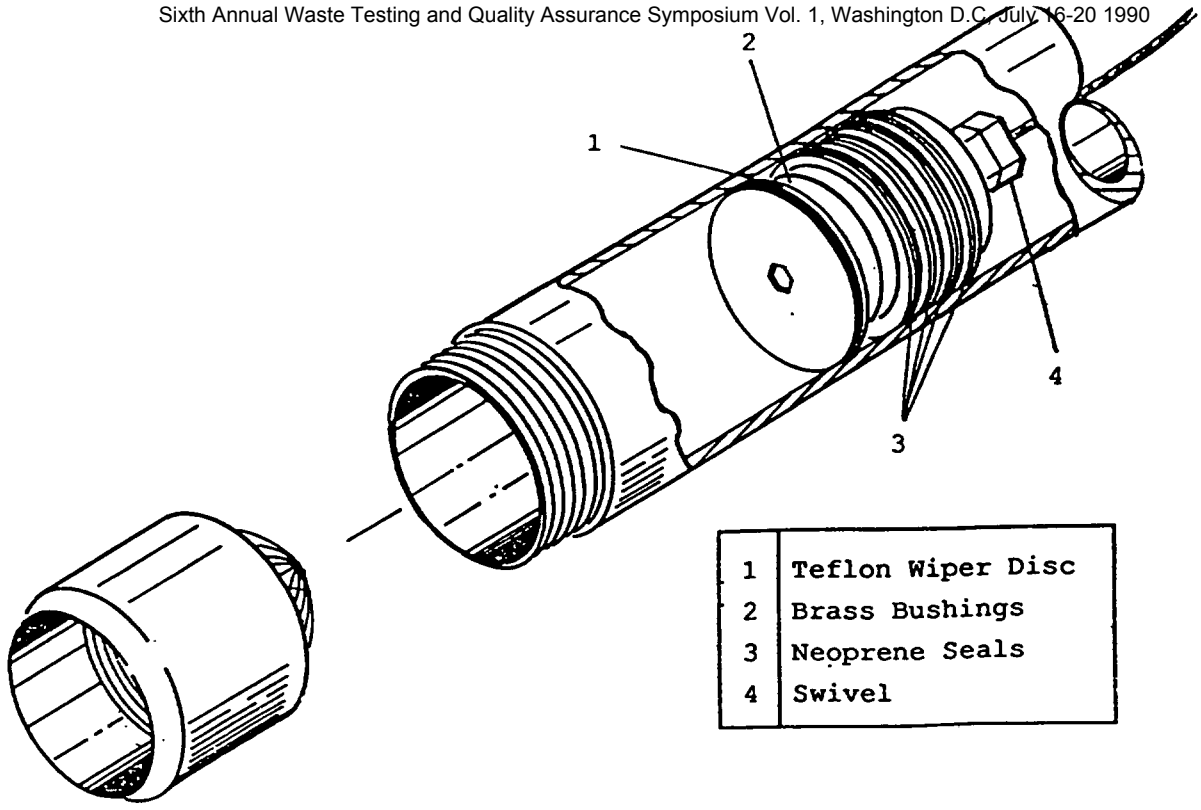

Figure 1. Modified Wireline Piston Design

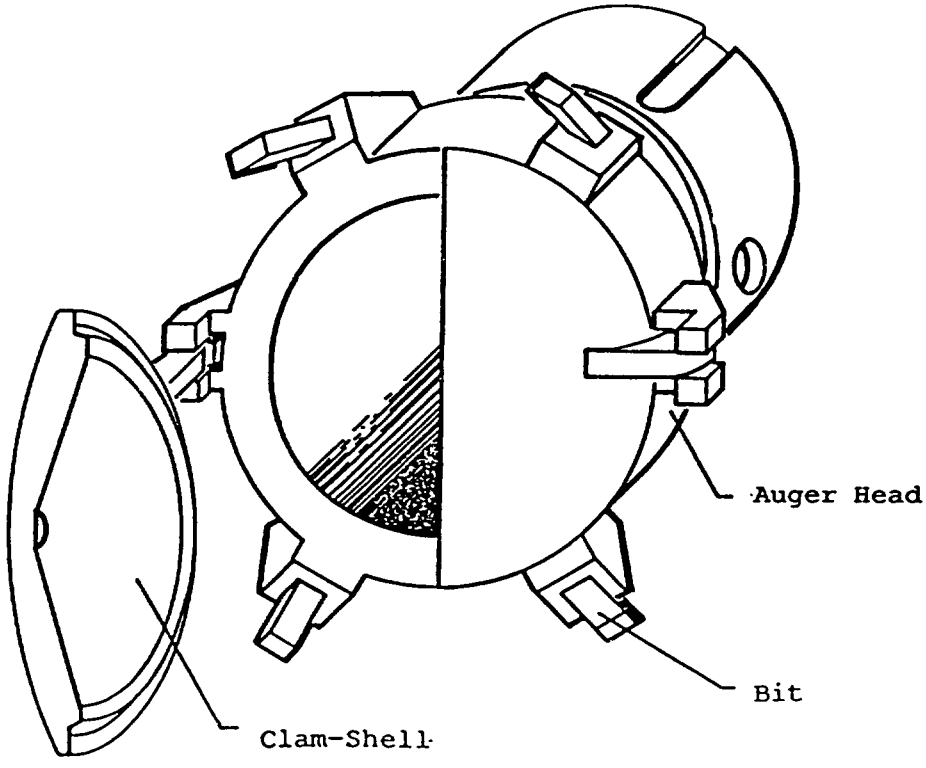

Figure 2. Clam-Shell Fitted Auger Head

The sample tube can be screwed into a special hydraulic core extruder located under the derrick at the rear of the drilling rig. During routine geotechnical sampling there is little need to protect sample from exposure to the atmosphere, therefore they can be collected and preserved in the field. In these cases the cutting shoe is replaced with a stainless steel paring device which peals away the outer 2.5 cm (i inch) of the core as it is extruded as shown in Figure 3.

Often the nature of the sample requirements is such that field preservation must be carried out in an oxygen free atmosphere. These requirements may result when sampling volatile organics or oily phase hydrocarbons in soils or when the in situ biological integrity would be destroyed in the presence of oxygen. As shown in Figure 4, these problems can be surmounted by inserting the end of the sample tube with the sealed cutting shoe into a glove box especially designed and constructed for this purpose. It can be prepared for field sample collection in about 30 minutes by filling with the proper number of sterilized containers and core paring devices and purging with nitrogen gas to reduce the oxygen level below detectable limits (Leach et al., 1989). Tests have shown that after 30 minutes of purging the oxygen content of the box is less than 0.02 percent.

In preparation for field sampling, a sufficient number of quart and pint glass sample containers are sterilized in the laboratory. Sterilization is done by washing the containers and lids and autoclaving at 120 degrees centigrade at 1 atmosphere of pressure for 60 minutes. As the containers and lids are removed from the autoclave, they are placed in a laboratory environmental chamber or glove box. When filled to capacity, the chamber is sealed and the interior air flushed by purging with nitrogen gas for 30 minutes at a flow rate of 2,500 L/hr at a pressure slightly above atmospheric. This procedure displaces gases inside the samples containers and fills them with nitrogen. After 30 minutes of purging, the sample containers and lids are wrapped in aluminum foil under a nitrogen atmosphere and the lids are screwed hand tight. The stainless steel paring devices are rinsed in distilled water and wrapped in foil for transport to the field.

In the field, the glove box is loaded with sufficient sample containers and steel paring devices to collect a minimum of 300 cm (9.8 feet) of cored sample (three separate 100 cm samples). About 10 minutes before being placed in the glove box, the three paring devices are rinsed with a 95 percent ethanol bath, placed in a stainless steel pan and ignited to fire-burn the excess ethanol. They are then wrapped in aluminum foil and placed in the glove box. The glove box in then closed and purged with nitrogen as discussed above. A positive pressure of nitrogen is maintained during all sampling activities.

After the extruder mounted sampler is inserted into the glove box through an Iris diaphragm, the cutting shoe and core catcher are

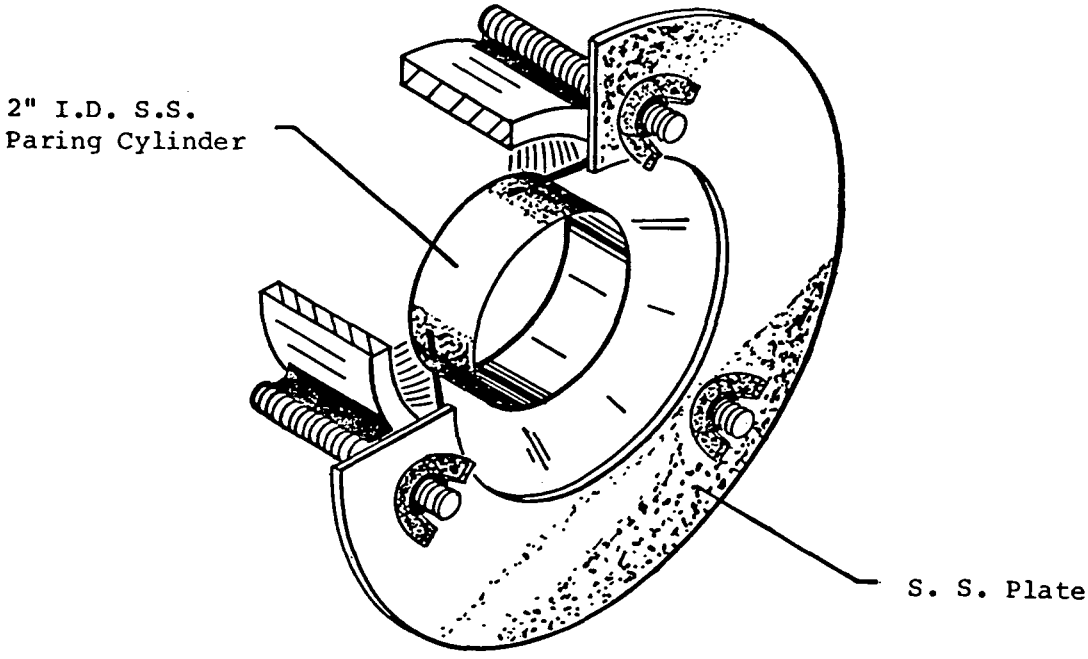

Figure 3. Core Paring Tool

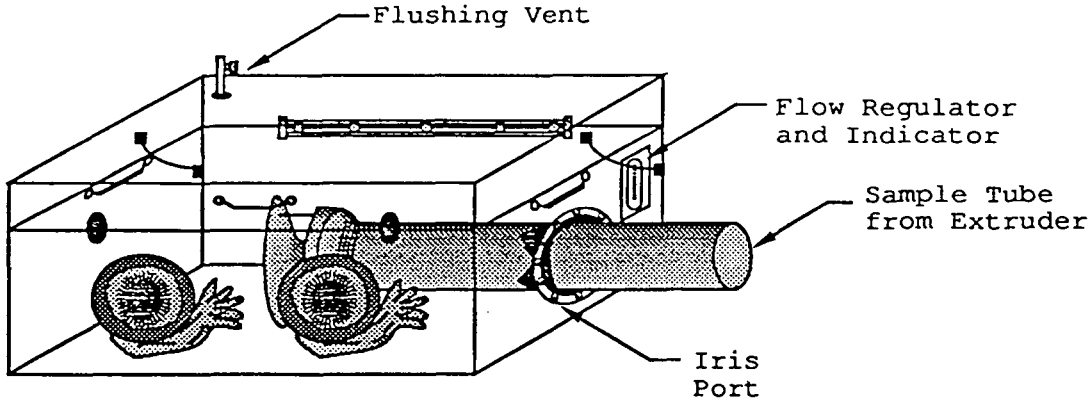

Figure 4. Field Sampling Glove Box

removed. A foil-wrapped paring tool is unwrapped and screwed to the sampling tube. About 10 cm (3.9 inches) of sample is extruded and carefully broken away exposing an aseptic face. Cores are then collected as the sample is extruded, sealed and numbered inside the glove box. Paring of the core is necessary to remove the slick exterior of the core which is in contact with the interior of the sampler where disruption and contamination could occur during collection.

After the samples have been processed, the box must be opened, thoroughly cleaned and prepared for repurging. Normally if the samples are to be analyzed for oily phase or volatile compounds, or used in microbiological investigations, they should be iced and transported to the laboratory.

It is not possible to close the clam-shell and continue to drill as the system is now designed, nor is it desirable since contaminated soils are generally inside the lead auger. Therefore, if deeper samples are required, the entire flight must be carefully removed from the borehole without rotation. The annulus of the augers, exterior flighting, and the clam-shell doors must be thoroughly cleaned with high-pressure steam to insure the integrity of additional samples.

The borehole should then be backfilled with clean sand or uncontaminated cuttings and redrilled to the next desired sample depth. In many situations, however, it may be advantageous to move the rig a few feet and drill a new hole to the next sampling depth. Although the process is slow, the tools must be clean and the clam-shell doors closed if high integrity sampling is to be consistently obtained.

DISCLAIMER

This paper has not been subjected to Agency review and therefore does not necessarily reflect the views of the U.S. Environmental Protection Agency.

REFERENCES

Armstrong, J.M., Kovreck, W.M., and Leach, L.E., 1988. Bioremediation of a Fuel Spill: Evaluation Techniques for Preliminary Site Characterization, Presented at the NWWA Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference, Houston, Texas, November, 1988.

Gillham, R.W., Robin, M.L., Barker, J.F., and Cherry, J.A., 1983. Ground Water Monitoring and Sample Bias. American Petroleum Institute, Publication 4367, 206 pp.

Hackett, G., 1987. Drilling and Constructing Monitoring Wells with Hollow-Stem Augers Part 1: Drilling Considerations, Ground Water Monitoring Review, Fall, 1987, pp. 51-62.

Haley,J.L., Roe, C., and Glass, J., 1989. Evaluation of the Effectiveness of Ground Water Extraction Systems, Proceedings of HMCRI's Superfund '89 Conference, November, 1989, Washington, D.C.

Keely, J.F., and Boateng, K., 1987. Monitoring Well Installation, Purging and Sampling Techniques, Part 1: Conceptualizations. Ground Water, v. 25, no. 3, pp. 300-313.

Leach, L.E., Beck, F.P., Wilson, J.T., and Kampbell, D.H., 1988. Aseptic Subsurface Sampling Techniques for Hollow-Stem Auger Drilling, Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods, Vol. I, pp. 31-51.

Leach, L.E., Kampbell, D.H., Cloud, J.E., and Kovacs, D.A., 1989. Statistical Performance of a Procedure for Aseptic Sampling at Hazardous Waste Sites Using Hollow Stem Auger Drilling, presented at the Tenth Annual Meeting of the Society of Environmental Toxicology and Chemistry, Toronto, Canada, Nov., 1989.

Munch, J.H., and Killey, R.W.D., 1985. "Equipment and Methodology for Sampling and Testing Cohesionless Sediments", Ground Water Monitoring Review, Winter, 1985, pp.38-42.

Parsons, P.J., 1960. "Movement of Radioactive Wastes Through Soil 1: Soil and Ground Water Investigations in Lower Perch Lake Basin", Atomic Energy of CanadaLtd., Report AECL-1038.

Patterson, R.J., Frape, S.K., Dykes, L.S., and McLeod, R.A., 1978. A Coring and Squeezing Technique for the Detailed Study of Subsurface Water Chemistry, Can. Jour. Earth Sci. 15, pp. 162-169.

Riggs, C.O, and Hatheway, A.W., 1986. Ground water Monitoring Field Practice- An Overview, Proceedings of the ASTM Conference on Ground Water Technology, CocoBeach, Florida, ASTM Special Publication 963.

Zapico, M.M, Vales, S. and Cherry, J.A., 1987. "A Wireline Piston Core Barrel for Sampling Cohesionless Sand and Gravel Below the Water Table", Ground Water Monitoring Review, Summer, 1987, pp. 74-82.

46 No paper available.

47 No paper available.

48

FIELD EVALUATION OF A MICROCHIP GAS CHROMATOGRAPH FOR THE ANALYSIS OF VOLATILE ORGANICS AT HAZARDOUS WASTE SITES

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ABSTRACT

A portable microchip gas chromatograph (GC) with dual capillary columns and dual thermal conductivity detectors (TCD) has been deployed at several hazardous waste sites for the identification and quantification of various volatile organic compounds. This GC, the Microsensor model M200, uses data reduction software based on traditional "correlation chromatography," made possible by the dual columns present. A portable sample concentrator has been developed to preconcentrate vapor phase samples prior to analysis by the M200 GC to lower detection limits to approximately 10 parts-per-billion volume (PPB-V). The M200 GC results from the analysis of soil gas vapor phase samples and other gas phase sample matrices were compared to other portable GCs (Photovac 10A and 10S models) and to Tenax/CMS adsorption tubes analyzed by standard GC/MS methodologies.

INTRODUCTION

The Microsensor M200 GC has two miniaturized TCDs embedded in a silicone wafer. An internal pump pulls the vapor samples through a loop etched onto a silicone wafer. Microvalves are actuated to inject variable amounts into the two analytical columns. The two 4 meter narrow bore capillary columns (DB5 and DB 1701) are of different

polarity. Therefore the same set of compounds will yield slightly different retention times for each column which will aid in peak identification. The columns can be individually heated, isothermally, from 30 to 180°C. The M200 GC was interfaced with a Macintosh Plus computer to both control GC operational parameters and to perform data reduction and compound identification routines. Louisiana State University (LSU) has written a software data package using "correlation chromatography" techniques to increase the level of confidence for identifying compounds. The software contains, at present, 30 or more components in its library. The entire library can be updated in terms of retention times indices (RTI) and TCD response using a small subset (minimum of three compounds) of the library. If the subset selected spans the range of RTIs of the standards of interest all the RTIs in the stored library can be updated to reflect any differences between the stored library and the current experimental conditions. Peaks with similar RTIs which could coelute may be resolved using various software routines. Levels of coelution can be selected in the software until unresolved peaks are separated. LSU has developed the software package under contract from both NOAA and the Emergency Response Team of the US EPA. As such this software may be available to the general public either directly or through licensing agreements in the near future.

The M200 equipped with dual TCDs yields nearly universal response for all volatile compounds tested at the 1-10 parts-per-million volume (PPM-V) range and above. Five to six orders of magnitude for linear range are possible with the three detector sensitivity settings. However, the TCDs of the M200 GC, as with most TCDs, lack sufficient sensitivity below the PPM-V range. To circumvent this, a portable sample concentrator has been developed by LSU for field use. This portable concentrator has two adsorbent traps filled with Tenax and sphearocarb (80-100 mesh). The two traps can be used alternately to increase sample throughput and reduce cleanout delays. An internal sample pump pushes the sample onto the trap at a known flow rate for a specified period of time. Using a calibrated rotameter and stop watch are used the exact volume loaded onto the trap can be calculated. The trap is heated to 240°C or other specified temperature, and back flushed into a small gas tight syringe. By knowing the total volume placed onto the trap and the exact volume desorbed into the syringe a concentration factor can be derived. Field studies have shown that the portable concentrator yields linear results on volatile aromatic and chlorinated hydrocarbons for a range of compounds from vinyl chloride to xylenes at concentration factors of 5X to 1000X.

SUMMARY

Soil gas and vapor phase samples in Tedlar samples bags were analyzed at a Superfund and at hazardous wastes sites in southern New Jersey. The M200 GC and Photovac models 10A10, 10S50, and 10S70 GCs were used to analysis for the following volatile organics: t-1,2

dichloroethylene, 1,1,1 trichloroethane, benzene, trichloroethylene, toluene, and tetrachloroethylene. The M200 yielded similar results to the Photovac GCs and in many cases showed results closer to the GC/MS results. Analytical time was drastically reduced with 1-2 minutes run times for the M200 GC compared to 10-20 minutes for the Photovacs. The M200 GC with the dual TCDs can theoretically respond to any compound heavier than the helium carrier gas. The Photovac GCs responds to only those compounds whose ionization potential is at or below that of the detector lamp (10.6 eV). As a result the Photovac GC were unable to detect 1,1,1 trichlorethylene at the ppb-v level. Table 1 compares the M200 GC results against GC/MS data . Table 2 compares the M200 GC verses the Photovac GC. These results are consistant with corrolations of GC / MS data with other field and bench top analytical instruments. A data base is being compiled to compare these field instruments, as well as others, with GC / MS analytical results on Superfund and hazardous waste sites throughout the USA.

TABLE 1.0

MICROSENSOR M200 G.C. DATA vs. GC / MS DATA

	BENZENE		TOLUENE		1,1,1 TCA	
CODE	M200	GC / MS	M200	GC / MS	M200	GC / MS
1356	50722	51000	147	290(J)	ND1	ND
1356	62290	45000	ND2	340(J)	ND2	ND
1613	4224	3700	159	610	ND1	ND
1613	5250	--	ND2	--	ND2	--
1685	ND1	ND	ND1	ND	2100	2000
1685	ND2	--	ND2	--	1780	--
1279	22800	31000	ND2	ND	ND2	ND
1283	ND1	ND	ND1	ND	403	1300
595	181	816	340	342	47	ND
596	168	259	342	814	27	ND
596DUP	--	247	--	814	--	ND
601	ND1	396	ND1	657	ND1	14
604	ND1	12	ND1	23	ND1	11
1165	ND1	17	ND1	33	ND1	10

TABLE 1.0 CONTINUED

	t-1,2 DCE		TRICHLOROETHENE		TETRACHLOROETHENE	
CODE	M200	GC / MS	M200	GC / MS	M200	GC / MS
1356	85	ND	ND1	ND	ND1	ND
1356	ND2	ND	ND2	ND	ND2	ND
1613	447	150(J)	2076	2300	ND1	ND
1613	ND2	--	2960	--	ND2	ND
1685	ND1	ND	ND1	ND	ND1	ND
1685	ND2	--	ND2	ND	ND2	ND
1279	ND2	ND	ND2	ND	ND2	ND
1283	ND1	ND	ND1	ND	ND1	ND
595	1080	ND	177	ND	269	ND
596	945	ND	195	ND	46	ND
596DUP	--	ND	--	ND	--	ND
601	ND1	27	ND1	ND	ND1	ND
604	ND1	ND	ND1	ND	ND1	ND
1165	81	ND	ND1	ND	ND1	ND

ND1 = NONE DETECTED, < or = 50 ppb-v (M200 GC)
ND2 = NONE DETECTED, < or = 1-2 ppm-v (M200 GC)
ND = NONE DETECTED, < or = 3-24 pppb-v (GC / MS)
(J) = DETECTED BUT BELOW QUANTITATION LIMIT (GC / MS)

TABLE 2.0

MICROSENSOR M200 G.C. vs. PHOTOVAC G.C.

	BENZENE		TOLUENE		1,1,1 TCA	
CODE	M200	PHOTOVAC	M200	PHOTOVAC	M200	PHOTOVAC
595	181	210	340	620	47	--
596	168	20	342	ND	27	--
601	ND1	430	ND1	300	ND1	--
604	ND1	ND	ND1	ND	ND1	--
605	48	ND	ND1	10	16	--
1165	ND1	ND	ND1	ND	ND1	--
1169	26	10	44	150	ND1	--
1162	ND1	ND	ND1	40	ND1	--
1163	ND1	ND	ND1	80	ND1	--
1164	ND2	ND	21	30	ND2	--

TABLE 2.0 CONTINUED

	t-1,2 DCE		TRICHLOROETHENE		TETRACHLOROETHENE	
CODE	M200	PHOTOVAC	M200	PHOTOVAC	M200	PHOTOVAC
595	1080	ND	177	ND	269	400
596	945	ND	195	40	46	ND
601	ND1	ND	ND1	ND	ND1	ND
604	ND1	ND	ND1	ND	ND1	ND
605	11	20	8	10	ND1	ND
1165	81	ND	ND1	ND	ND1	ND
1169	17	131	17	ND	ND1	20
1162	52	ND	ND1	ND	21	ND
1163	60	ND	ND1	ND	ND1	ND
1164	76	ND	13	ND	ND2	ND

ND1 = NONE DETECTED, < or = 50 ppb-v (M200 GC)
ND2 = NONE DETECTED, < or = 1-2 ppm-v (M200 GC)
ND = NONE DETECTED, < or = 10-20 ppb-v (PHOTOVAC GC)

49 # The Use of Quality Assurance Samples in Three Tiered Soil Gas Investigations and Their Impact on the Interpretation and Integration of the Different Levels of Acquired Data

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For several years now the U.S. Environmental Response Team (ERT) typically uses a three tiered sampling approach during their soil gas sampling programs. The three tiers are 1) the measurement of total VOCs, 2) the determination of selected target compounds using a portable GC, and 3) the analysis of Tenax/Carbonized Molecular Sieve (CMS) tubes that are pulled from a selected subset of the samples analyzed in step 2. Typically, the data interpretation had consisted of merely comparing the contours generated from the total VOC data and from the portable GC and confirming that the GC/MS analyses had detected the same compounds as the portable GC. Also, initially there were no true guidelines for the selection of samples for the GC/MS confirmation analyses. However, recently the ERT has started to implement several steps to insure a more rigorous interpretation of the portable GC data in light of the smaller GC/MS database. The first step involved establishing some general guidelines on the selection of portable GC samples for further GC/MS analyses. The second step involved the use of field standard samples which are then run as samples through the final two steps. This data then provided a key for discriminating negative biases in the GC/MS data due to sample losses from positive biases in the portable GC data. These steps will be illustrated using data obtained from several ERT soil gas surveys.

50 A FAST FIELD METHOD FOR THE IDENTIFICATION OF ORGANICS IN SOIL BY MOBILE GC-MS

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ABSTRACT

Over the last few years, much has been made of the need for fast screening techniques that can provide information as to the presence/absence of EPA listed organics during site characterization and/or remediation of superfund sites. Toward that end, research in our laboratory has focused on developing both screening and quantitative GC-MS methods for the identification of organics in soil media. Methods development has centered on the use of thermal desorption GC-MS (Bruker Instruments) as the means for direct introduction of the organics from the soil/sediment matrices into the instrument. A thermal desorption sampling probe is attached to the mass spectrometer. The probe consists of a stainless steel head and hose that can be independently temperature programmed over a wide range of temperatures, e.g., 25 to 260 °C. In addition, the hose contains a 3.5 m fused silica capillary column which serves to provide minimum separation of organics. The MS is operated in the selected ion monitoring (SIM) mode with between 4 and 8 ions selected depending on the nature of the analytical application.

For screening analyses, the stainless steel sampling head is placed over a known quantity of soil for which a known concentration of standard has been added. The relative standard deviation for PCBs, PAHs, and pesticides is between 25 and 30% with no sample pretreatment. For higher precision measurements, soil/solvent extraction is performed. The extract is co-injected onto an aluminum covered dish with a known amount of standard(s). The extract and standard(s) are thermally desorbed into the GC-MS as described above. Measurement precision is between 10 and 20% for these compounds.

Typical dynamic ranges are between 7 and 2500 ng on-column. The GC uses ambient air from the site as the carrier gas. The membrane used to preclude air components from entering the MS retards ~ 8% of the organic from entering the MS. Research will be presented illustrating the linear dynamic range and minimum detectable quantities for these compound classes.

Selected "targeted" PCB, PAH, and pesticide isomers can be preprogrammed for SIM MS detection. Thus, in a single five minute experiment a wide range of contaminants can be monitored during site remediation or characterization. In addition, methods have been developed that can provide both total and chlorination level PCB concentrations as well as individual isomeric PAH and pesticide measurements in soil/sediment media. Results of analogous experiments for VOCs will be discussed. Actual on-site measurements will be presented intercomparing mobile and laboratory GC-MS findings.

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