Jerry Pan

FIFTH ANNUAL
WASTE TESTING
AND
QUALITY ASSURANCE
SYMPOSIUM

July 24-28, 1989

OMNI SHOREHAM HOTEL
WASHINGTON, D.C.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

PROCEEDINGS

VOLUME I

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Symposium Managed by American Chemical Society

Fifth Annual Waste Testing and Quality Assurance Symposium
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AIR AND GROUND WATER

INFLUENCE OF WELL CASING MATERIALS ON CHEMICAL SPECIES IN GROUND WATER

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ABSTRACT. In this study four well casing materials were examined: polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), stainless steel 304 (SS 304) and stainless steel 316 (SS 316) to determine their suitability for monitoring both inorganic and organic constituents in ground water. Analyte solutions exposed to the well casing materials were compared to controls that consisted of an identical solution and container, but were devoid of the well casing material. For the inorganic studies, solutions containing two concentrations of As, Cr, Pb, and Cd, at two pHs, with and without added organic carbon, were tested. Samples were taken after 0.5, 4, 8, 24, and 72 hours of exposure. Results showed that PTFE well casings had no significant effect on the concentration of any of the aqueous metals monitored. Both stainless steels were susceptible to surface oxidation in ground water solutions. Rusting of the metal casings appears to create both active sites for sorption and a mechanism for the release of impurities and major constituents. The sporadic occurrence of surface oxidation makes the solutions prone to random error. PVC showed release of Cd and sorption of Pb after 72 hours of exposure. The magnitude of these effects is most likely not a major concern for purging times of less than 24 hours. Overall PTFE was the best-suited material for monitoring these trace inorganic species in ground water, followed by PVC, SS 304, and SS 316. The well casings were also tested for sorption of the following organic substances: RDX, trinitrobenzene (TNB), cis-and trans-1,2-dichloroethylene (c-DCE, t-DCE), m-nitrotoluene (m-NT), trichloroethylene (TCE), chlorobenzene (CB), and 0-, p-, and m-dichlorobenzene (0-DCB, p-DCB, and m-DCB). The two sets of isomers were selected to examine the effect of the structure on sorption. Samples were taken after 0 hours, 1 hour, 8 hours, 24 hours, 72 hours, 7 days, and approximately 6 weeks. Even after 6 weeks there was no loss by sorption for either stainless steel, although they did show signs of rusting. The greatest losses were due to PTFE with the chlorinated organics. While there was some slight sorption by PVC, after 72 hours the concentrations of analytes were still not significantly different from those of the glass controls. The results of these studies indicate that the choice of a well casing material for ground water monitoring of both inorganic and organic constituents is a compromise, but that PVC is probably the best overall choice.

THE EFFICACY OF INDICATOR PARAMETERS IN DETECTING INCIDENTS OF GROUND WATER CONTAMINATION

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ABSTRACT: The detection of ground water contamination requires the application of extensive and expensive testing. While, a numer of indicator tests are available to detect the presence or absence of chemcial groups, compounds or substances in ground water, there has been no systematic comparison of the application of indicator analytes or parameters to the detection and quantification of analytes on the Hazardous Substance List and other compunds as identified as a result of automated library searches.

Indicator parameter analyses and hazardous substance compound analyses for a group of 58 waste management sites are examined. The correlation between the results of indicator parameter analyses and the detection of specific hazardous substances at hazardous waste sites is assessed.

The efficacy of indicator parameters as predicators for specific classes of compounds such as organic volatile compounds, phenolics and halogenated species is also studied.

AN INTERLABORATORY STUDY OF VOLATILE ORGANIC COMPOUNDS IN GROUND WATER BY CAPILLARY COLUMN GC/MS

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ABSTRACT

The Environmental Monitoring Systems Laboratory - Cincinnati, (EMSL-Cincinnati) develops analytical methods and provides quality assurance (QA) support for U.S. Environmental Protection Agency (USEPA) programs involving water regulations. One of these QA support activities is to conduct interlaboratory method validation studies to evaluate analytical methology selected for the Agency's operating programs. These studies establish the reliability and legal defensibility of the data collected by the Agency, state regulatory authorities and commercial laboratories performing compliance analyses.

EMSL-Cincinnati has completed a method validation study (MVS) for Method 524.2, "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography/Mass Spectrometry" using reagent water and well water at a Superfund hazardous waste site as the relevant matrices. Nine laboratories were selected to participate in the study based upon laboratory experience, quality control practices, and satisfactory completion of a performance evaluation sample.

Analysts from the participating laboratories performed analyses of reagent water and ground water which were spiked with known concentrations of 60 volatile analytes. Six concentration levels, as three Youden pairs were examined for each matrix. After elimination of outliers, approximately 5500 data points were used to develop regression equations for the recovery, overall precision and single laboratory precision estimates for each of the sixty analytes. Also, any matrix effects between the water types were identified.

Percent recoveries for all compounds indicate a general high bias for the method. The pooled mean recovery for 59 compounds in reagent water, excluding dichlorodifluoromethane, was 111% with a range of 99 to 133% for the individual components; whereas, the recovery in groundwater samples was 110% with a range of 89% to 130%. Several of the gases exhibited quite high recoveries for the study.

Overall precision expressed as percent relative standard deviation (%RSD) for reagent water samples was 15.4% for all compounds in a range of 6.8% to 40%. Only 6 compounds had RSD of greater than 20%. For groundwater samples, the pooled %RSD was 16.4%, range 6.3% to 34.7%; indicating no major differences due to the matrix.

Single analyst precision for the pooled data in reagent water was 9.4% RSD with a range of 3.2% to 25.7%. Seven of the analytes exhibited RSD greater than 15% in reagent water. In groundwater, the pooled %RSD was 10.9% over a range of 5.8 to 32.3%.

Statistically significant matrix effects were identified for 14 of the volatile analytes; however, these effects were considered of practical significance for only 8 cases.

THE DETERMINATION OF FIXED GASES AND TOTAL HYDROCARBONS IN SOIL GAS AND AIR

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The growing number of emission sources in the industrial, municipal, and transportation areas makes source gas and ambient air monitoring necessary. The safety of existing landfill sites requires the monitoring of soil gas and/or ambient air both inside and outside the perimeter of the disposal area. The presence and amounts of O_2 and CO_2 can provide important information about aerobic and anaerobic reactions inside the landfill. The monitoring of methane to follow its migration can eliminate explosion hazards by preventing its collection in airpockets in residences or in other populated areas.

To attain the requirements of the Clean Air Act, total hydrocarbon monitoring is necessary since many organics behave as precursors in ozone formation.

The system described here is intended for measuring CO_2, N_2, CH_4 and total hydrocarbons (THCs) in aerial matrices. (See Figure 1).

The two-loop gas sample valve delivers a one milliliter sample directly to the FID for the detection of the THC's and one milliliter to a three column set for the separation of the fixed gases, the heavies being backflushed to vent.

The FID is capable of detecting THCs and CH_4 from ppm to low percentage levels while the TCD can detect CO_2, O_2, N_2, and CH_4 from low ppm to high percentage levels.

A propane standard is used as a calibration compound for the quantitation of the THC response as ppm Carbon providing excellent results for all hydrocarbons. Substituted organic compounds may give a lower Carbon response resulting in somewhat low biased results. In most cases this bias can be neglected.[1]

Figure 2 shows the chromatogram of a standard gas mixture. This system exhibits excellent reproducibility (% standard deviation, n=8). In addition a wide linear range may be covered from low ppm to % levels for the fixed gases and total hydrocarbons.

The instrument can be used in the manual or automated mode. With a Stream Selector Valve, 16 samples, blanks or calibration mixtures can be analyzed unattended. The automation can be GC based or directed by the Varian DS-650 data system.

[1] Absolute values of Non-Methane Organic Carbon as methane may be obtained as described in Application Note #12.

Instrument:	Varian 3400 GC
Detector:	FID; 220° Range 12 TCD; 120° Filament 160°
Columns:	Dedicated Column Set
Carrier:	Helium, 30 ml/min Air, 30 ml/min
Column Temp:	90° isothermal
Concentration:	300 ppm CO_2 300 ppm CH_4 800 ppm THC in air

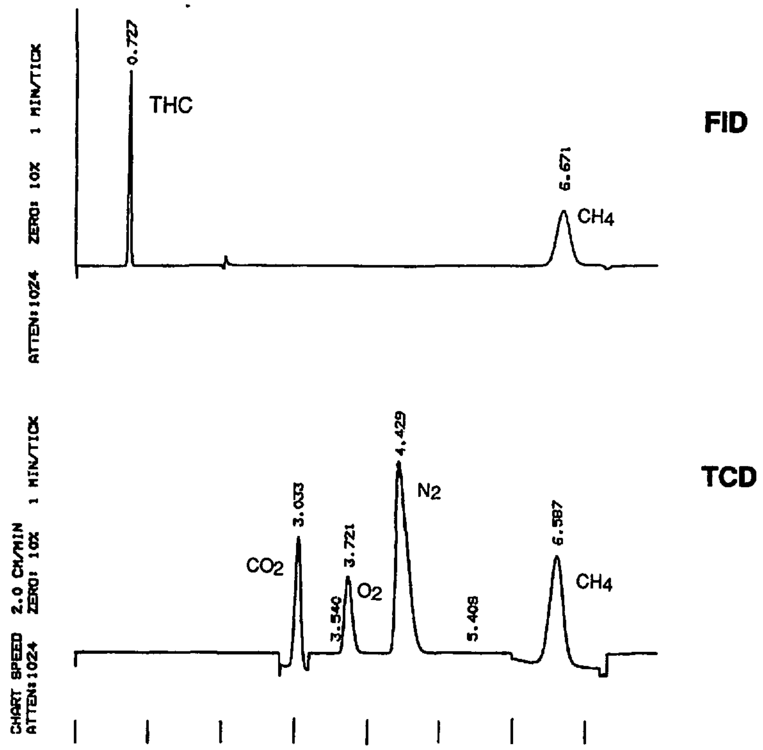

Figure 2
Chromatogram of Standards

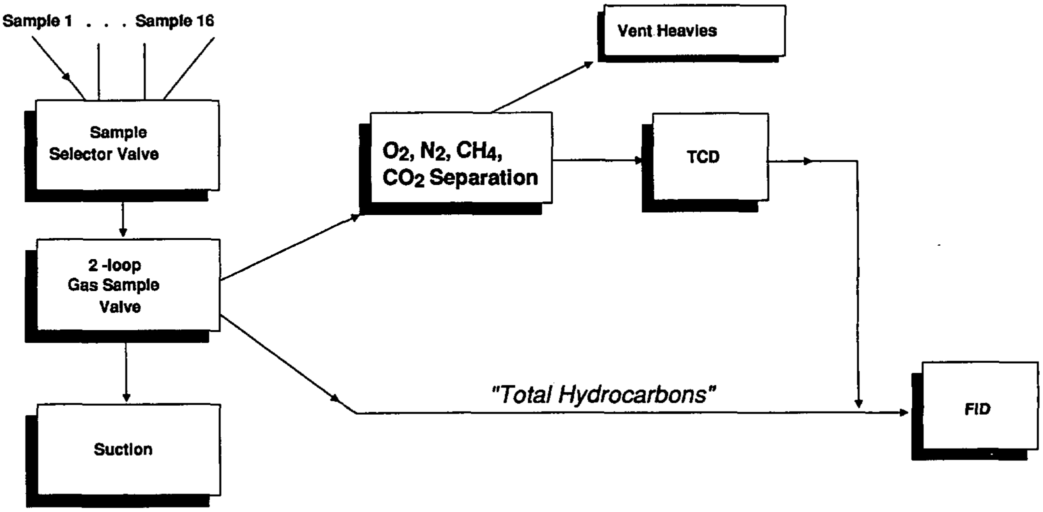

Figure 1
Total Hydrocarbons - Fixed Gases

A CASE STUDY OF THE USE OF THE "SUMMA CANISTER" FOR PASSIVE "OFF GAS" VENT SAMPLING AND ANALYSIS

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ABSTRACT

The "SUMMA CANISTER" with a restricted flow orifice was used to collect and preserve "off-gas" vent samples from a landfill in Illinois. Since the method is rarely used for vent sampling, standard accepted methods were used to confirm the integrity of the technique. The technique presented some problems in analytical procedures. They were overcome however, and the analysis was continued. The problems encountered are presented here with possible solutions. The method appears, to have the potential, to be one of the more efficient ways currently available for collecting and preserving gas samples.

INTRODUCTION

This paper describes the use of the "SUMMA CANISTER" with a restricted flow orifice for the collection of gases from a passive "off gas" venting system, in an actual case study. This method has rarely been used or documented in the past for this type of vent sampling. Charcoal tubes and Tedlar bags were used as a back-up in the event the "SUMMA CANISTER" method was deemed invalid, since they are methods commonly used for this type of sampling.

The site is in north central Illinois. It had been a sand and gravel pit for thirty years prior to its conversion to a sanitary landfill in 1941. The landfill was in operation until 1978. At the request of the State of Illinois a "Remedial Investigation/Feasibility Study" (RI/FS) was performed between 1983 and 1985. The site was placed on the National Priority List (NPL) for hazard remediation, as the result of that study. Based on the RI/FS interim remedial measures were proposed and accepted. The proposed action was to repair the cap, install a leachate collection system, which included a large leachate storage building, and fence the perimeter. This was completed by 1987.

In 1988, the United States Environmental Protection Agency (USEPA) Region V office requested the activation of the USEPA/Evironmental Response Team (ERT). The ERT was asked to sample the off-gases of the passive venting system on the site. There are five vents.

In May of 1988 an on-site evaluation was made. The initial site entry was performed by the ERT and Remedial Engineering Analytical Contract (REAC) support personnel. A "site-safety plan" was established prior to entry based on a previous study performed by the regional Technical Assistance Team (TAT). This study indicated that "dichloromethane" was the main contaminant of concern to on-site personnel. In addition to the results of the TAT study, the entry team found quantities of hydrogen cyanide, vinyl chloride and methane near the base the vents. At this time the "site safety plan" was changed to reflect the new findings and the appropriate safety precautions were established and enforced. Logistical support requirements, equipment staging and perimeter sampling locations were also established.

Since the venting system is passive, flow rates were monitored systematically throughout the sample period. This was done in order to establish an example of the daily trend of gas flow out of each vent. The data can also be used for modeling efforts that may be undertaken in the future.

The chemical compounds of concern at the landfill were methylene chloride, 2 butanone (methyl ethyl ketone), 2 propanone (acetone), 1,1 dichloroethene (vinylidene chloride) and 1,2 dichloropropane (propylene dichloride). These compounds were established as those of concern by the remedial response manager (RPM).

METHODOLOGY

The sampling occurred over a four day period. The first day "grab" samples were taken to establish an analysis criterion and to observe if certain compounds are more prevalent during certain times of the day.

The samples, from each vent, were collected in 1-liter Tedlar bags. This was accomplished by inserting a Teflon tube approximately 2 feet down into the vent using a vacuum pump and desiccator to fill the bag. A sample was to be taken every two hours for the first twenty-four hours. A temporary laboratory was set-up at a local hotel. The samples collected were taken to the temporary laboratory for analysis. The laboratory was equipped to do flame ionization and photo ionization gas chromatography analysis.

Due to diffusion, the bags could not hold the high volatiles in the gas causing them to escape the bags. This forced the lab personnel to dispose of the bags for safety reasons before analysis could be completed. Afternoon and evening samples that were brought to the lab were immediatly extracted on to "Tenax" tubes and shipped back to the ERT-TAT lab in Edison, New Jersey for analysis via gas chromatography/mass spectroscopy. The Tedlar bags were, obviously, not suitable for our purpose at the site. Since the bags had a high potential for leaking, they should not be shipped. It was not feasible to make the temporary lab capable of extracting the samples from tubes, therefore the temporary lab was eliminated and the technique was discontinued.

Activated charcoal tubes rated at 150mg were used for the second two days of sampling. A vent extension was constructed of sheet metal and attached to each vent. It extended two feet above the top of the vent. This was to reduce the influence of the wind on the actual vent. A hole was drilled into the extensions so that the intakes of the tubes were adjacent to the tops of the original vent pipes. The off-gases were drawn through the tubes with a vacuum type sampling pump. The pump was set at a flow rate of 350 cc/min for 180 minutes. An air sample was also taken from the leachate storage building using this method, at the same time period as the "SUMMA CANISTER" and "Anderson" pump described below. The tubes were analyzed in accordance with NIOSH 1500 for Hydrocarbons, NIOSH 1501 BP 36^{o}-126^{o}C for Aromatic Hydrocarbons and NIOSH 1003 Halogenated Hydrocarbons.

In tandem with the charcoal tubes, two-stage silica-gel tubes were used to determine concentrations of inorganic acids in the vent off-gasses. The silica-gel tubes were set at a flow rate of 200 cc/min for 180 minutes. These tubes were analyzed in accordance with NIOSH 7903 for inorganic acids.

The sampling procedure was repeated four times each day for the two days. The tubes were sent to the ERT-REAC laboratory in Edison via overnight delivery at the end of each of the sampling days. This was to insure that the sample tubes would be stored properly until the analysis could be completed.

The "SUMMA CANISTER" sampling occurred on the fourth day. The canisters were evacuated and verified to 0.1 psi pressure within each canister, prior to sampling. Two methods of injecting the sample into the canisters were used, a preset critical orifice and "Anderson" type sample pumps.

Two sampling periods were used one began at approximately at 1030 and the other began at approximately a 2100. This time span allowed for optimum daily changes in atmospheric stability. During these same periods samples were taken upwind, downwind and in the leachate storage building. The upwind and downwind samplers were placed no closer than 150 feet to the nearest vent. The "Anderson" type pumps were used to sample these locations, since it was assumed that the concentrations of the chemical constituency would be relatively low. The flow rate for the pumps were set at 27 ml/min for 360 minutes. This method pressurizes the canisters relative to atmospheric pressure.

It was determined the high concentrations coming out of the vents would ruin the Anderson pumps. The "Anderson" type pumps therefore, could not be used for these vents. The critical orifice was used to sample the off-gas vents. Each orifice was preset at 10 cc/min. This allowed the canisters to fill over a six hour period to between 10 psi and 14.7 psi. Making them near neutral to the atmospheric pressure for the period. The orifice, being a clear orifice (no traps) allowed pure off-gas to enter the canister. The canister was then attached to the vent and the intake tube was inserted into one of the holes used for the flow measurements. The intake tube was made of "Teflon."

The canisters were sent back to the ERT-TAT laboratory in Edison for analysis by gas chromatography/mass spectroscopy (GC/MS). Some of the canisters filled with critical orifice were not sufficiently pressurized for the sampling train. Pressure had to be added via "ultra zero air." Figure 1 shows a schematic of the dilution-pressurization train used. Upon attempting to analyze the vent samples it was discovered that the samples had higher concentrations of methane and carbon dioxide than expected. This caused the cryogenic traps to condensate and freeze. This rendered them useless and they had to be completely replaced. After a delay of approximately eleven weeks the analysis was continued. To overcome the problem aliquots of sample were adsorbed on to TENAX/CARBON MOLECULAR SIEVE (TENAX/CMS) cartridges by way of the following method: The TENAX/CMS cartridge were placed in a desorb oven CMS side down to allow a helium purge through the TENAX portion first. An aliquot of sample of 15 or 20 cc was injected into a 20 to 30 cc/min gas stream. Following a five minute purge, the sample cartridge was reversed and replaced in the desorb oven for analysis. This allowed for an accurately measured dilution of the sample, thus methane and carbon dioxide was reduced to a safe level. The GC/MS was able to analyze these samples with no difficulty.

The canisters filled by the "Anderson" type samplers were already pressurized. this allowed them to be attached directly to the analysis train, see Figure 2. The train extracts an accurately measured aliquot of sample using a mass flow controller, dries the aliquot and cryogenically traps it for subsequent GC/MS analysis.

P-Bromofluorobenzene and Bromochloromethane were added as surrogates to all samples and standards prior to analysis. The TENAX/CMS cartridges were spiked concurrently with the thermal desorb procedure described above. The standards analyzed contained eighteen components. The sample component identification/quantitation were done using the Aquarius software available on the RTE-6 data system.

Proper quality assurance procedures were adhered to. A sufficient amount of blanks and duplicate samples were provided as well as a chain of custody.

RESULTS

The laboratory attempted to analyze the "SUMMA" vent samples approximately five weeks after they arrived from the site. However, as stated in the methods section, the concentrations from the samples were so high the cryogenic traps were ruined and new traps had to be ordered, postponing the analysis.

The Tenax tubes, which contained the off-gas taken from the Tedlar bags, were then analyzed via the methodology stated above. The lower detection limits were in the 10 part per billion range. Table 1 shows the chemical compounds found in those tubes from an early afternoon and late evening's sampling for each vent.

The data from the charcoal tubes are contained on Table 2. The table includes data acquired from a morning and evening sample periods. This data was done by the ERT laboratory under the REAC contract as opposed to the TAT laboratory that performed the SUMMA and Tenax tube analysis. The samples were analyzed by gas chromatography only. The high volatiles, such as vinyl chloride and trichloroflouromethane, eluted too rapidly and were undetected.

As explained above the off-gas samples taken directly from the vent by the "SUMMA CANISTERS" with the critical orifice were adsorbed on to a Tenax/CMS cartridge just prior to analysis. The samples were stored for eleven weeks in the "SUMMA CANISTERS" under no special conditions, awaiting the arrival of the replacement cryogenic traps. Table 3 contains a list of the compounds found in those samples.

The data from the leachate storage building samples collected with the "SUMMA CANISTER" connected to the Anderson sampler compared very closely with the charcoal tube data. As expected of the compounds tested for, trace amounts of benzene and toluene appeared. META and Ortho xylene only appeared on the SUMMA data. All other compounds were indicated in the raw data as not detected.

DISCLAIMER: The data recovered from this project is immense. We therefore did not list all of the compounds found in the samples. The compounds listed are those of concern for the project and those usually of concern for this type of landfill. We feel we have shown a sufficient representative sample of the data for the reader to understand the point of this paper.

DISCUSSION

Of the compounds of concern only 1,1 dichloroethene appeared. Many other common landfill compounds also appeared and are listed in the tables. Although the samples were collected on different days the results were fairly close in compound content, especially between the Tedlar bag samples and the "SUMMA CANISTERS." The compounds from the charcoal tubes that coelute on the gas chromatograph were identified by correlating the data with that found in the gc/ms data from the Tedlar bag and "SUMMA CANISTER" samples. This is with the exception of ortho-xylene and styrene which coelute and are both compounds of concern. As can be seen in the tables the quantities measured varied between the three methods.

Several factors can be attributed to the differences found in the quantities. The first is that the sampling was performed over several days. This means that if the quantities of the compounds varies periodically a true comparison of quantitation can not be accomplished. The second factor is that the size and purity of each sample was different. The Tedlar bag sample was taken over a few seconds to fill a 1-liter bag of pure off-gas then evacuated on to a TENAX tube. Evacuating on to a tube is not the standard practice in the field normally the bags are either analyzed in the field or shipped as they are. The charcoal tubes were taken over a three hour period allowing 63-liters of off-gas to pass through the trap. The "SUMMA CANISTER" collection method extended over a six hour period allowing approximately 3.6-liters of pure off-gas to be trapped in the canister. Just prior to the analysis a 15 or 20 cc sample was removed from the canister. This aliquot was then purged through a TENAX/CMS trap prior to analysis (as described in the METHODS section). The same questions arise with all three of these methods: How many of the compounds of concern and how much of each were actually trapped, and does each tube contain a representative sample of each parcel of off-gas from the vent? The third factor is the durability of the samples during shipping and storage. The important factor here is time, how long will the compounds of concern remain trapped in each sample container. Currently with these questions, certain assumptions are made, giving the methods the benefit of the doubt.

CONCLUSION

This was the first time that the ERT used the "SUMMA CANISTER" to collect and store off-gas samples from a passive venting system of a landfill. As shown in this report several problems were encountered that had to be overcome to make the method work. Solutions to those problems encountered were also presented.

The study compared some of the problems with the current methods being used for this type of sampling to the "SUMMA CANISTER" method. It is the feeling of the group that the "SUMMA CANISTER" method, although does not eliminate, reduces the impact of the normal problems encountered with the standard methods. The largest impact, due to its construction, is on the preservation of the sample during shipping and storage. Since each canister is shipped under slightly positive or at atmospheric pressure, and in its own shipping crate there is little chance of infiltration from other samples or surrounding contaminated atmospheres. The valving is well protected so there is little chance of breakage which could contaminate the surrounding atmospheres. The canister shell is made of metal so there is little chance of cracking or shattering as with the glass tubes of the different types of traps.

The "SUMMA CANISTER" can hold several liters of pure sample. This allows the pure sample to be transported to a laboratory for more ideal conditions should the transfer on to tubes become necessary. Also, depending on the analysis scheme, the large volume makes it possible to do more than one type of analysis on each sample. At the time this paper was written critical orifices for the canister have been improved to collect sample over an eight hour period. For passive venting this is ideal since the flow of off-gas is not consistent throughout the day. This type of vent releases off-gas when a build-up occurs within the landfill. The long sampling time span means that there is more of a chance of collecting the release when it occurs. By using the critical orifice type valving it is not necessary to have power at the vents which cuts down on the logistical problems often encountered at a landfill. Due to less moving parts, such as with powered pumps, there is less chance of malfunction during the sampling period.

These are only some of the advantages we found in using the "SUMMA CANISTER" method of sampling. The problems we encountered due to inexperience with the system were easily overcome. There is no question that we will use the system again for this type of project and expand and try it in other situations.

SUMMA CANISTER
SAMPLE DILUTION LINE

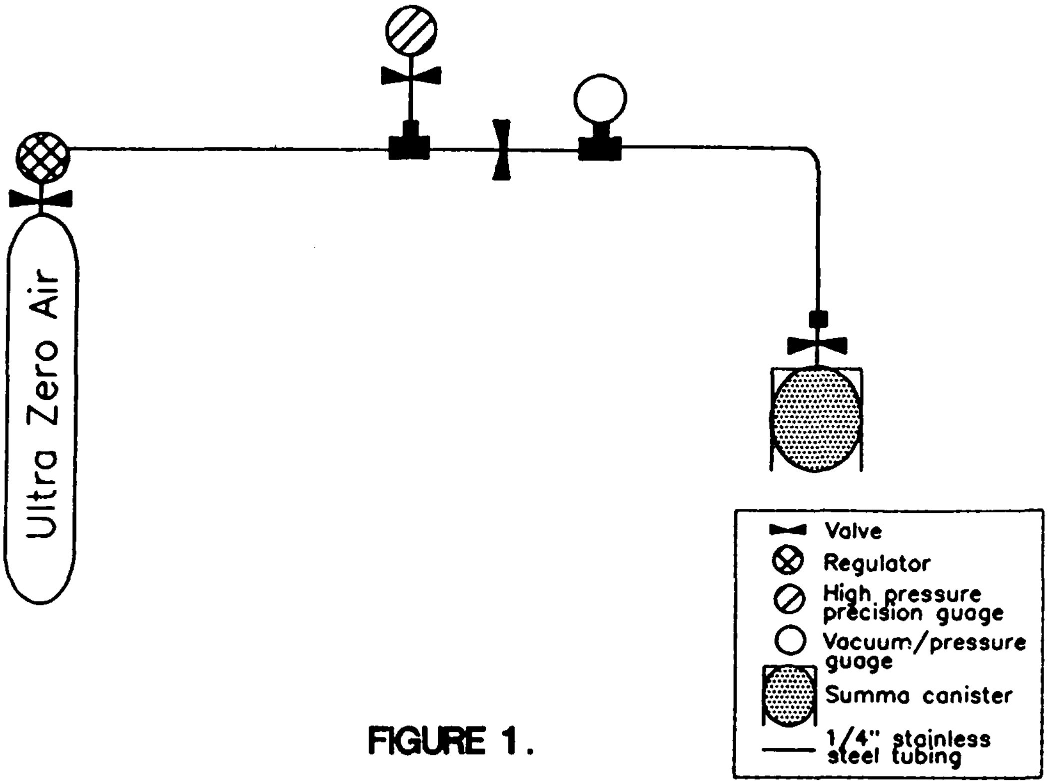

FIGURE 1.

SUMMA CANISTER
ANALYSIS TRAIN

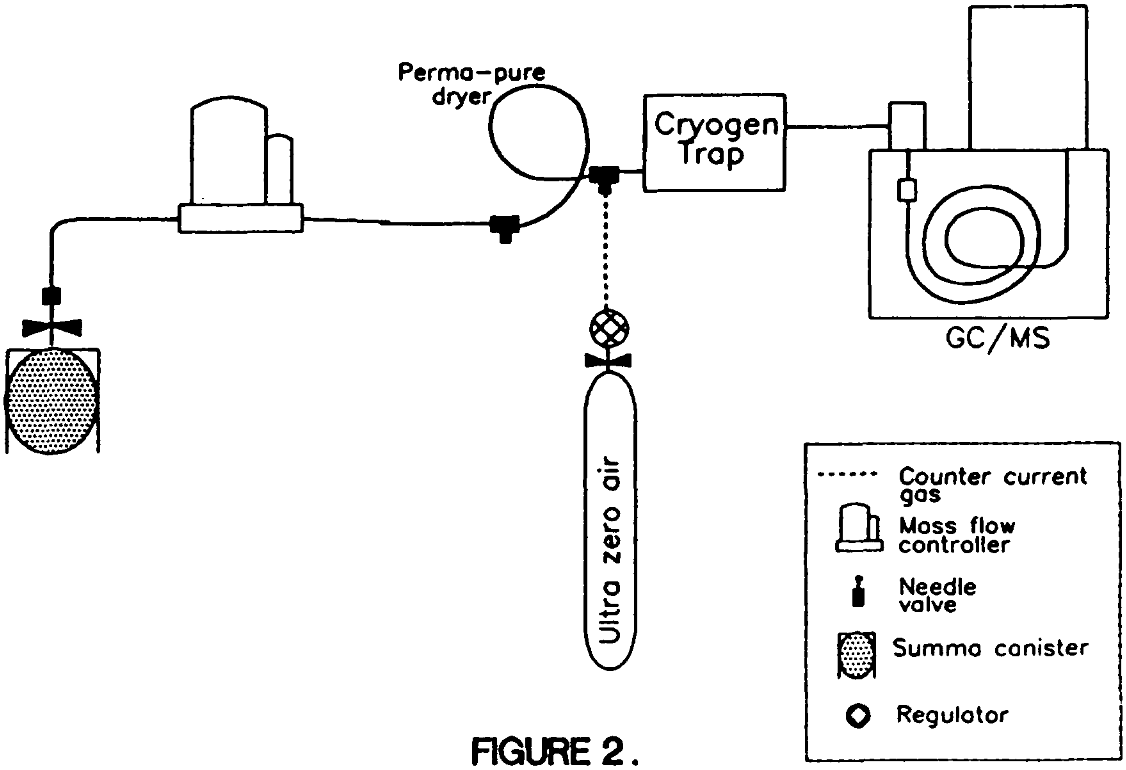

FIGURE 2.

TABLE 1: TEDLAR BAGS TO TENAX TUBES IN PPB

	VENT1A	VENT1E	VENT2A	VENT2E	VENT3A	VENT3E	VENT4A	VENT5A	VENT5E
VINYL CHLORIDE	536	698	22400	20000	3530	2730	ND	ND	ND
TRICHLORO-FLOUROMETHANE	1530	2290	9510	4510	6540	1700	78	1420	2,790
1,1 DICHLOROETHENE	ND	BLOQ	1170	263	565	420	ND	549	312
METHYLENE CHLORIDE	ND	608	5970	12400	17200	11100	ND	1140	663
TRANS 1,2 DICHLOROETHENE	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1 TRICHLOROETHANE	53.5	69.5	1290	1310	637	880	ND	2860	580
BENZENE	71.3	146	1400	1410	1050	771	ND	384	110
TRICHLOROETHYLENE	ND	37.5	1260	ND	ND	ND	ND	ND	ND
TOLUENE	928	1810	22500	25000	5650	5260	42.2	278	263
TETRACHLOROETHYLENE	BLOQ	44.3	2940	3440	ND	ND	ND	ND	ND
ETHYL BENZENE	1240	3110	3260	4010	8060	5580	BLOQ	BLOQ	BLOQ
M-XYLENE	1810	4520	6520	9680	13500	9540	BLOQ	324	219
O-XYLENE	400	1780	1790	2440	4320	2660	BLOQ	BLOQ	ND
STYRENE	ND	340	2060	3690	859	510	ND	214	279
META ETHYLTOLUENE	49.4	706	1030	1680	1970	1330	ND	ND	BLOQ
LIMIT OF QUANTITATION (PPB)	40	20	200	200	200	200	10	200	114

BLOQ=BELOW LIMIT OF QUANTITATION
ND= NON DETECT
VENT W/A= AFTERNOON
VENT W/E= EVENING

TABLE 2: CHARCOAL TUBES ANALYZED BY GC ONLY IN PPB

	VENT1M	VENT1E	VENT2M	VENT2E	VENT3M	VENT3E	VENT4M	VENT5M	VENT5E
VINYL CHLORIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRICHLORO-FLOUROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1 DICHLOROETHENE	ND	26.2	99.4	ND	25.7	ND	ND	ND	ND
METHYLENE CHLORIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRANS 1,2 DICHLOROETHENE	1442.2	1881.4	508.4	4751	997.4	2289	ND	58.6	ND
1,1,1 TRICHLOROETHANE	195.9	202.7	478	2175.9	513.5	1146.7	ND	ND	ND
BENZENE	333.4	164.1	453.25	913.4	447.8	569.3	100.3	112.3	100.6
TRICHLOROETHYLENE	ND	ND	ND	ND	ND	ND	ND	ND	ND
TOLUENE	772	1414	20634	198802.	368	2806	ND	ND	ND
TETRACHLOROETHYLENE	ND	ND	ND	ND	ND	ND	ND	ND	ND
ETHYL BENZENE	1558	135	4440	6605	6929	7943	ND	75.48	
M-XYLENE	2966	5900	7528	6864	6780	6873	ND	70.8	ND
O-XYLENE @									
STYRENE @	113	2379	3034	ND	2725	1434	ND	3505	775
META ETHYLTOLUENE	ND	ND	ND	ND	ND	ND	ND	ND	ND

NOTES:

BLOQ=BELOW LIMIT OF QUANTITATION
ND= NON DETECT
VENT W/M= MORNING
VENT W/E= EVENING
@=COELUTE CAN NOT DESCRIMINATE

TABLE 3: TENAX/CMS CRTRDGS FM SUMMA CNSTRS IN PPB

	VENT1M	VENT1E	VENT2M	VENT2E	VENT3M	VENT3E	VENT4M	VENT5M	VENT5E
VINYL CHLORIDE	477	1180	6920	6240	1460	1360	ND	ND	ND
TRICHLOROFLOUROMETHANE	ND	88.5	474	57.7	156	202	ND	ND	ND
1,1 DICHLOROETHENE	ND	ND	ND	ND	ND	ND	ND	ND	ND
METHYLENE CHLORIDE	ND	110	2350	1770	5170	7000	ND	ND	ND
TRANS 1,2 DICHLOROETHENE	ND	ND	108	118	ND	ND	ND	ND	ND
1,1,1 TRICHLOROETHANE	ND	ND	ND	66.4	ND	ND	ND	ND	ND
BENZENE	263	556	1380	1430	638	796	650	62.9	93
TRICHLOROETHYLENE	63.9	155	1360	1400	83.5	185	ND	ND	ND
TOLUENE	1970	4790	13100	12550	5004	6040	107	49.1	134
TETRACHLOROETHYLENE	73.1	155	2270	2180	96.7	106	ND	ND	ND
ETHYLBENZENE	3360	7220	2290	2230	3170	3620	32	179	807
M-XYLENE	5560	11400	4840	4680	5200	6140	83	474	757
O-XYLENE	1740	3750	1450	1540	1590	1830	25	238	180
STYRENE	ND	ND	245	ND	ND	ND	ND	ND	ND
META ETHYLTOLUENE	621	1260	814	760	776	902	ND	170	ND
LIMIT OF QUANTITATION (PPB)	20	20	15	20	20	15	20	20	20

BLOQ=BELOW LIMIT OF QUANTITATION
ND= NON DETECT
VENT W/M= MORNING
VENT W/E= EVENING

ABSTRACT: DEVELOPMENT OF A HIGHLY RELIABLE FIELD DEPLOYABLE ANALYZER FOR VOC

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Release of toxic volatile organic compounds can cause a particularly hazardous situation because of the compounds mobility and routes of exposure. Effective chemical hazard assessment of a given situation requires a knowledge of the identities and toxicity of airborne contaminants that can be obtained within the time frame before exposures occur. This requirement translates into the need for a highly reliable qualitative identifier with rapid response times and sensitivities well below the IDLH concentrations. We have investigated a microchip gas chromatographic system that can be field deployed and will provide rapid, highly reliable qualitative and quantitative analyses of volatile organic compounds (VOC). The microchip GC has essential components etched into a silicon wafer providing a small, rugged and rapid analyzer for VOC. The unit uses, simultaneously, narrow-bore high resolution gas chromatographic separation on two different liquid phases to achieve highly reliable qualitative and quantitative analyses. Alternatively, we have used the microchip GC as the front end to a small mass spectral detector. Both units have analysis times in the one to two minute range with detection limits around 1 ppm for most VOC analytes. If lower detection limits are needed for ambient air monitoring, a modular concentration device can be used to pretreat air and/or water samples prior to analysis with the microchip GC systems. We have used the devices for a variety of applications including analyses of ambient air, industrial effluents, hazardous waste, and groundwater. Additionally, the data is readily tied into a database, CAMEO, to provide information on the physical, chemical and toxic properties of compounds detected at the scene of an incident.

AN EVALUATION AND COMPARISON OF THE PHOTOVAC TIP II AND HNU PI 101 TOTAL ORGANIC VAPOR ANALYZERS

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ABSTRACT. Since the beginning of EPA's national hazardous waste site investigation program in the late 1970s, one of the objectives of on-site screening for contaminants at hazardous waste sites has been the health and safety monitoring for on-site personnel. While there are several hand-held air monitoring instruments currently available, Ecology and Environment, Inc. (E & E) has primarily used the HNU PI 101 photoionization detector (PID) based instrument for field investigations and site safety determinations. Photovac, Inc. has more recently introduced the TIP II, which operates on the same principles and serves the same purpose as the HNU PI 101. Both instruments can provide nonqualitative, semiquantitative data regarding the presence of ionizable species in ambient air. However, there is little published information which documents the effectiveness of the TIP II in hazardous waste site investigative work. E & E, under its Zone II Field Investigation Team (FIT) contract with the EPA, has completed a comprehensive side-by-side evaluation of the TIP II and PI 101 to determine the utility of the TIP II for the EPA pre-remedial program.

Evaluation of the TIP II and the PI 101 involved collection and interpretation of both objective data and subjective evaluations. The study conducted at E & E included a discussion of instrument theory and applications in order to provide background information. Manufacturer's literature on operating parameters were considered, including instrument descriptions, and design specifications, as well as a comparative evaluation of instrument user manuals. Laboratory test results of instrument operational parameters were evaluated, including battery tests, evaluation of controls, zero stability, flow rates, instrument response time, and response fluctuation. Instrument performance with selected standard gases was compared in a controlled environment. As the instruments are used under a wide variety of ambient conditions, an examination of field instrument performance was necessary to complete the evaluation. Observations of experienced PI 101 users are also presented as they apply specifically to EPA pre-remedial waste site investigations. Test results indicate that there are differences in the performance and operation of the PI 101 and TIP II. These differences should be considered by field personnel when the use of an air monitoring instrument is required for field operations.

DISCLAIMER. This report has been prepared by Ecology and Environment, Inc. under EPA Contract 68-01-7347, and reviewed and approved for public release by the U.S. Environmental Protection Agency (EPA). Mention of commercial products does not constitute endorsement by the U.S. Government. Editing and technical content of this report are the responsibility of Ecology and Environment, Inc., Seattle, Washington, and do not necessarily reflect the views or policies of the EPA.

1.0 INTRODUCTION

Air monitoring survey instruments are routinely used by E&E to assess site conditions relative to health and safety protocols during the performance of hazardous waste investigative work. Under EPA's Remedial Planning/Field Investigation Team (REM/FIT), Field Investigation Team (FIT), and Technical Assistance Team (TAT) programs, the primary air survey instruments used by E&E have been the Foxboro OVA-128, a flame ionization detector- (FID-) based instrument, and the HNU System, Inc.'s PI 101, a photoionization detector- (PID-) based instrument.

Recently, Photovac, Inc. introduced a PID-based air survey instrument, the TIP II. The TIP II is similar in operation to the PI 101, but is contained in a single unit (as opposed to two distinct components for the PI 101). The TIP II also utilizes a liquid crystal display (LCD) readout (versus an analog meter readout for the PI 101). Unlike the PI 101, which has been extensively field-tested and described in several articles, little published information is available to document the effectiveness of the TIP II in hazardous waste site investigative work.

To facilitate an assessment of the TIP II's utility to FIT Preliminary Assessment/Site Inspection (PA/SI) activities, E&E's Seattle-based FIT purchased a TIP II and initiated a comparative evaluation of the TIP II and the PI 101. A single instrument representing each manufacturer's model was employed for all tests. The objectives of the study were to:

- Evaluate and compare the specifications and operating parameters of both instruments in a controlled environment; and
- Evaluate and compare the field performance of each instrument.

2.0 THEORY AND APPLICATIONS

2.1 Photoionization Detector Theory

The PID, which is used in both the Photovac TIP II and the HNU PI 101, is a non-specific organic and inorganic vapor/gas detector. Ambient air is drawn through a probe and into a sensor chamber. Inside the sensor chamber, an ultraviolet lamp emits photons with a prescribed energy. The photons emitted from the lamp pass through an ultraviolet transmitting window and enter the ionization chamber. Molecules with a lower ionization potential (IP) than the energy of the photons will absorb a photon and become ionized as described in the equation:

$$RH + h\nu \rightarrow RH^+ + e^-$$

where RH = molecule
$h\nu$ = photon with energy greater than IP of RH
RH^+ = ionized molecule
e^- = electron

The ionization chamber contains a pair of oppositely charged electrodes. Ionized molecules migrate to the negative electrode, called the collector electrode. The resulting current is proportional to the concentration of ionizable species in the air.

Clean air constituents (e.g., O_2, N_2, CO, CO_2, H_2O) have IPs which are higher than the energy of any ultraviolet lamp source commercially available, and therefore are not detected by the instrument. Although most volatile organic contaminants in air have a sufficiently low IP, certain contaminants with very high IP may not be detected by the PID, even with the highest energy lamp available. For example, CH_4, HCN, and acetonitrile all have IPs greater than 12 eV and are not detected by the PID.

The detector is calibrated by adjusting the span control so that the instrument readout matches the concentration of a calibration gas. Benzene is the usual calibration gas for the PI 101. Isobutylene is used for the TIP II.

The PID does not detect all contaminants with the same sensitivity. The only gas or vapor which will be detected quantitatively is the calibration gas. All other vapors are measured as calibration gas equivalents whose "true" concentrations will depend on individual response factors relative to the calibration gas.

2.2 Applications and Limitations of the TIP II and PI 101

The TIP II and PI 101 are both direct reading instruments designed for real-time monitoring of contaminants in air. Both instruments measure total ionizable gases and vapors present in air samples. Neither is compound-specific within the range of the IP of the instrument lamp. As stated in Section 2.1, all compounds have unique IP values. In addition, not all compounds respond with quantitative equivalency. Response factors for both instruments are compound-specific. For example, equivalent concentrations of toluene and methyl ethyl ketone (MEK) do not yield the same response on the PI 101 after calibration with benzene. The response of a 500 ppm MEK sample is approximately 850 while the response for an equal concentration of toluene is over 1,500.

For a known contaminant, the actual concentration of the vapor or gas can be calculated from the instrument reading based on its response factor relative to the response factor of the calibration gas. However, if the contaminant(s) are unknown, the instrument readout can yield only semi-quantitative estimates of the actual levels detected.

These limitations do not preclude use of these instruments when the objective is to obtain real-time, non-specific "scoping" assessments of environmental conditions of a site. Applications include: general air monitoring, leak detection, spill control, site characterization, environmental surveys, and emergency response.

3.0 LITERATURE COMPARISONS OF OPERATING PARAMETERS

3.1 Instrument Descriptions

3.1.1 Photovac TIP II

The TIP II weighs approximately 3.5 pounds and is contained in a single, hand-held unit.

The instrument readout is a lighted digital LCD with a range of 0 to 1,999 ppm. The display update frequency is greater than one per second. The LCD is visible through a clear curved plastic cover which is flush with the instrument casing.

TIP II standard equipment includes a 10.6 eV lamp with four other interchangeable lamps available: 8.4, 9.5, 10.2, and 11.7 eV. Lamps have a one-year warranty, except for the 11.7 eV lamp, which has a 90-day warranty because of its inherent instability. The standard 10.6 eV lamp was used throughout this study.

The TIP II field kit includes a carrying case, span kit containing standard gases, adjustable headset for audio monitoring, power cord for battery pack, power cord for portable recorder, three-meter probe extension, and a wrist strap. Reported instrument specifications are summarized in Table 1.

3.1.2 HNU PI 101

The PI 101 weighs approximately 9 pounds and is comprised of a readout unit and a probe. The readout unit weighs 7 pounds and is usually carried with a shoulder strap; the probe weighs 1.5 pounds and is hand-held.

The instrument has an unlit analog meter readout with a needle that deflects proportional to the concentration of contaminants. There are three range settings: 0-20 ppm, 0-200 ppm, and 0-2,000 ppm. The scale is divided into one-hundred 0.2 ppm increments (0-20 ppm range). The operator should use the 0-20 ppm range when in the field, unless a higher range is indicated by the meter response.

TABLE 1

REPORTED PHOTOVAC TIP II AND HNU PI 101 INSTRUMENT SPECIFICATIONS

Specifications	TIP II	PI 101
Calibration Gas	Isobutylene	Benzene
Safety Class	Division I	Division II
Detection Limit	0.1 ppm	0.1 ppm
Range	0-1,999 ppm	0.2-2,000 ppm
Linear Range	0-100 ppm, ±10% 100-1,000 ppm, ±15%	0.1-600 ppm
Response Time	3 seconds	Less than 3 seconds
Zero Drift	1% Precision	Less than 1% over 10 hrs
Zero type	Need zero gas	Electronic
Weight	3 lbs	Readout unit: 7 lbs Probe: 1.5 lbs
Dimensions	45 x 6.3 cm diameter	Readout unit: 21 x 13 x 24 cm Probe: 28.5 x 6.3 cm diameter
Number of Controls	3	3
Warm-Up Time	2 minutes	20 seconds
Battery Type	NiCd	Gel Cell
Battery Life	4 hours	10 hours
Charge Time	16 hours	3 hrs, 90%; 14 hrs, 100%
Operation Using A/C	No	Yes
Different Energy Light Source	Change Lamp	Use different probe
Operating Temperature	Not reported	Ambient to 40°C
Operating Humidity	Not reported	0 to 95% R.H.
Sample Injection	Pump	Fan
Service	Charged by the repair, average 8-day turn-around, free loaners available, no extended warranty available	With Super Warranty, 24-hour service, free loaners after 72 hours

The PI 101 comes with one of three probes: 9.5, 10.2, or 11.7 eV. Additional probes may be purchased separately. Different energy lamps are not interchangeable within a single probe. For example, a 10.2 eV probe could not be converted to 11.7 eV by changing the lamp. The 10.2 eV probe is used for most fieldwork, and was used for this study.

No field kit is available for the PI 101. All accessories must be purchased separately. Table 1 lists reported instrument specifications.

3.2 Comparative Evaluation of Instrument User Manuals

Both instruments have extensive user manuals which include sections on unpacking the instrument, operating instructions, PID theory, detailed diagrams of the instrument, maintenance and servicing instructions, troubleshooting guides, lists of accessories, and replacement parts lists. The manuals do differ somewhat in their organization and completeness.

3.2.1 Photovac TIP II Manual

The TIP II manual includes an explicit table of contents and an introductory section with a brief overview of the contents of each following section. Step-by-step operating instructions are detailed, with separate sections for qualitative and quantitative operation. A table of specific span settings for various compounds is presented for quantitative use. The maintenance section includes brief procedures for troubleshooting and servicing the instrument, as well as normal maintenance procedures. Also included in the manual is an appendix which describes how to prepare span gas.

3.2.2 HNU PI 101 Manual

The PI 101 manual contains a more general table of contents than the TIP II manual. A detailed instrument specification table follows the introductory section. Operating and calibrating instructions are in narrative form. The manual contains an extensive table of ionization potentials for different compounds and a reference table of instrument sensitivities for selected compounds. The PI 101 troubleshooting section is more extensive than the TIP II manual. Maintenance and servicing of the PI 101 are not explicitly described. However, complete disassembly instructions and detailed electrical diagrams are included.

4.0 LABORATORY TEST RESULTS FOR OPERATIONAL PARAMETERS

4.1 Batteries

Batteries are an important factor in field instrumentation and must satisfy certain criteria for use in the field. Battery life must meet or exceed the expected period of active use anticipated between time periods allotted for battery recharge. Time required for recharge must be sufficiently brief to avoid delays in fieldwork due to equipment down-time. The battery must be versatile in order to accommodate a variety of field applications, such as intermittent use or prolonged monitoring. Some type of low battery warning system is also desirable. The battery must also be convenient to carry, since weight may become a significant factor.

Each battery was fully charged according to manufacturer's specifications prior to the tests. Battery life was measured by allowing each unit to operate without interruption or intermittently. Each battery was considered expended when the low battery indicator was internally activated.

4.1.1 Photovac TIP II

The TIP II is equipped with a four-hour NiCd battery. An indicator in the upper left-hand corner of the LCD will read "LOBAT" when the battery is low and needs recharging. The instrument should not be used after the "LOBAT" indicator appears. When the NiCd battery was tested, it was found to have a three-hour life. Also, NiCd batteries may develop a "memory." For example, if it is repeatedly used for only one-hour intervals between charges, the battery will eventually have only a one-hour maximum life. Therefore, it is preferable to run the TIP II until the "LOBAT" indicator appears before complete recharging of the battery. Recharge time for the TIP II NiCd battery is mandated by the manufacturer at a minimum of 16 hours to prevent battery damage. Continuous overcharging may also reduce battery life. The test results showed that the NiCd battery life was approximately 3 hours.

The shelf life of the charged battery is less than one month. After approximately 1.5 hours of use, the unit was stored for 34 days. When the instrument was turned on, no LCD reading appeared, indicating that the battery was dead.

For extended use of the TIP II, gel cell batteries are available with 12- or 36-hour operating lives. These batteries are worn over the shoulder and connected by an electrical cord to the hand-held probe. The power cord for the battery fits loosely into the main unit and has a tendency to become disconnected even during limited activity.

4.1.2 HNU PI 101

The PI 101 uses a lead gel cell battery contained in the readout unit. A low battery is indicated by a red LED light. Also, a battery protection circuit in the PI 101 shuts down the instrument when the battery is discharged to below 11 volts. This prevents deep discharging and extends the battery life. The manufacturer's literature states that the life of this battery is greater than 10 hours. Tests showed that the battery life was approximately 16 hours. Partial or incomplete discharge and/or recharge of the gel cell battery will not affect battery life. PI 101 battery recharge follows an exponential curve in which a three-hour recharge will bring the battery to 90% capacity, but 14 hours are required to achieve 100% recharge.

Shelf life tests were not conducted since the PI 101 is continuously charged when not in use. Overcharging and operation of the unit during recharge is not detrimental to the battery.

4.2 Controls

The controls on both instruments were examined in detail to determine ease of use for fieldwork. The power ON/OFF, zero, and span controls are the most frequently used and are critical for proper instrument operation. The zero control is used to set instrument baseline at 0 or no concentration of ionizable species in a sample of clean air. Instrument sensitivity is controlled by the span setting. Increased sensitivity will result in higher concentration readout even if actual sample concentration remains unaltered. Span control is employed to match the instrument's concentration readout to that of a known standard.

4.2.1 Photovac TIP II

The TIP II has an ON/OFF button, and zero and span control knobs with locking rings. Readout is from 0-1,999 ppm. Both control knobs are marked from 0 to 9 in 0.5-unit increments over approximately 300 degrees. Controls are coarse compared to the PI 101. Turning the zero control knob from 2 to 3, a 30° rotation, altered the readout from -11.4 to 3.3 ppm when the unit was calibrated with isobutylene. When sampling 100 ppm isobutylene, the readout changed from 65.8 to 122.5 ppm with a rotation of the span control from a setting of 7 to 8, a 30° turn.

4.2.2 HNU PI 101

The PI 101 controls consist of a function knob, an electronic zeroing knob and a multi-turn rotations venier span control knob (Figure 7). The function knob is used to turn the unit on and off and set the readout range (0-20 ppm, 0-200 ppm, or 0-2,000 ppm). Since the zero control is electronic, no "zero air" is needed to calibrate the instrument before sampling ambient air. The zero control is finer than the control on the TIP II -- one 360° rotation of the zero control knob covered a range of 0.5 to 6.2 ppm on the 0-20 ppm scale. The span control is also finer than the TIP II's; a full 360° rotation, from 7 to 6, altered the readout from 96 to 110 ppm on the 0-200 ppm scale when sampling 100 ppm benzene.

TIP II sensitivity increases as the span is increased from 0 (lowest sensitivity) to 9 (maximum sensitivity). PI 101 sensitivity increases as the span setting is decreased from 10 (lowest sensitivity) to 0 (maximum sensitivity).

4.3 Zero Stability

Because action levels for site safety are often in the 1 to 5 ppm range, it is critical that low end instrument sensitivity be subject to minimal fluctuation; that is, the instrument should exhibit a high degree of precision over time. Drift of the zero setting was measured after each instrument was charged, zeroed, and calibrated according to manufacturer specifications.

4.3.1 Photovac TIP II

Zero was set at 0.0 ppm according to the manufacturer's calibration instructions. The instrument was then used for 0.5 hour. The unit was turned off for approximately 16 hours. Power was then restored to the unit and resampling of "clean" zero air continued for another two hours. The zero calibration held steady at 0.0 during the initial period of operation. Upon restart, the reading was 0.5 ppm. Zero readings ranged from -0.4 to +1.0 ppm during the second operating period. The unit was recharged for 16 hours, after which the zero reading was -0.7 ppm.

4.3.2 HNU PI 101

The PI 101 was used to sample zero air for six hours. The zero readout remained constant at 0.0 during the entire period. The unit was then recharged for approximately 60 hours at which time zero air analyses yielded a reading of +0.4 ppm.

4.4 Flow Rates

The operating flow rate should not affect the quantitative output of these PIDs, if the concentration of available sample does not change. The combination of flow rate and response time (Section 4.5) together dictates the minimum sample volume required for accurate analyses. To compare flow rates of the two instruments, a Buck Calibrator was used to collect readings over 10-minute intervals. Ten tests were run on each instrument, after fully recharging the batteries. Percent relative standard deviation (%RSD) statistics were calculated and are necessary to accurately compare flow rate variability of two such different flows.

4.4.1 Photovac TIP II

The average flow rate of the TIP II was 765 ml/min. Flows ranged from 715 to 822 ml/min. The standard deviation for ten readings was 765 ±28 ml/min, which was used to calculate a %RSD of 3.7%.

4.4.2 HNU PI 101

The average flow rate of the PI 101 was 168 ml/min. Flows ranged from 163 to 173 ml/min. The standard deviation for ten readings was 168 ±3.2 ml/min, which yielded a %RSD of 1.9%. The impact, if any, of these fluctuations on instrument performances is unknown.

4.5 Response Times/Fluctuation

Response time is the time required by an instrument from the onset of sampling until a defined percentage or maximum (100%) response is achieved. The times required to achieve both 90% and 100% response of 100 ppm calibration gases were measured after both the TIP II and PI 101 were prepared for use according to manufacturer specifications. The time required for return to a zero reading from 100 ppm was determined by measuring the time from removal of the 100 ppm standard and immediate onset of zero air sampling until instrument readout returned to zero. Fluctuation of the response at 100 ppm was measured to provide an estimate of instrument precision above the zero or low end range.

4.5.1 Photovac TIP II

The TIP II had a 10-second 100% response time. When analyzing 100 ppm isobutylene, the TIP II display read 98.5 after four seconds. The 90% response time was less than four seconds. The final reading of 100.2 ppm required 10 seconds. The display fluctuated between 99.5 and 100.2 ppm over a two-minute period. It took approximately 20 seconds for the instrument to return to zero after changing the sample source to zero (clean) air.

4.5.2 HNU PI 101

The PI 101 100% response time was 30 seconds. When calibrated with 100 ppm benzene, the 100 ppm isobutylene standard was analyzed. After 10 seconds, the meter read 54 ppm, approximately 87% response. At 30 seconds, the reading was stable at 62 ppm (100% response) and during a three-minute period the level varied between 62 and 62.5 ppm. Fifteen seconds after resumption of clean air sampling, the meter read 3.4 ppm, and after three minutes the level stood at 1.2 ppm. Approximately 15 minutes of zero air sampling were required for the meter to return to zero.

5.0 LABORATORY STANDARD GAS ANALYSIS TEST RESULTS

5.1 Choice of Gas Standards

In order to test the analyzing capabilities of these instruments, it was necessary to choose standards with varying IPs, varying sensitivities, and at least one standard with varying concentrations to verify the linearity of the instruments.

Compounds on the Target Compound List (TCL) and/or those most frequently encountered at National Priority List (NPL) sites were chosen as standards because they would be the most applicable for field use of the instruments. The limiting factor was availability of the preferred gases. Benzene, xylenes, and vinyl chloride are all on the TCL and also are ranked in the top 25 most frequently detected compounds on NPL sites. Isobutylene was chosen because it is the normal calibration gas for the TIP II. It was also used for the linearity test for both instruments since certified benzene gas standards were not available in concentrations greater than 350 ppm. Isobutane was used because its high IP tested the upper energy limits of the lamps. See Table 2 for a complete listing of gas standards used.

TABLE 2

GASES USED TO TEST PHOTOVAC TIP II AND HNU PI 101 RESPONSE

Standard	Concentration*	Ionization Potential (eV)
Isobutylene, in air	5.8 ppm	9.24
	22 ppm	
	100 ppm	
	539 ppm	
Benzene, in air	100 ppm	9.24
p-Xylene, in air	39 ppm	8.44
Vinyl chloride, in air	205 ppm	9.99
Isobutane, in air	512 ppm	10.57

* Gas concentrations were certified to ±2%.

5.2 Method for Standard Analysis

Standards were purchased from Byrne Specialty Gases, Inc. in Maxicyls containing 8 cubic feet of gas at 240 psi. One 0-15 psi regulator was shared for all cylinders. Gases were transferred from the Maxicyls into tedlar bags through inert tubing. Each tedlar bag and connecting tube was filled with only one type of gas to minimize potential cross contamination.

Tedlar bags were rinsed before use by partially filling them with standard gas and then emptying. The bags were then filled with standard gas just prior to analysis. For analysis, the full bag was connected to the instrument probe with inert tubing. After a stable reading was achieved, the bag was emptied until immediately before the next analysis.

5.3 Standard Gas Analyses/Response Factors

The instruments were calibrated and standards were analyzed with both instruments in three separate tests. The PI 101 uses benzene as a calibration gas while the TIP II uses isobutylene. The PID is more sensitive to benzene than isobutylene. An instrument calibrated to a 100 ppm benzene standard reading would display only 70 ppm for a 100 ppm isobutylene standard. In order to directly compare the actual readouts of the two instruments, standards were analyzed on the PI 101 twice: first with the instrument calibrated to benzene, the usual calibration gas, and second with the instrument calibrated to isobutylene. Only the TIP II isobutylene calibration and PI 101 isobutylene calibration data are directly comparable. The PI 101 benzene calibration data must be adjusted for varying response factors before they may be compared to either of the other data sets.

For isobutylene, the TIP II had a greater response to the high (539 ppm) level standard, while the PI 101 had a greater response to the low (5.8 ppm) level standard. The PI 101 had a greater response to vinyl chloride at 205 ppm. The TIP II had a greater response to isobutane at 512 ppm. The results for the p-xylene analyses may not be reliable because it gave unstable readouts on both instruments, with the observed concentration constantly rising.

Standard gas analysis results indicate that, in general, the instruments perform comparably when sampling air. The TIP II, however, yields a slightly larger and more linear response than the PI 101. Both instruments show some variance in results between calibrations.

As previously stated, the PID does not detect all contaminants with the same sensitivity. Table 3 presents the calculated response factors (normalized to a benzene value of 10.0) for the data.

Isobutylene response factors were more consistent on the TIP II than on the PI 101. Vinyl chloride response factors were approximately half the expected value on either instrument. As noted earlier, the p-xylene data were suspect. The measured response factor was one quarter the expected value on both instruments. No data were available for an expected isobutane response factor.

Despite the difference in reported lamp energies (TIP II - 10.6 eV, PI 101 - 10.2 eV), no significant difference in instrument sensitivity was noted during the analysis of isobutane (IP = 10.57 eV).

5.4 Calibration Hold and Response vs. Battery Life (Charge Level)

In this test, both instruments were calibrated according to the manufacturers' recommended protocols immediately after charging the batteries to maximum capacity. Samples were analyzed at regular intervals over the life of the batteries to determine the effect of charge level on instrument response. Following the manufacturers' recommendations, the TIP II was calibrated with isobutylene while the PI 101 was calibrated using benzene.

The PI 101 appears to maintain calibration, that is, respond more consistently than the TIP II throughout the life (charge level) of the battery. Both instruments' responses varied from reading to reading, but the TIP II appeared to indicate a more definite downward trend with time.

TABLE 3

PHOTOVAC TIP II AND HNU PI 101
MEASURED STANDARD RESPONSE FACTORS
(Based on Benzene Response Factor of 10.0)

			Average Response Factors		
Compound	Certified Conc. (ppm)	Reported Response Factors	TIP II Isobutylene Calibration	PI 101 Benzene Calibration	PI 101 Isobutylene Calibration
Isobutylene	5.8	7.0	6.6	7.2	7.7
Isobutylene	22	7.0	6.1	6.1	6.1
Isobutylene	100	7.0	6.3	5.5	6.0
Isobutylene	539	7.0	5.9	3.9	4.8
Benzene	100	10.0	10.0	10.0	10.0
p-Xylene	39	11.4	3.4	2.9	2.7
Vinyl Chloride	205	5.0	2.4	2.8	3.0
Isobutane	512	*	5.2	4.1	4.9

* None found.

6.0 FIELD MEASUREMENTS

All preceding tests were performed in a controlled environment (the E&E Region X Mobile Support Base). Since the TIP II and PI 101 are used under a wide variety of ambient conditions, a field comparison of instrument performance was necessary to complete the study.

Before the field comparisons were made, both instruments were fully charged, zeroed, calibrated, and checked for operational readiness. For field testing, air from various outdoor sources was monitored with the two instrument probes held side-by-side (approximately six inches between sampling probe inlets). Simultaneous readouts for both units were recorded. Field comparisons were conducted on two separate days. Meteorological conditions were similar during both field tests: temperature, approximately 60°F; winds, light; relative humidity, low with bright sun.

An overview of the field test results reveals differences in instrument performance in an uncontrolled environment. In general, the PI 101 meter response was lower than the TIP II meter response. Since the PI 101 was calibrated to benzene and the TIP II was calibrated to isobutylene, this difference in response was expected. The TIP II has a significantly wider range in responses than the PI 101, especially when sampling highly contaminated air. After the first field test was completed, the ionization chambers were rechecked, and the PI 101 chamber appeared to be contaminated. Dust from the drums is the suspected cause of this contamination. After the second round of field sample analyses was completed, both instruments were again checked and no problems were noted.

7.0 OTHER CONSIDERATIONS

7.1 Maintenance

Both the TIP II and PI 101 require routine maintenance to insure optimum instrument performance. The TIP II ultraviolet lamp window requires regular cleaning. The dust filter, which protects the ionization chamber from contamination, must be changed when it becomes clogged, or a drop in instrument sensitivity will result.

The PI 101 also requires periodic cleaning of the ultraviolet light source window. In addition, the ionization chamber must be checked regularly for contamination.

Instructions for maintenance are provided in both instruments' operating manuals. HNU and Photovac will provide on-site training for normal field maintenance. HNU also offers an in-depth repair course.

Routine maintenance on the PI 101 was completed without incident. A problem was encountered during routine maintenance of the TIP II. During removal of the lamp, the lamp holder was allowed to rotate slightly, which caused an electrical connection between the bulkhead and the PC board to disconnect. Repairs could not be accomplished in the field and the unit was returned to the manufacturer for service.

7.2 Manufacturer Service

Photovac does not offer field service for the TIP II. However, their representatives will talk users through troubleshooting and repairs over the phone whenever possible. If the unit must be returned to the manufacturer for repairs, a loaner unit is provided free of charge. Manufacturer repair costs are based on the type of repair needed. Average turn-around for repair is eight days. No extended warranty is available beyond the initial one-year warranty.

HNU offers a "super warranty" which includes a toll-free 24-hour phone line for technical assistance, priority turn-around (usually 72 hours) for repair with a free loaner if repairs take longer than 72 hours, and all parts and labor except lamp and battery. Annual inspection and calibration for the instrument are also included. HNU offers maintenance and support training for the PI 101 at negotiated rates. Additionally, certification training is available for servicing units.

7.3 Photovac TIP II Upgrade Notice

Photovac has introduced an upgrade program for the TIP II Analyzer. Changes include: adding a coarse zero control which allows for 10 times finer adjustment, changing the span control to a logarithmic scale which would give three times finer adjustment in the most used range, and reducing the display update frequency to one second.

8.0 SUMMARY

Like the HNU PI 101, the Photovac TIP II can provide non-qualitative, semi-quantitative data regarding the presence of ionizable species in ambient air. Results for both instruments are dependent upon several factors, including lamp energy and age, sample flow rate, battery charge level, specific compound(s) detected, calibration gas used, instrumentation operating procedures, and ionization chamber cleanliness. Test results for this study indicate that there are certain differences in the performance of these two instruments (Table 4). The PI 101 has some drawbacks when compared to the TIP II, such as an unlit meter readout, greater size, greater weight, and longer purge time between samples. However, the HNU PI 101 tends to be more suited to the overall needs of E&E FIT for PA/SI work. Battery life, battery type, ease of control knob manipulation, readout stability, and greater low range sensitivity are the major advantages the PI 101 offers over the TIP II.

TABLE 4

SUMMARY OF SELECTED PHOTOVAC TIP II AND HNU PI 101
COMPARISON TEST RESULTS

Feature Tested	TIP II	PI 101
Response Time, 90%	4 sec.	10 sec.
Response Time, 100%	10 sec.	30 sec.
Sample Flushing Time	20 sec.	15 min.
Fluctuation (60 sec.)	<1%	<1%
Zero Drift (1 day)	+ or - 1 ppm	+ or - 0.4 ppm
Warm-Up Time	10 min.	5 min.

(cont.)

Feature Tested	TIP II	PI 101
Battery Life	3 hrs., may develop memory	16 hrs.
Charge Time	16 hrs., 100%	3 hrs., 90% 14 hrs., 100%
Mean Flow Rate	765 ml/min.	168 ml/min.
Flow Rate Range	715-822 ml/min.	163-173 ml/min.
Average % Response after prolonged use (near end of battery life), compared with original response	82%	102%
Response Drift %$\overline{\text{RSD}}$ for all compounds tested	12.1%	5.6%
Readout	Digital	Analog
Readout Design	Difficult to read without sample probe extension or in bright light	Acceptable
Controls	Difficult to adjust, unprotected against accidental changes	Acceptable
Total Weight	3 lbs.	8.5 lbs.

GENERAL REFERENCES

1. Photovac Inc., TIP II User's Manual, Version 2.1, October 1986.
2. HNU Systems Inc., Instruction Manual for Model PI 101 Photoionization Analyzer, 1975.
3. Ecology and Environment, Inc., FIT Operation and Field Manual, March 1982.
4. Driscoll, J.N. and M. Duffy, Photoionization Detector: A Versatile Tool for Environmental Analysis, Chromatography, pp. 21-27, May 1987.

THE AUTOMATED DETERMINATION OF VOLATILE ORGANIC CONTAMINANTS IN AMBIENT AIR AND/OR SOIL GAS BY GAS CHROMATOGRAPHY WITH SELECTIVE DETECTORS

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INTRODUCTION

VOCs and light gases are major air pollutants in our environment. They enter the ambient air from industries such as refineries, dry cleaners, power plants and even bakeries. But the major source of ambient air pollution is from mobile sources, i.e., automobiles and trucks. Some of these pollutants can contribute to the ozone formation by acting as precursors. The indoor air we breathe at home may be polluted with VOCs originating from disinfected water, cigarettes or from household products such as air fresheners, deodorants and moth balls. The use of industrial solvents or paints and finishing products in the workplace is another source of exposure to VOCs.

The discovery of toxic air contaminants in homes adjacent to hazardous landfill sites and in parks or other facilities which are built on former landfills (active and inactive) has led to recently enacted legislation in California, AB3525 and AB3374, authored by Charles M. Calderon. This legislation requires testing at all landfills to determine the chemical composition of air contaminants above, within, and adjacent to the site to determine the possibility of contaminant migration beyond the solid waste disposal site's perimeter.

The contaminants that must be screened are shown below:

VOCs

Vinyl Chloride
Benzene
1,2-Dibromoethane
1,2-Dichloroethane
Dichloromethane
Tetrachloroethene
Carbon Tetrachloride
1,1,1-Trichloroethane
Trichloroethene
Chloroform

Light Gases

Total Hydrocarbons

Methane
Oxygen
Nitrogen
Carbon Dioxide

Several analytical methodologies exist for the analysis of VOCs in ambient air and soil gas. Solid phase adsorption followed by either solvent or thermal desorption has been used for many years in industrial hygiene applications and in stack gas monitoring. This technique suffers from problems such as adsorbent contamination, imprecision, and low recoveries for low boiling VOCs.

Whole air sampling has become the primary method for sampling air with the introduction of EPA method TO-14. With this technique a whole air sample is drawn through a cryogenically cooled trap to freeze out and concentrate VOC contaminants. The trap is then quickly heated and the VOCs are transferred to a cryogenically cooled capillary column. The column is temperature programmed and the VOCs chromatographed to either multiple selective GC detectors or to a mass spectrometer. While this technique provides sub part per billion detection limits, several improvements are possible: (1) automation for multiple samples, (2) use of a variable temperature adsorption trap to eliminate the necessity for water removal and (3) elimination of the requirement for a cryogenically cooled oven.

Two automated analytical systems have been developed to analyze sub part per billion levels of VOCs: one a fixed volume system and the other a variable volume system. Both systems use a variable temperature adsorption trap (VTAT), a 0.53 mm capillary column (DB-624) and the photoionization (PID) and Electrolytic Conductivity Detectors (ELCD) or Electron Capture Detector (ECD) in series.

Herein is provided a description of these two systems, their operation, and the general analytical procedures followed. In addition, the results of the following studies are reported: 1) chromatographic retention time and peak area precision, (2) method detection limits, (3) system linearity, and (4) run-to-run carryover. Finally, ambient, dry-cleaner, and indoor air samples are analyzed using the techniques described.

EXPERIMENTAL

Two types of gas chromatographic systems have been developed for the determination of volatile organic chemicals in soil gas and ambient air, one a fixed volume and the other a variable volume system. A description of these two systems follows.

Fixed Volume Mode

The fixed volume system shown in Figure 1 includes the following: (1) a two loop gas sample valve (2-ml and 100-ml), to handle high and low concentration samples, respectively, (2) a surrogate standard valve for introduction of a surrogate sample with each run, (3) a variable temperature adsorption trap (VTAT) packed with Tenax/activated charcoal and suitable for trapping all VOCs studied, (4) a packed or 0.53 mm column for compound resolution, (5) a Photoionization and either an Electrolytic Conductivity Detector or Electron Capture Detector plumbed in series and an optional (6) 16-port stream selector valve (SSV) for automatic selection of up to 16 samples, calibration mixtures, or blanks.

The two-loop gas sample valve (GSV) provides the option of introducing a small (2-ml) or large (100-ml) volume air sample, standard or blank into the system. Therefore, soil gas samples which might have high VOC concentrations or ambient air samples which usually have low concentrations may be analyzed over a wide concentration range. Samples are drawn into the loop with a slight vacuum provided by a small diaphragm pump or are allowed to purge the loop from a pressurized canister.

A surrogate standard GSV with a loop <1 ml is filled from a pressurized tank of a known concentration of a surrogate standard. An 8 PPM concentration of 1,3-bromochloropropane was used in this work.

The VTAT (Figure 2) is coiled about a 1 inch grooved aluminum mandrel which contains a heating cartridge and temperature probe. This is housed in a small insulated chamber into which cryogenic fluid is delivered. The trap may be cooled to -190^{O}C and temperature programmed at rates up to 180^{O}/min to a maximum temperature of 400^{O} with all temperature parameters selectable from the GC keyboard. A 1/8" o.d. stainless steel trap containing 14 cm of Tenax TA and 8 cm of activated charcoal was used in this system. Glass beads may also be used requiring cryogenic (-180^{O}C) temperatures for trapping VOCs.

While a 1% SP-1000 on Carbopack B (60/80) packed column was used in earlier work, a 30M X 0.53 mm DB-624 column provides improved chromatography.

Fixed Volume Procedure

Samples of ambient air, soil gas, calibration mixtures or blanks are collected in either Tedlar^{TM} bags or canisters and connected to the SSV. If automation is operative, the appropriate GC method is automatically activated and the sample is drawn into or allowed to purge the 2- or 100-ml loop depending upon sample concentration. The sample loop is then flushed for 5 minutes (see Table 1) to the adsorbent trap (20^{O}C) where VOCs are trapped, the air and moisture being vented. Simultaneously the surrogate sample is flushed into the trap. When trapping is completed the trap is isolated, preheated to 250°C, and the VOCs are backflushed to the analytical column for separation. Subsequently the trap is baked out for seven minutes and then cooled to 20°C with LN_2 or LCO_2 in preparation for the next analysis.

Variable Volume Mode

The variable volume system shown in Figure 3 consists of the following: (1) a multi-port valve for switching sample to VTAT, introducing surrogate sample, and allowing direct injection to column, (2) the VTAT with trap isolation valve, (3) mass flow controllers, (4) an optional SSV and (5) column and multi-detectors as described above.

Unlike the fixed volume system, the variable volume system allows volumes from 50 ml to 800 ml or greater to be sampled, depending upon the mass flow controller setting, trapping time, and trap temperature. The air or soil gas sample is first drawn through the multiport valve from a Tedlar™ bag or canister while the surrogate loop is flushed. Then a fixed volume of surrogate standard along with the sample flow is diverted to the trap for a set time and mass flow rate. When the trapping is complete, the trap is isolated and preheated to 250° and then backflushed to the column for chromatography and detection. Subsequently trap baking and cooling occurs prior to the next run.

RESULTS AND DISCUSSION

Two gas standards (Table 2) were purchased for use in the evaluation and development of the fixed and variable volume systems. These high and low concentration standards possess concentration levels possible in soil gases and ambient air, respectively. The low concentration standard was used for approximately one year only because of degradation.

Ten VOCs plus a surrogate standard, 1,3-bromochloropropane, are shown well resolved in Figures 4 and 5 on packed and capillary columns.

The analyses times for these two columns are very similar. But the capillary column provides several advantages: (1) a more efficient column for resolving many additional VOCs of interest, (2) narrower peak shapes to improve sensitivity, and (3) lower bleed allowing for the screening for higher molecular weight VOCs.

To evaluate the VOC systems the following studies have been performed:

1) Retention time and peak area precision
2) Run-to-run carryover
3) System linearity
4) Method detection limits
5) Variable volume sampling

All parameters were evaluated on the fixed volume system while Nos. 1, 4 and 5 were evaluated on the variable volume system.

A series of ten low-concentration and high-concentration standard runs were made on the system. Relative standard deviation (RSD) of retention times and responses were determined. Results are shown in Table 3. With the exception of vinyl chloride, the RSDs of the retention times are generally less than 0.03%. The response RSDs are less than 5% for low- and less than 2% for high-concentration VOC gas standards. Surrogate standard response RSD is 1.5%. Retention time and response RSDs were similar with the variable volume system.

When analyzing standards, blanks and samples of varying concentrations, it is necessary to be aware of run-to-run carryover. This has been investigated in the fixed volume system by running the high-concentration standard in the 100-ml loop followed by a blank. Results are shown in Figures 6. Only EDB is seen as a carryover peak and this is due only to its high sensitivity on the ECD. Its estimated carryover is <0.1%.

The linearity of response of the system to varying concentrations of VOCs is not necessarily determined by detector linearity. Bag permeation, if using Tedlar™ bags, adsorption, and decomposition are mechanisms that may be operative and difficult to gauge in a complex gas analysis system. Nevertheless, the linearity of several VOCs has been studied over a wide range of concentrations using the PID, ECD and ELCD detectors. Results are shown in Figures 7 and 8. The data shown in Figure 7 was generated using a 100 ml sample for the most dilute standards and 2 ml for the most concentrated standards. Only 100 ml standards were used to obtain data shown in Figure 8. The system linearity is demonstrated by the constancy of the calibration factors over a wide concentration range.

The flexibility of choosing either the 2- and 100-ml loop in the case of the fixed volume system or the virtually unlimited choice of sample volume in the variable volume system allows one to choose the sample volume that will cover the concentration range of interest.

Method detection limits (MDL) were determined using 100 ml of gas mixtures prepared from primary standards. VOC concentrations of approximately five to ten times estimated detection limits were prepared and analyzed at least seven times after which standard deviations of the results were determined. Standard deviations were multiplied by a T factor 3.14 (99% confidence level) giving the MDLs shown in Table 4. Limits obtained using the PID, ECD and ELCD are shown compared with those required under the California Calderon Bill.

The experimental MDLs meet these requirements, the ECD providing its greatest sensitivity for those VOCs having the highest electronegativity and the ELCD in the halogen mode providing relatively uniform response for all the listed VOCs with better response for the mono- and dichloronated solutes. Therefore, the requirements of a particular application would dictate the selection of either the ECD or ELCD for the halogenated components: (1) sensitivity, (2) selectivity, and (3) response uniformity.

APPLICATIONS

Several grab samples of air were collected in evacuated canisters after which the canisters were pressured to 20 psi. These canisters were then attached to the stream selector valve on the fixed volume system and 100-ml aliquots flushed through the trap and the trap subsequently desorbed to the 0.53 mm DB-624 column. The ambient air sample (Figure 9) exhibited only a trace of tetrachloroethene on the ELCD and a unidentified trace VOC on the PID. On the other hand the grab sample of air taken from the dry cleaner establishment (Figure 10) showed significant levels of tetrachloroethene, ethylbenzene, and toluene and traces of methylene chloride, carbon tetrachloride and trichloroethene. Figure 11 shows an air sample taken from the moist room air following a shower. As expected from chlorinated water, traces of trihalomethanes, methylene chloride, and tetrachloroethene are found. Finally, a trace level standard was collected in a canister and sample volumes of 100 and 300 ml were drawn through the trap of the variable volume system. As expected the 300 ml sample provides three times the VOC response of the 100 ml sample (See Figure 12). This system is capable of extremely high sensitivity limited only by the breakthrough volume of the trap which is approximately 700 - 800 ml at $20^{o}C$.

CONCLUSIONS

Two gas chromatographic techniques are applicable to the multilevel determination of VOCs in soil gas and ambient air. One is a fixed volume and the other a variable volume technique. The fixed volume system allows either two milliliter or one hundred milliliter samples while the variable volume system allows sample volumes of from fifty to about eight hundred milliliters. Central to these systems is a variable temperature adsorption trap. This trap adsorbs and concentrates the VOCs from the sample while allowing moisture to pass through thereby eliminating the need for a dryer. Excellent precision is obtained both for retention times and peak areas. And carryover from highly concentrated samples is minimized. The method detection limits possible are in most cases under 0.5 ppb and depend upon the detector and the sample size chosen. Selectivity, sensitivity, and response uniformity must be considered in detector choice. Finally, the flexibility of these systems is paramount with applications ranging from soil gases in hazardous waste sites to indoor atmospheres to ambient air and source emissions.

Table 1
Timing of the Air Analysis

Time		0.01	5.0	7.0	10.0	17.0 25.0
Analysis Sequence	**SAMPLING**	**CONCENTRATION**		**SEPARATION ON ANALYTICAL COLUMN**		
	GC/DS to Ready	VOC Trapping	Trap Isolation Preheat	Trap Desorbtion to Column	Trap Bake	
Trap Temperature	Cooling to 20°	20°	180°/min	250°	250°	Cooling to 20°
Column Temperature	Cooling to 35°	35°	35°	35°	35°	10°/min 135°
VOC's					CH_2= CHCl; CH_2 Cl_2	$CHCl_3$; 1,2 DCE; CCl_4; 1,1,1 TCE ..

Table 2

Air/Soil Gas Analysis

Standard VOC Mixtures

Compounds	**Concentrations (PPB)**	
	High	Low
Dichloromethane	4000	5.0
Chloroform	500	0.2
1,2-Dichloroethane	*	2.0
1,1,1-Trichloroethane	400	0.4
Carbon Tetrachloride	50	0.5
Trichloroethene	300	0.5
1,2-Dibromoethane	5	0.2
Tetrachloroethene	50	0.5
Vinyl Chloride	5000	6
Benzene	2000	5

* Not included in this mixture

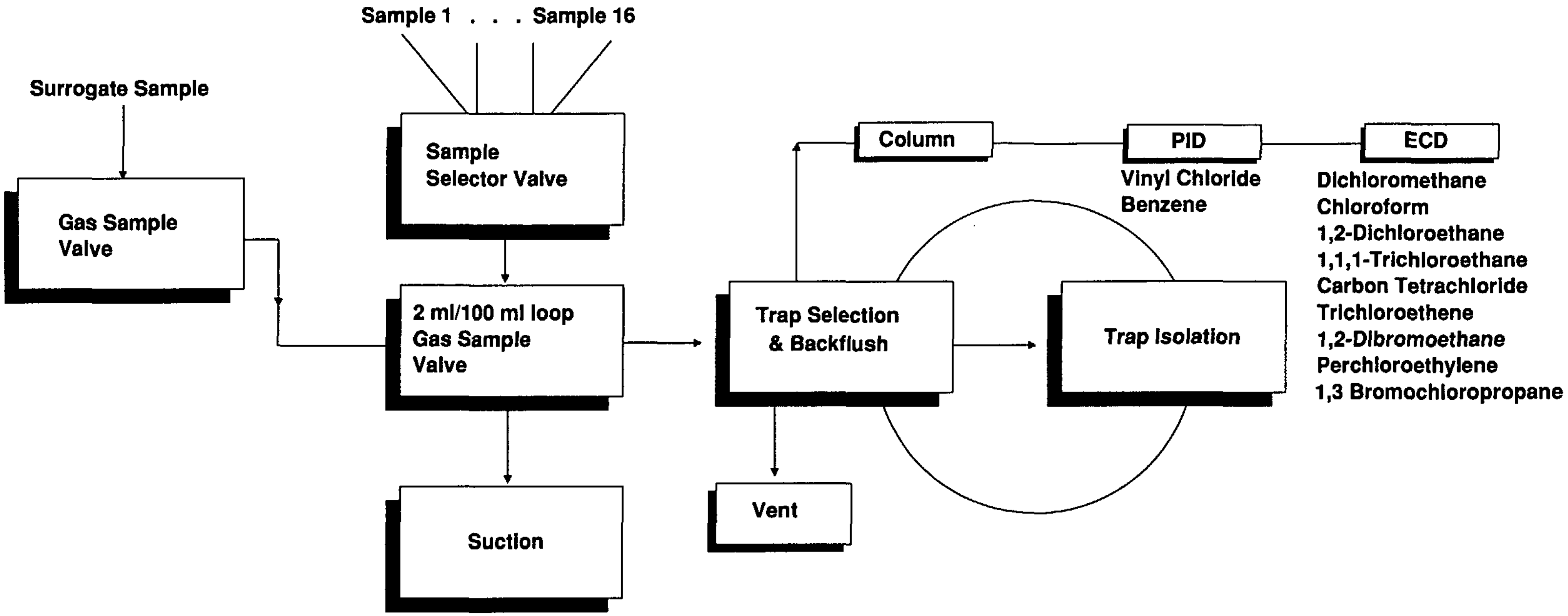
Table 3
Retention Time and Response Reproducibility % Standard Deviations

		Response	
Components	Retention Times	Low Concentrations	High Concentrations
Vinyl Chloride	0.50	2.2	0.38
Dichloromethane	.035	3.8	0.21
Chloroform	.017	3.1	0.55
1,2-Dichloroethane	.025	3.4	—
1,1,1-Trichloroethane	.020	0.61	0.82
Carbon Tetrachloride	.018	2.41	4.0
Trichloroethylene	.014	0.77	0.90
Benzene	.022	3.90	0.35
1,2-Dibromethane	.017	5.80	0.48
Perchloroethylene	.013	3.80	1.14

Table 4
Air/Soil Gas Analysis
Method Detection Limits in PPB (V/V)

Compound	**ARB Guideline**	**ELCD/0.53 Cap Column**	**ECD/Packed Column**
Vinyl Chloride	2.0	.20	.80
Benzene	2.0	.20	.25
1,2-Dibromoethane	0.5	.10	<.01
1,2-Dichloroethane	0.2	.05	.19
Dichloromethane	1.0	.05	.60
Tetrachloroethane	0.2	.05	<.01
Carbon Tetrachloride	.02	.04	<.01
1,1,1-Trichloroethane	0.5	.03	<.01
Trichloroethane	0.6	.02	.01
Chloroform	0.8	.03	<.01

Figure 1
Air/Soil Gas Analyzer
VOCs



System Operation

Function	*Duration (min)*	*Trap Temperature*
Sampling	7	30°
Trapping	5	30°
Trap Preheat	2	30° to 250°
Desorption	3	250°
Trap Bake	7	250°
Trap Cooldown	10	250° to 30°

Figure 2
VTAT

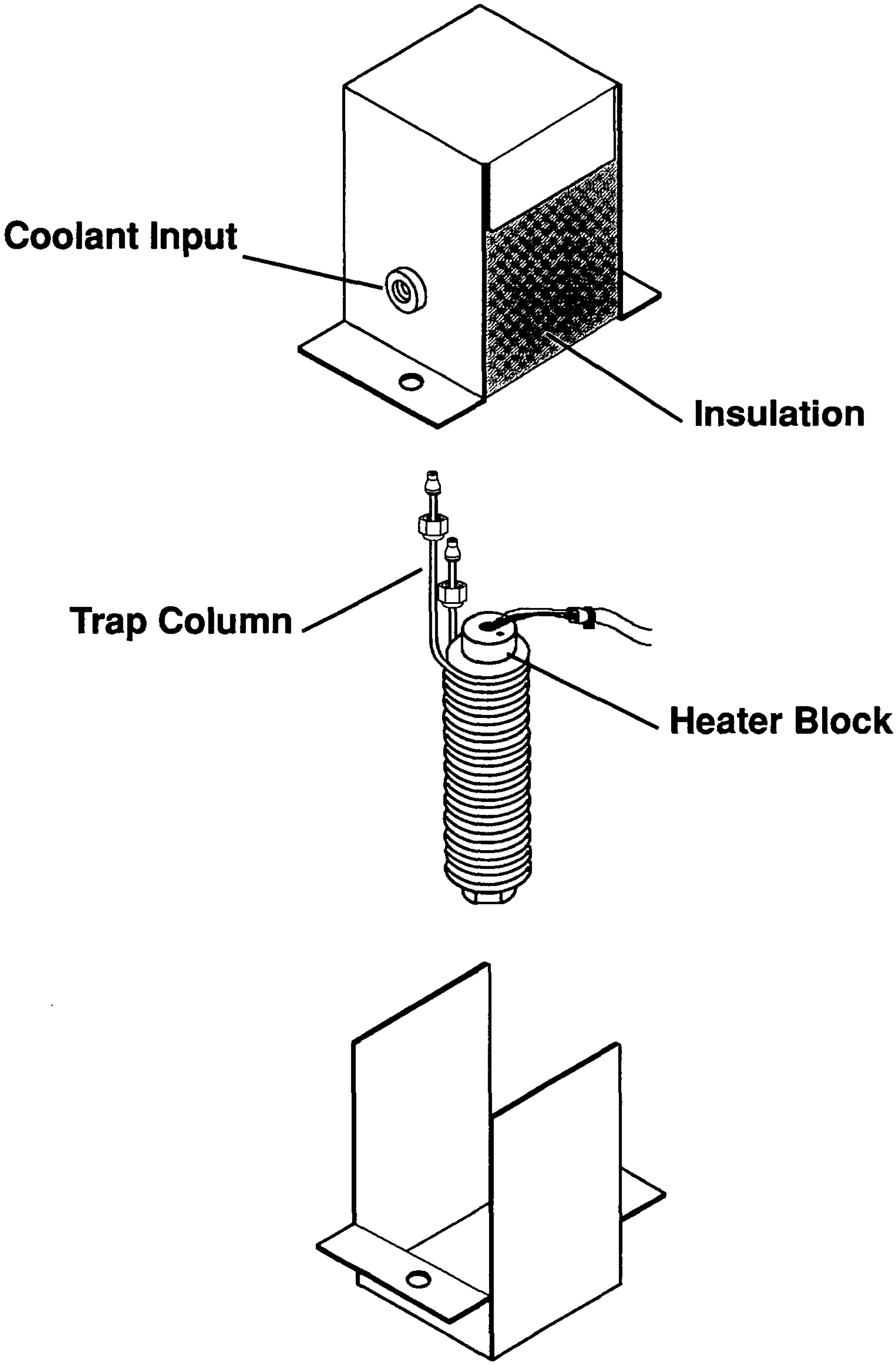


Figure 3
Air/Soil Gas Analysis - VOCs
Variable Volume Mode

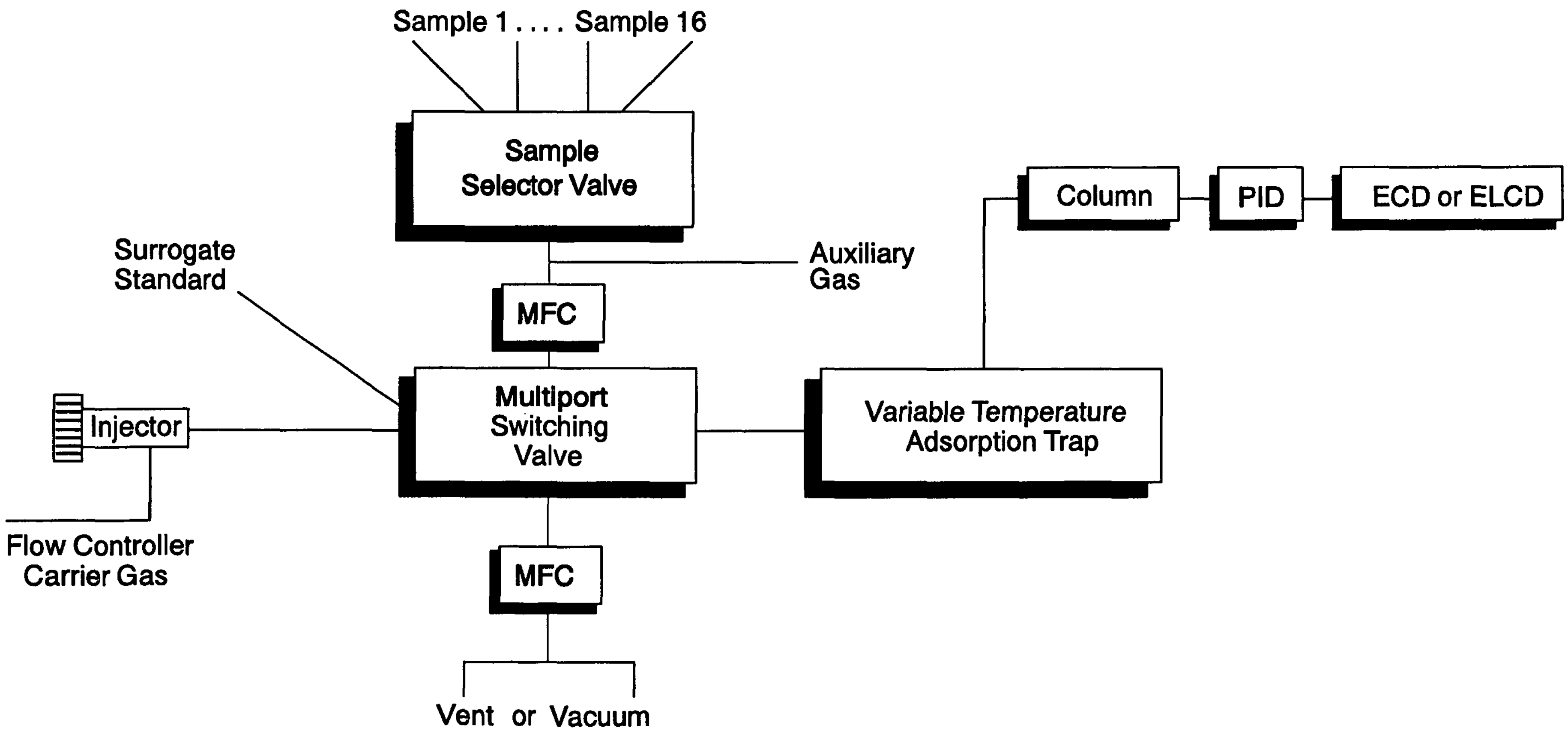
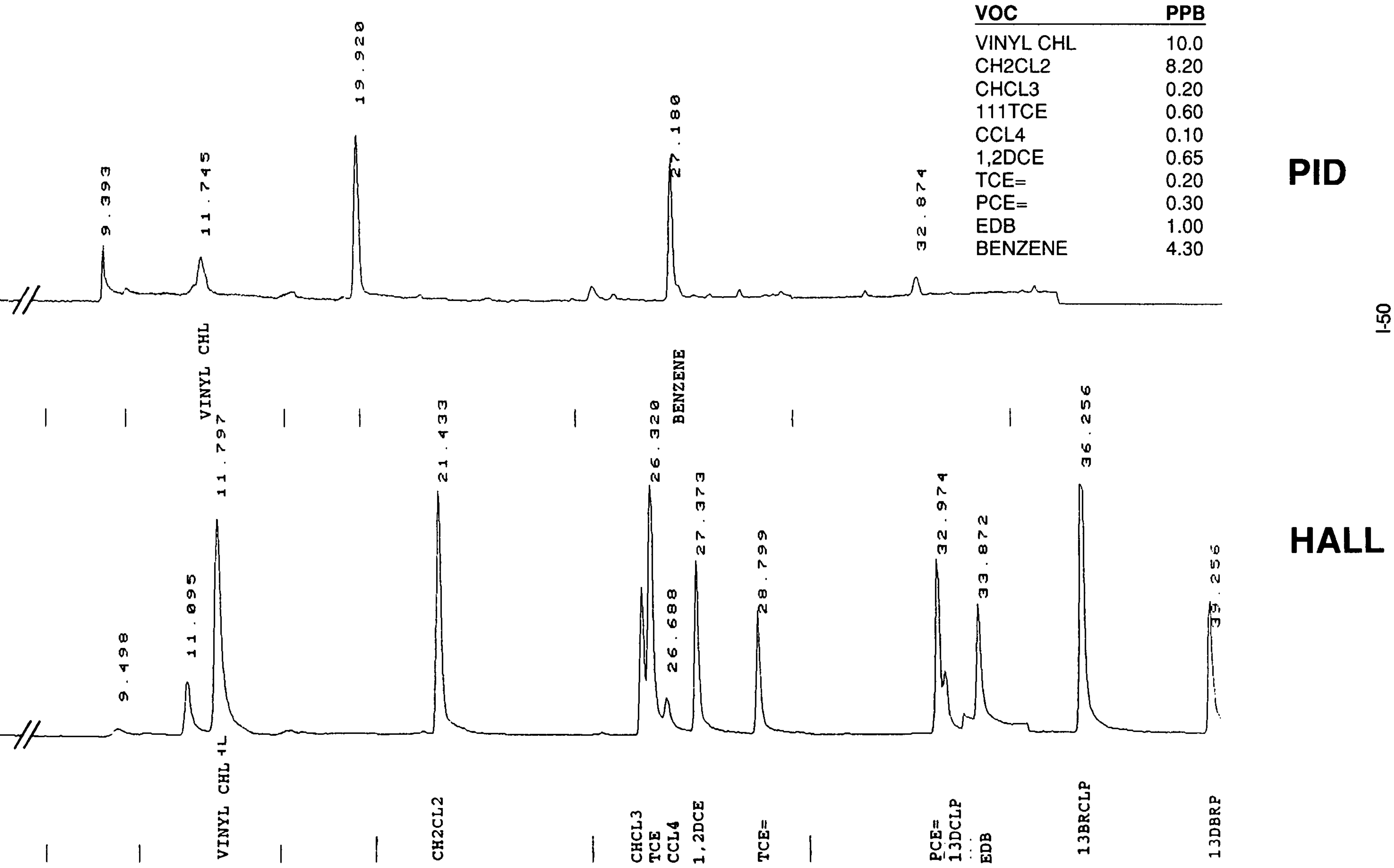


Figure 5
Landfill Gas/Air Analysis
Low Levels of VOC's on DB-624 Column



VOC	PPB
VINYL CHL	10.0
CH2CL2	8.20
CHCL3	0.20
111TCE	0.60
CCL4	0.10
1,2DCE	0.65
TCE=	0.20
PCE=	0.30
EDB	1.00
BENZENE	4.30

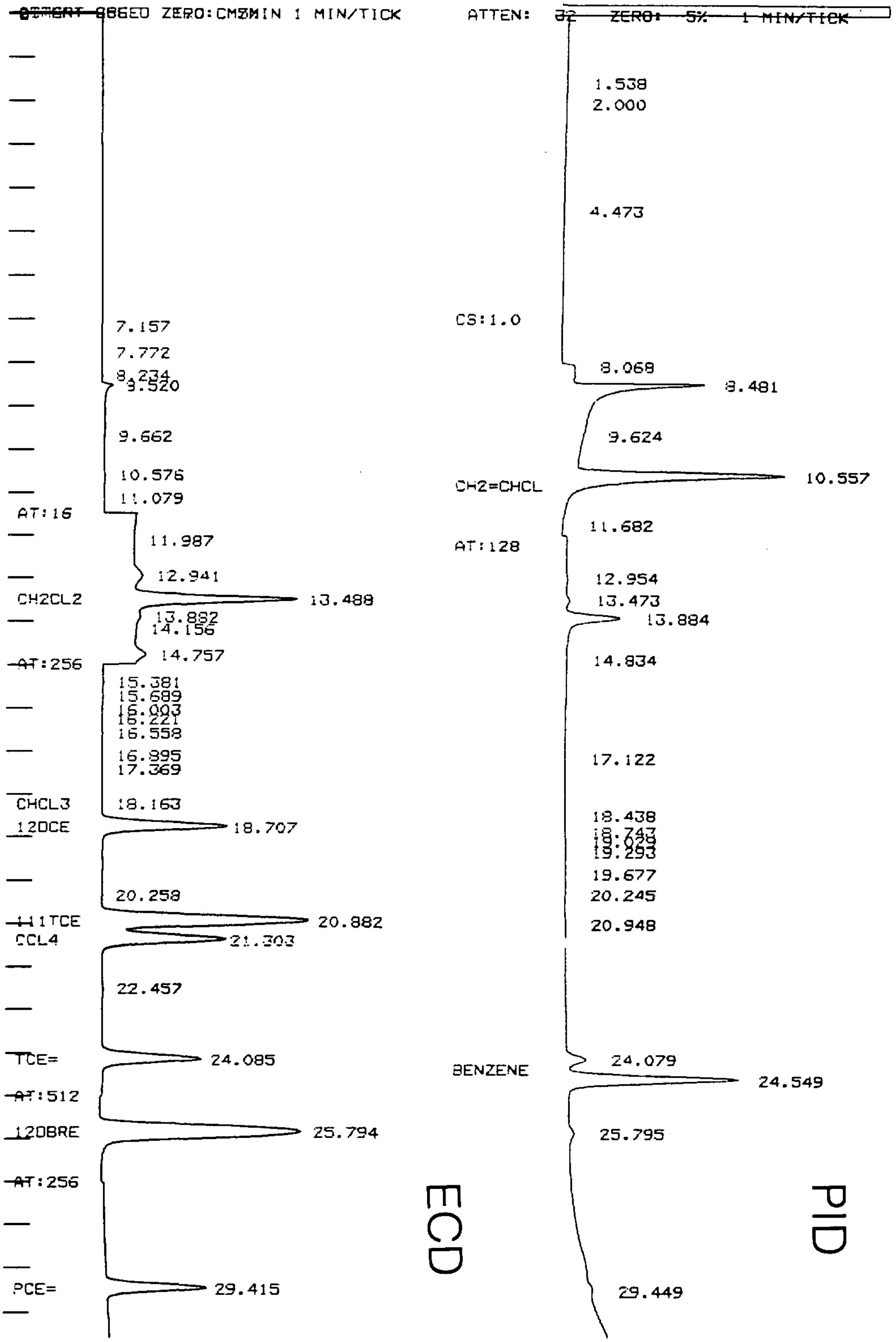
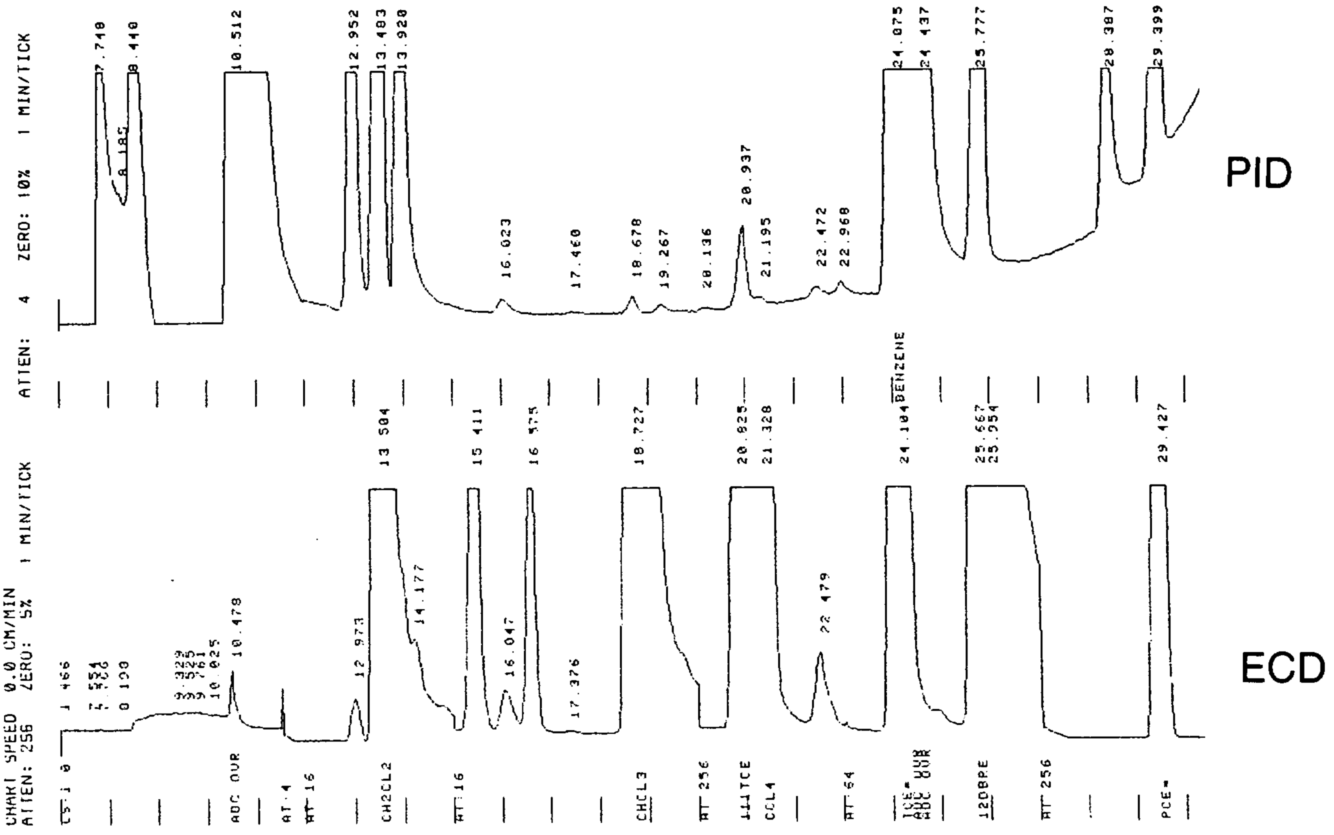


Figure 4
Air/Soil Gas Analysis
Column: 1% SP-1000/Carbopack B (60/80)

Figure 6

Carryover, VOC's
100-ml Loop

High Concentration Standard



Blank

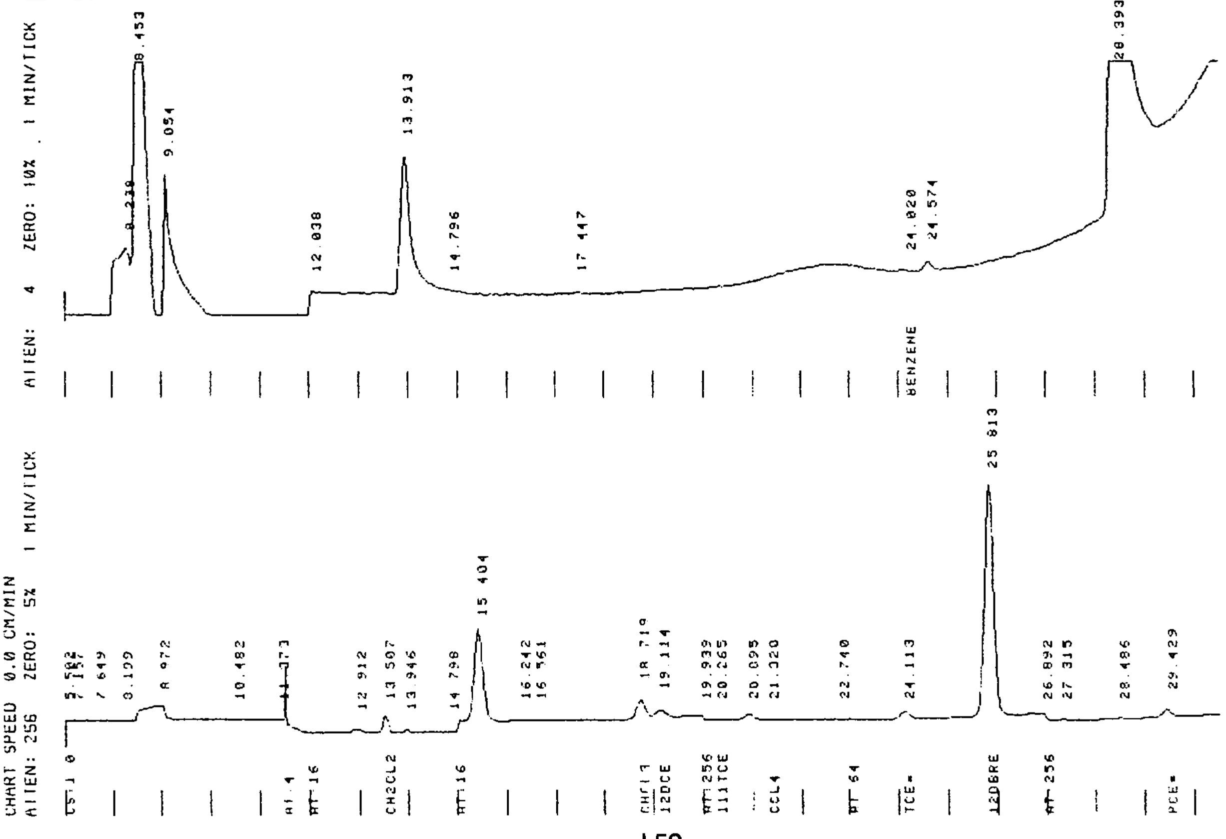


Figure 7
Air/Soil Gas Analysis
System Linearity

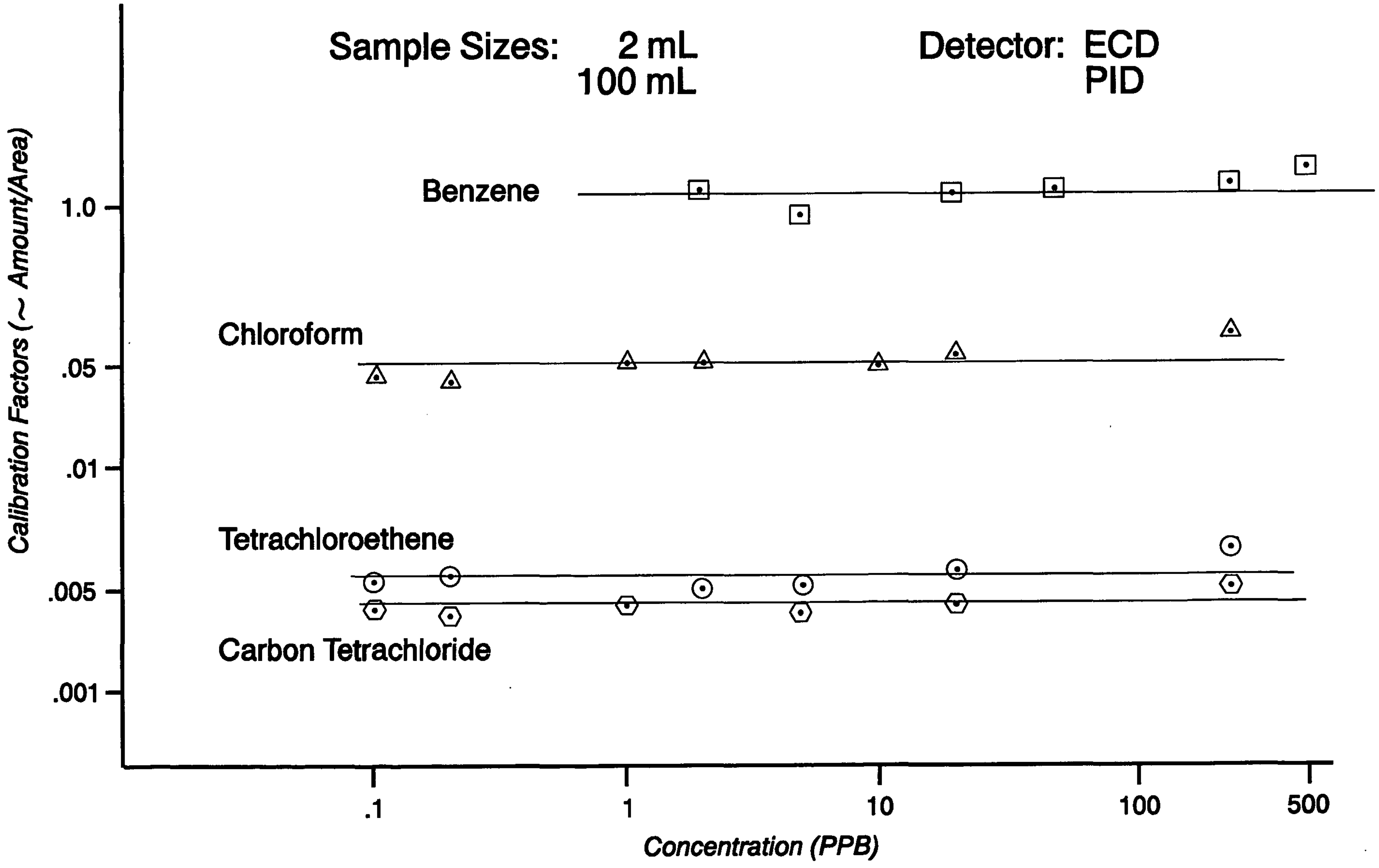


Figure 8
Air/Soil Gas Analysis
System Linearity

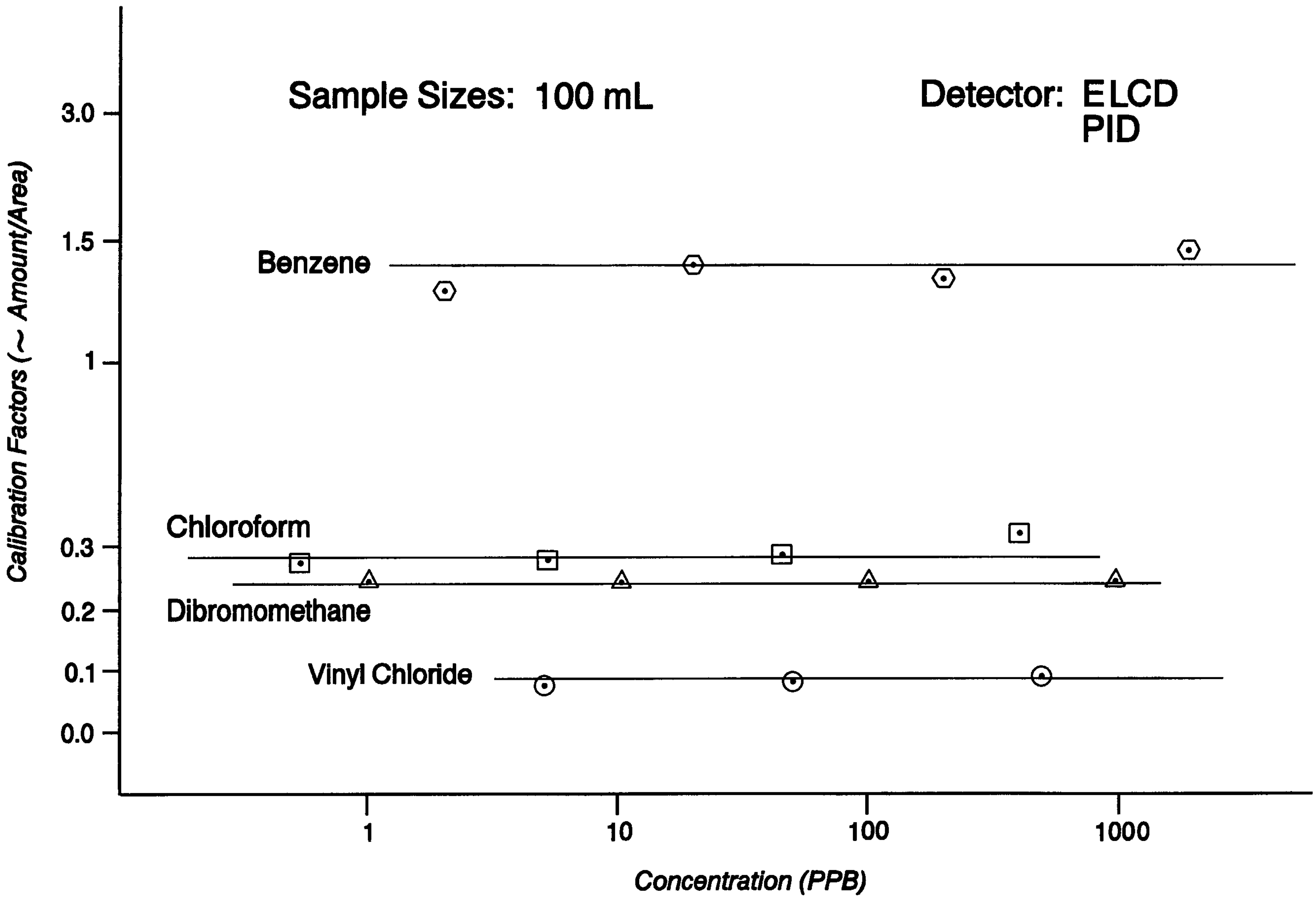


Figure 9
Ambient Air Sample
100 ml

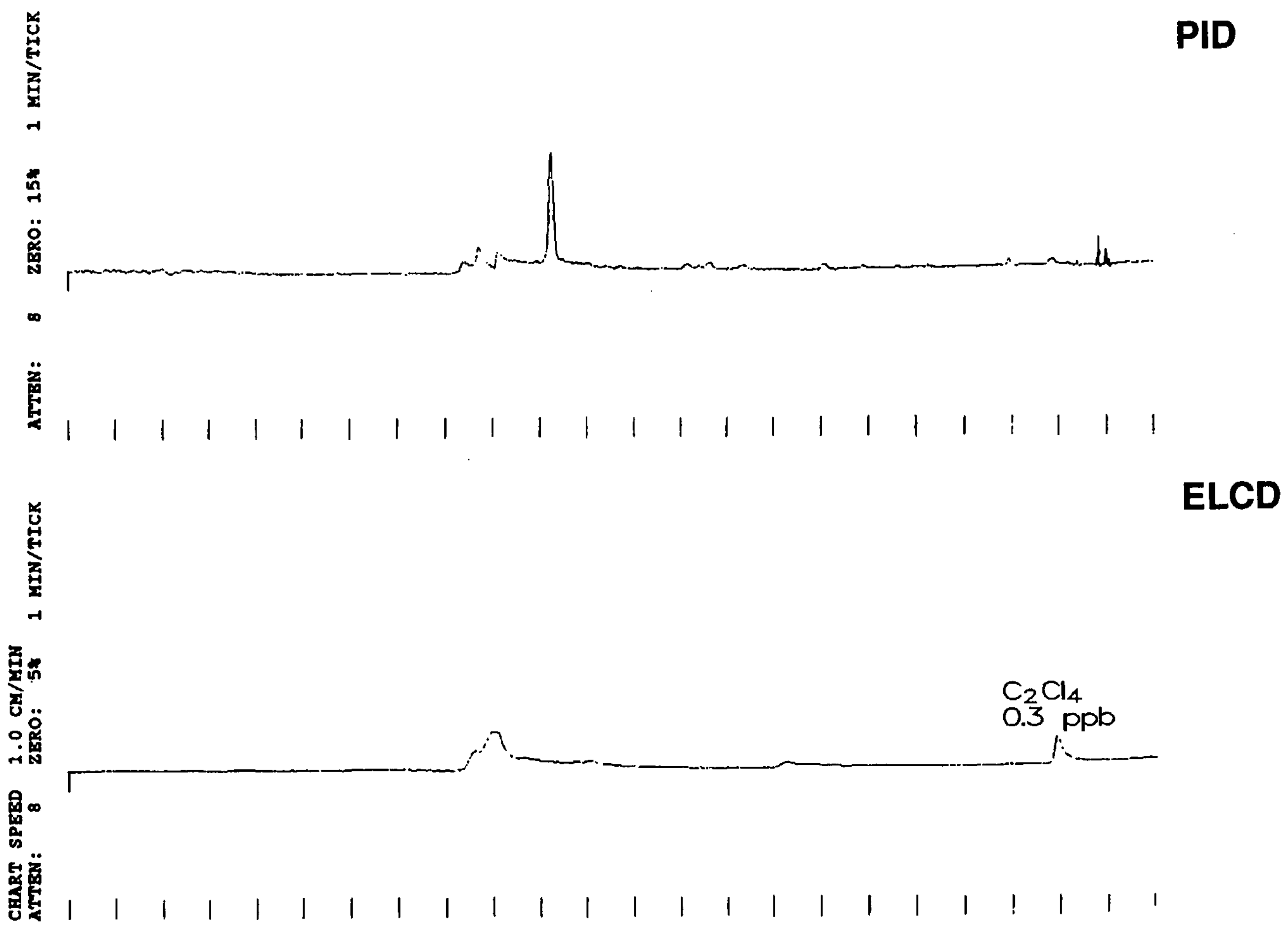


Figure 10
Dry Cleaner Air Sample
100 ml

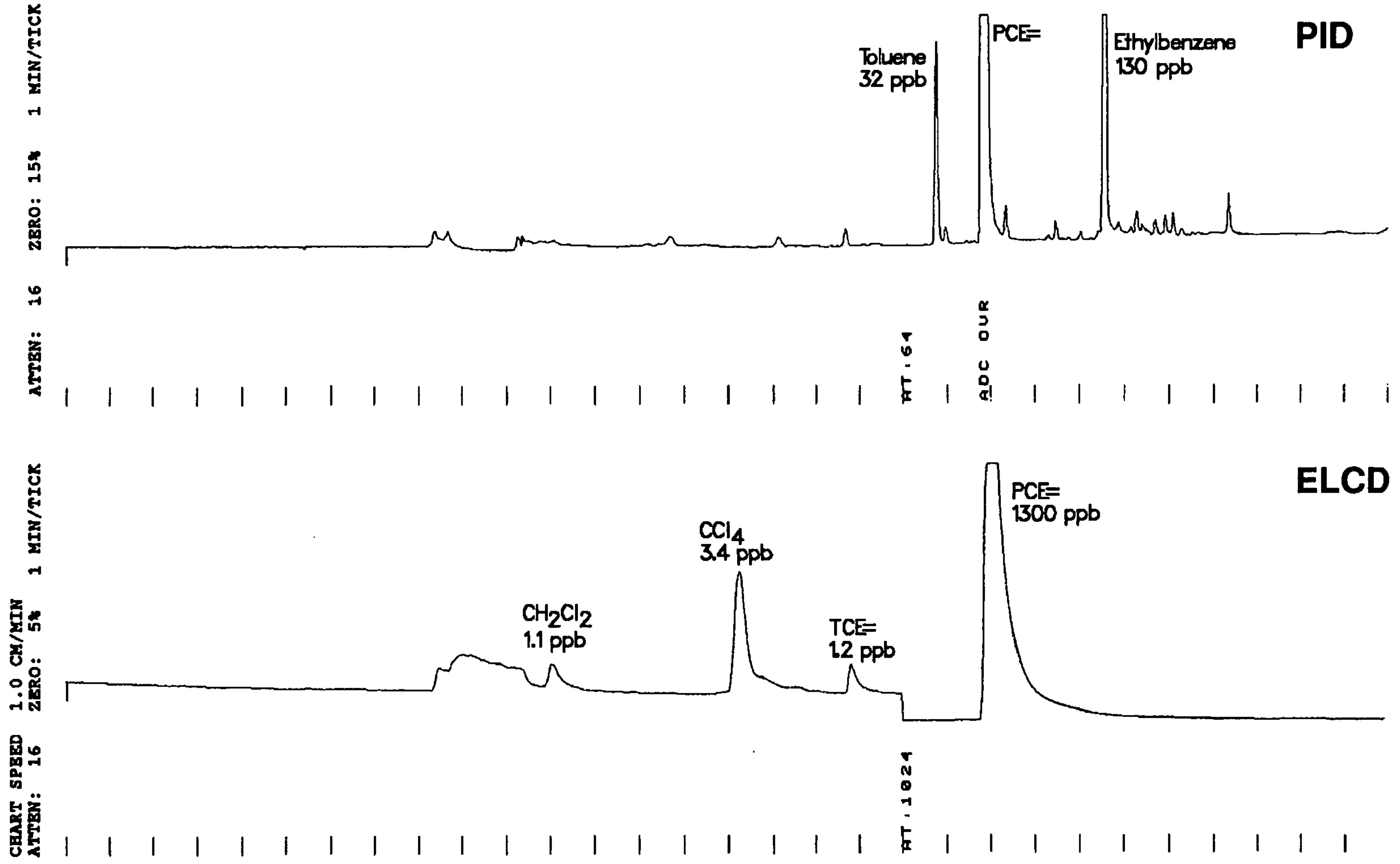


Figure 11
Shower Room Sample
100 ml

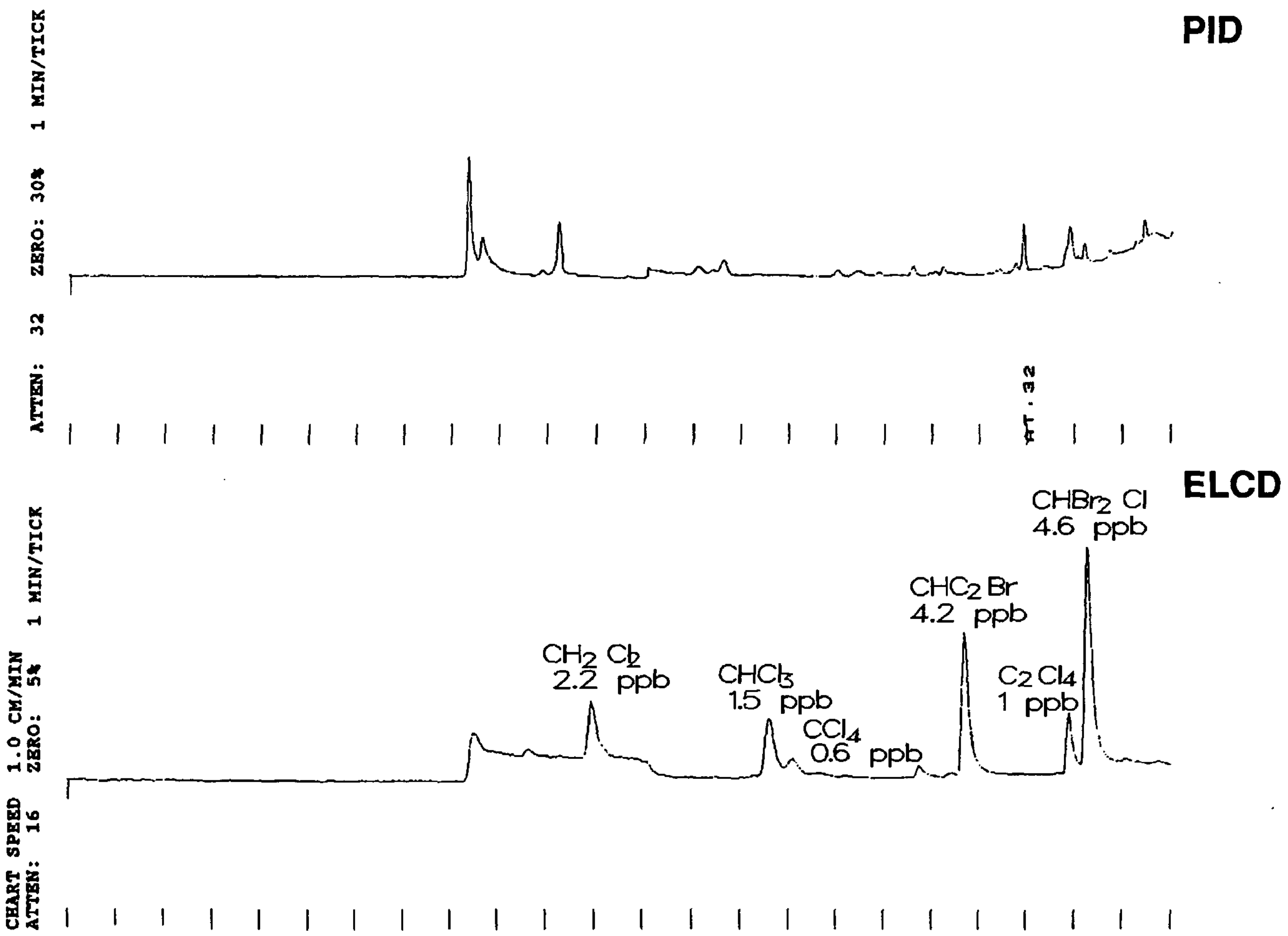
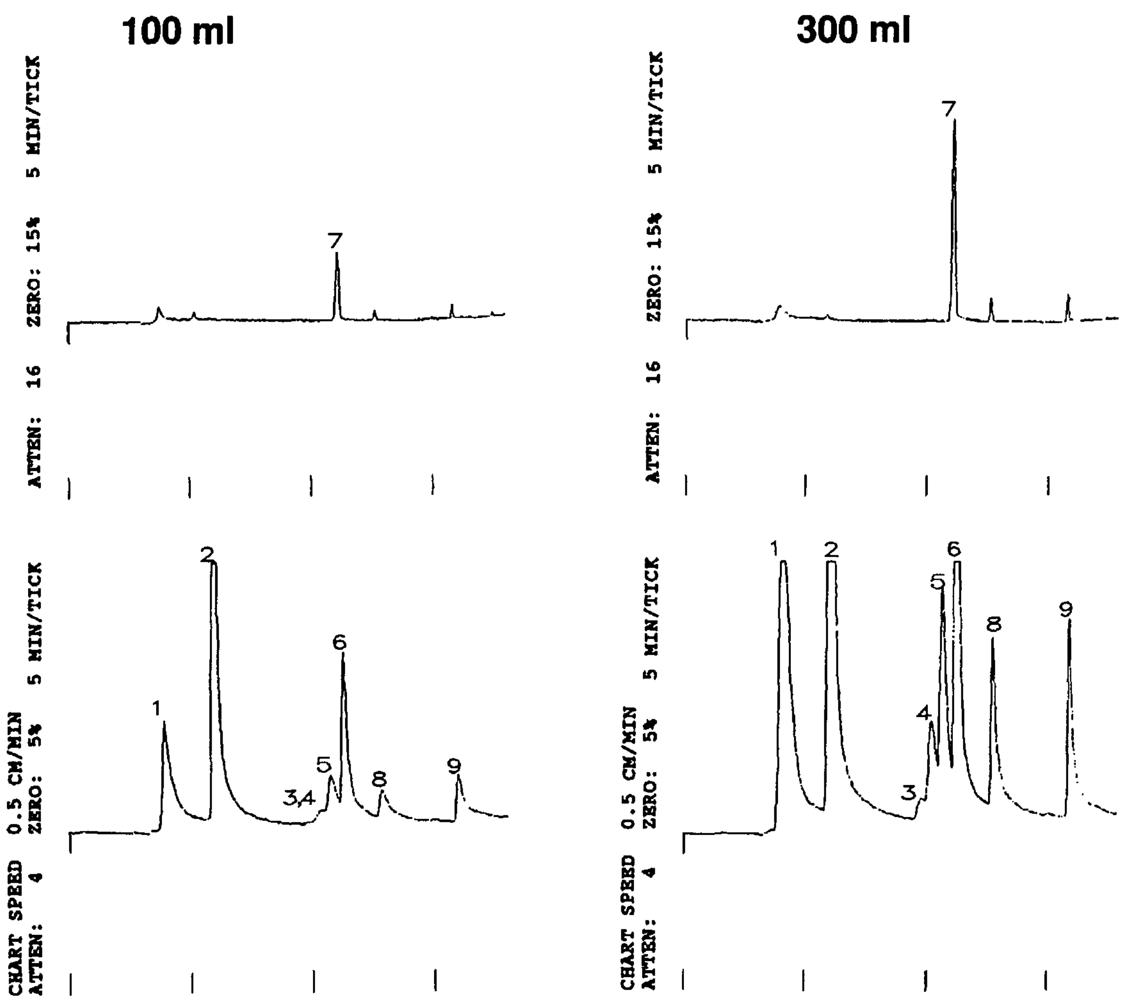


Figure 12
Variable Volume Sampling



		ppb
1.	Vinyl Chloride	5
2.	Methylene Chloride	6
3.	Chloroform	.2
4.	1,1,1-Trichloroethane	.4
5.	Carbon tetrachloride	.5
6.	1,2-Dichloroethane	2
7.	Benzene	5
8.	Trichloroethene	.5
9.	Tetrachloroethene	.5

THE DETERMINATION OF FIXED GASES AND NON-METHANE ORGANIC COMPOUNDS IN SOIL GAS AND AIR

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The growing number of emission sources in the industrial, municipal, and transportation areas makes source gas and ambient air monitoring necessary. The safety of existing landfill sites also requires the monitoring of soil gas and/or ambient air both inside and outside the perimeter of the disposal area. The presence and amounts of CO and CO_2 can provide important information about aerobic and anaerobic reactions inside the landfill. The monitoring of methane to follow its migration can eliminate explosion hazards by preventing its collection in airpockets in residences or in other populated areas.

To attain the requirements of the Clean Air Act, total hydrocarbon monitoring is necessary since many organics behave as precursors in ozone formation. It is also necessary to measure CO levels since they reflect the general ambient air quality.

The system described here measures CO, CO_2, CH_4, and non-methane organic compounds (NMOCs) in aerial matrices. The light gases CO and CO_2 are converted to CH_4 enhancing their detectability (<1ppm) on the flame ionization detector (FID). The catalytic oxidation of NMOCs with Hopcalite catalyst to CO_2 and the subsequent reduction to CH_4 eliminates the varying responses of NMOCs to the FID depending upon their degree of substitution. For example, propane carbon has a relative response of 1 on the FID while carbon tetrachloride carbon provides a relative response of only 0.5 resulting in a biased low response for the latter. In the present system calibration is simple since only one compound, propane, is required to determine the carbon response for all organics.

The system can be used in a manual or automated mode. With a Stream Selector Valve, 16 samples, blanks or calibration mixtures may be analyzed unattended. The automation can be GC based or directed by the Varian DS-650 data system.

Figure 2 shows the chromatogram of the standard gases at 50 ppm and Figure 3 shows the chromatogram of a typical soil gas. The CH_4, CO and CO_2 are individually quantitated where the NMOC's are grouped. The linearity of response is exhibited in Figure 4. A wider linear range can be achieved when a Thermal Conductivity Detector (TCD) is added to the system and connected in series with the FID.

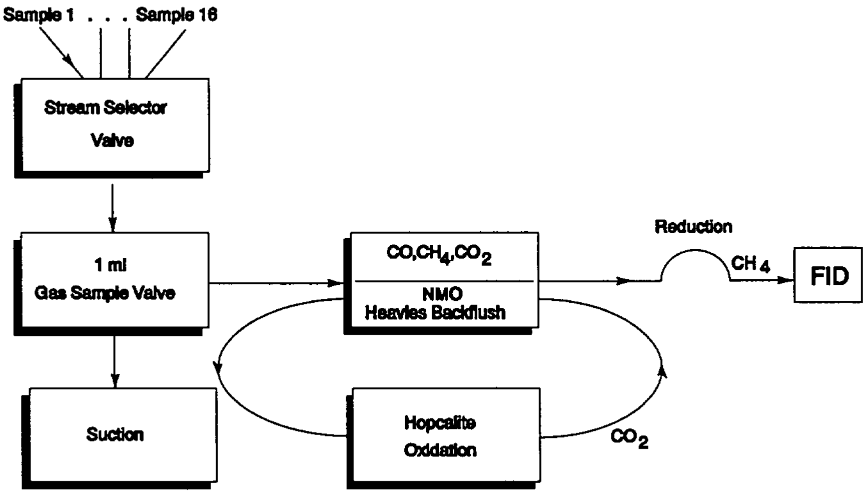


Figure 1
NMOC Analyzer

Column: Dedicated column set, 80° isothermal
Flow: 30 ml/min N_2
FID: Range 12
Concentration: 50 ppm each

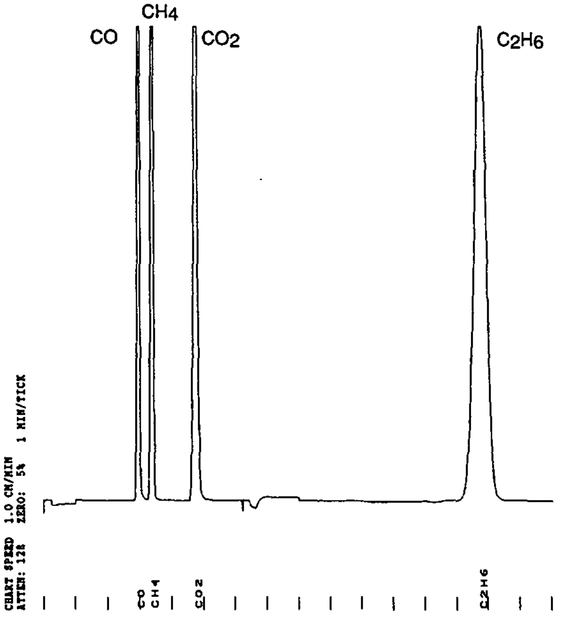


Figure 2
Chromatogram of Standards

Column: Dedicated column set, 80° isothermal
Flow: 30 ml/min N_2
FID: Range 10

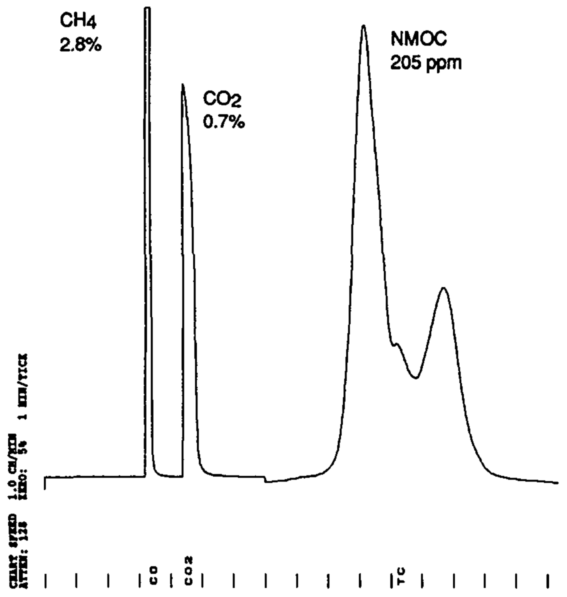
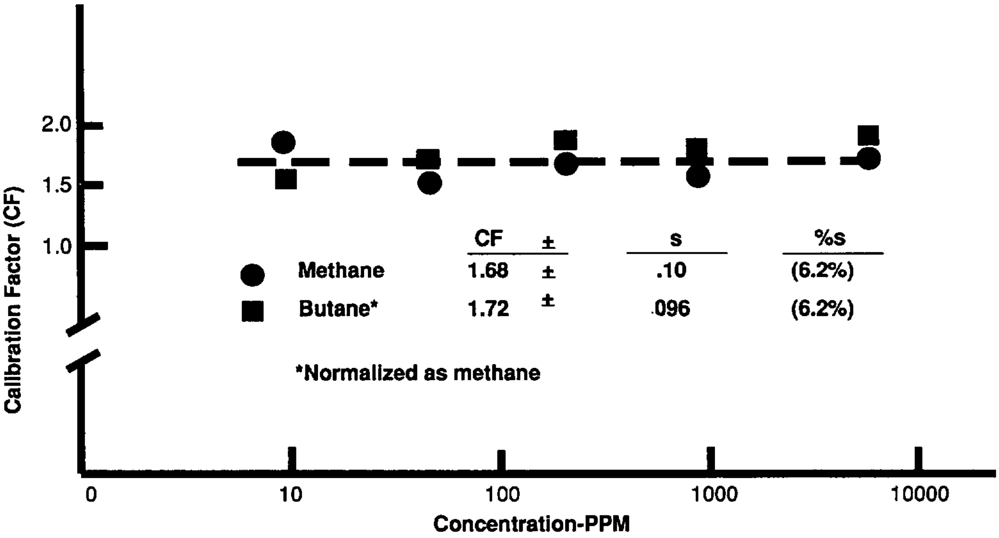


Figure 3
Chromatogram of a Typical Sample



	CF	±	s	%s
● Methane	1.68	±	.10	(6.2%)
■ Butane*	1.72	±	.096	(6.2%)

*Normalized as methane

Figure 4
Linearity of Response

BIOLOGICAL TEST METHODS

EFFECT OF CHEMICALS ON SOIL NITRIFYING POPULATIONS USING A CONTINUOUS-FLOW CULTURE TECHNIQUE

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ABSTRACT

This study examines the effects of Roundup [N-(phosphonomethyl)glycine] and N-Serve [2-chloro-6-(trichloromethyl)pyridine] on nitrifying organisms in static batch, perfusion soil columns, and a new continuous-flow soil column system. The continuous-flow method is new to nitrification studies and was shown to produce greater nitrifier activity than either static batch or perfusion techniques. Both N-Serve and Roundup were shown to significantly inhibit nitrification in treated soils over untreated controls. N-Serve completely inhibited nitrification at concentrations greater than 42 ug nitrapyrin g^{-1} dry soil, and Roundup significantly reduced nitrification at 6.8 and 68 mg glyphosate g^{-1} dry soil. Heterotrophic bacterial populations increased significantly in continuous-flow columns treated with 42 mg nitrapyrin and 68 mg glyphosate g^{-1} dry soil. Numbers of heterotrophs were not significantly different from controls in soils at lower concentrations. Numbers of nitrifying bacteria did not appear to change following treatment, although nitrification was inhibited. Fluorescent antibody analysis of nitifiers revealed that Nitrosolobus was more numerous than Nitrosospira and Nitrosomonas. Nitrosolobus increased in number, whereas the other two genera remained unchanged.

In this study, the continuous-flow system proved to be both reliable and useful in the culture of nitrifying bacteria. This method is an alternative to traditional static and perfusion culture techniques for evaluation of the effects of chemicals on microbial biogeochemical cycles, and can benefit soil toxicity assessment at hazardous waste sites.

INTRODUCTION

Traditional laboratory culturing of nitrifiers involves the use of static soil cultures or perfusion columns (Lees and Quastel, 1946). Although useful, both techniques suffer from continual changes in substrate concentration and soil chemistry. A continuous-flow method has recently been developed for the culture of heterotrophic soil microorganisms (Hendricks *et al.*, 1987). This technique provides a fixed concentration of nutrients continuously to a soil column and alleviates the limitations mentioned above. Recently, Rhodes and Hendricks (1989) have modified the technique and have shown that the continuous culture of nitrifying bacteria in soil has promise as an alternative to traditional methods.

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This study was designed to evaluate the new continuous-flow method by comparing it with the static and perfusion techniques for culturing nitrifying bacteria in soil, and to determine the response of nitrifying and heterotrophic bacteria to treatments of N-Serve and Roundup. N-Serve is a commercial nitrification inhibitor and Roundup is one of the commonly used herbicides in agriculture today. Preliminary experiments conducted as part of this study determined that, of the three cultural methods, the continuous-flow method supported high nitrifier activity and was the most sensitive in measuring nitrification. For this reason, the continuous-flow method was used to examine the effects of treatment on specific genera of ammonium oxidizing bacteria, denitrifying microorganisms, and heterotrophic microbial populations within the soil columns.

MATERIALS AND METHODS

Soil

The soil selected for this study was obtained from plots in Benton County, Oregon. The soil is a dark brown fine-silty mixed mesic Argiaquic Xeric Argialboll classified in the Amity series. Amity silty clay loams are typically deep, poorly drained, and were formed in mixed alluvium terraces. Soils of the Willamette Valley of Oregon receive approximately 60 cm of annual rainfall, but are dry for most of the summer months (Knezevich, 1975). Soil used in this study was randomly collected from the surface 4 cm, air dried at room temperature, sieved through a 2 mm pore screen, and stored in plastic bags at 4°C.

Culture Technique

The continuous-flow method of Hendricks et al. (1987) was modified (Rhodes and Hendricks, 1989) to culture nitrifying bacteria. The nitrification medium was based upon Schmidt and Belser (1982) and amended with 250 mg NH_4-N l^{-1}. Each column received 15 g dry weight Amity soil, and the medium was metered into the column at a rate of 10 ml day^{-1} for 16 days. Effluent was removed at the same rate and samples were collected every two days and analyzed for NH_4, NO_3, and NO_2. Each experiment was conducted for 16 days.

Treatment Chemicals

Roundup [N-(phosphonomethyl)glycine] (Monsanto Agricultural Products Company, St. Louis, MO)] and N-Serve [(2-chloro-(trichloromethyl)pyridine (A. T. Talcott, Dow Chemical Company, Midland, MI)] were obtained as commercial formulations.[2] Both compounds were well-mixed and added

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[2] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

directly to the soil on day 8 at applications of 0, 0.042, 0.42, and 4.2 mg active ingredient (AI) g^{-1} dry soil for N-Serve and 0, 0.68, 6.7, and 68 mg AI g^{-1} dry soil for Roundup.

Microbiological Analysis

Heterotrophic bacteria were enumerated by plate counts using soil extract agar amended with 1% glucose and starch casein agar (Wollum, 1982). Denitrifying bacteria were enumerated using the MPN technique of Focht and Joseph (1973). Nitrifying bacteria were enumerated by the Most Probable Number (MPN) technique using a 96 well microtiter plate (G. Stotzky, personal communication) and the medium of Schmidt and Belser (1982). This medium is an ammonium sulfate based, chemically defined substrate for nitrifying bacteria. All cultures were incubated at 25° ± 0.1°C. Agar plates were incubated for 7 days, denitrifier MPN tubes for 14 days, and nitrifier MPNs for 6 weeks.

Direct Counts

Nitrifying bacteria were also enumerated by epifluorescent direct counts. Fluorescent antibody cocktails specific to Nitrosomonas, Nitrosospira, and Nitrosolobus were used to stain soil extract samples (Schmidt, 1974; Demezas and Bottomley, 1986). All samples were viewed using a standard Zeiss microscope (Carl Zeiss, Inc., New York, NY) configured for epifluorescence. For the purpose of enumeration, 25 fields per slide were counted and bacterial numbers calculated per gram of dry soil.

RESULTS

Nitrification rates using the static, perfusion, and continuous-flow techniques are shown in Figure 1. The effect of application of the various concentrations of the two chemicals on continuous-flow cultures is shown in Figure 2 (N-Serve) and Figure 3 (Roundup). Inhibition of nitrification by Roundup appears to be transient and suggests recovery of the bacterial of activity towards the end of the experiments.

Table 1 summarizes results for heterotrophic and denitrifying bacterial populations in both N-Serve and Roundup treatments. Numbers of organisms cultured were statistically significant from controls in columns treated with 4.2 mg AI g^{-1} dry soil and 68 mg AI g^{-1} dry soil for N-Serve and Roundup, respectively.

MPN analysis for both ammonium and nitrite oxidizing bacteria are shown in Table 2. No change in nitrifier numbers is evident over the course of these experiments.

Table 3 lists the number of Nitrosomonas, Nitrosospira, and Nitrosolobus enumerated by the Fluorescent Antibody procedure (FA). Nitrosolobus was the most numerous at all treatment levels over the course of the experiments. However, no statistical change in populations was determined.

DISCUSSION

Roundup has been shown to be an inhibitor of soil nitrifying capability in continuous-flow soil columns (Rhodes and Hendricks, 1989). The mechanism of toxicity in other bacteria is thought to involve disruption of protein synthesis (Fisher et al., 1986). In our studies, Roundup does not appear to inhibit protein synthesis in soil based upon the significant increase in heterotrophic and denitrifying populations in continuous-flow columns by day 16.

The mechanism of nitrification inhibition cannot be determined from our studies. However, the MPN and FA data indicate that nitrifying bacterial densities do not change between untreated controls and treated columns. Our data suggest that of inhibition of the soil nitrification process is probably the result of an effect on cellular metabolism rather than inactivation of the nitrifier population.

It has been reported that glyphosate may not be inhibitory to all microorganisms. Pipke et al. (1987) have shown that an Arthrobacter sp. can utilize glyphosate as its sole source of phosphorus. They found that Arthrobacter does possess a glyphosate transport system, but this has not been reported for other bacteria. The uptake of glyphosate was inhibited by organophosphates, organophosphonates, and orthophosphates in their study.

Currently, only one study has examined the effects of glyphosate on soil nitrogen processes. Carlisle and Trevors (1986) demonstrated that glyphosate and Roundup induced inhibition of indigenous nitrifiers in perfusion columns containing a Canadian sandy loam soil. They found that pure glyphosate was more inhibitory than Roundup when applied at the same concentrations based upon active ingredient g^{-1} dry soil. Inhibition by Roundup was observed only at levels greater than 76.7 ug of glyphosate g^{-1} dry soil. Field studies conducted by Ana'yeva et al. (1986) indicate that high concentrations of glyphosate and other commercial pesticides disrupted the soil microbial population for several months following treatment. Since nitrifying bacteria have been found to be sensitive to a number of chemical compounds, and many of these compounds do not produce the same response in other physiological groups of organisms, nitrifying bacteria may prove to be unique and useful organisms to study the impacts of xenobiotic chemical compounds on soil microbial processes.

ACKNOWLEDGEMENTS

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Table 1. Effect of Various Concentrations of N-Serve and Roundup on Heterotrophic Bacteria Growing on Soil Extract Agar (SEA), Starch Casein Agar (SCA), and Nitrate Broth (DN) in Continuous-Flow Cultures

Chemical Concentration (mg/g Dry Soil)	DAY											
	0			8[1]			12			16		
	DN	SEA	SCA	DN	SEA	SCA	DN	SEA	SCA	DN	SEA	SCA
N-Serve												
0.00	8.01[2] (0.15)[3]	8.36 (0.15)	8.22 (0.15)	7.04 (0.08)	8.26 (0.11)	8.23 (0.16)	7.15 (0.58)	8.17 (0.09)	7.17 (0.21)	8.10 (0.34)	8.07 (0.17)	8.05 (0.07)
0.042							7.40 (0.41)	8.12 (0.09)	8.90 (0.21)	7.34 (0.34)	8.42 (0.17)	8.20 (0.07)
0.42							7.86 (0.41)	8.38 (0.09)	8.07 (0.21)	7.94 (0.34)	8.23 (0.17)	8.32 (0.07)
4.2							8.51 (0.41)	8.51* (0.09)	8.20 (0.21)	7.89 (0.34)	8.65* (0.17)	8.64** (0.07)
Roundup												
0.00	8.02 (0.15)	8.36 (0.15)	8.22 (0.15)	7.04 (0.08)	8.26 (0.11)	8.23 (0.16)	6.88 (0.28)	7.98 (0.18)	7.96 (0.20)	7.01 (0.17)	8.21 (0.16)	8.14 (0.16)
0.68							7.34 (0.22)	8.36 (0.16)	8.36 (0.18)	7.40 (0.17)	8.56 (0.16)	8.64* (0.16)
6.8							7.95* (0.28)	8.82** (0.18)	9.07** (0.20)	7.44 (0.17)	8.68* (0.16)	8.68* (0.16)
68							7.48 (0.40)	7.71 (0.26)	8.38 (0.23)	7.94** (0.17)	9.02** (0.16)	8.99** (0.16)

[1] Cultures were treated with the chemicals on Day 8.
[2] Data represents mean Log (CFU or MPN)/g dry soil.
[3] Numbers in parentheses indicate standard error.
* = Significant difference from control (0.05 > p > 0.01).
** = Highly significant difference from control (p < 0.01).

Table 2. Effect of N-Serve and Roundup on Ammonium (AO) and Nitrate Oxidizing Bacteria (NO) in Continuous-Flow Culture

Chemical Concentration (mg/g Dry Soil)	DAY							
	0		8[1]		12		16	
	AO	NO	AO	NO	AO	NO	AO	NO
N-Serve								
0.00	6.28[2] (0.15)[3]	6.46 (0.32)	6.23 (0.21)	6.21 (0.33)	5.80 (0.56)	6.01 (0.34)	5.87 (0.43)	6.37 (0.15)
0.042					5.81 (0.49)	6.15 (0.37)	5.10 (0.43)	6.33 (0.15)
0.42					5.10 (0.49)	5.82 (0.37)	5.19 (0.37)	6.07 (0.15)
4.2					4.04 (0.97)	5.57 (0.42)	6.86 (0.75)	5.74 (0.15)
Roundup								
0.00	6.28 (0.15)	6.46 (0.32)	6.23 (0.21)	6.21 (0.33)	5.80 (0.18)	6.01 (0.08)	5.87 (0.26)	6.37 (0.13)
0.68					5.93 (0.18)	6.18 (0.08)	5.74 (0.26)	6.30 (0.13)
6.8					5.61 (0.18)	6.08 (0.08)	5.77 (0.30)	5.86 (0.15)
68					6.13 (0.21)	5.94 (0.10)	5.45 (0.26)	5.85 (0.13)

[1] Cultures were treated with the chemicals on Day 8.
[2] Data represents mean Log (MPN)/g dry soil.
[3] Numbers in parentheses are standard error.

Table 3. Effect of Various Concentrations of Roundup on the Growth of Nitrosolobus (Nl), Nitrosospira (Np), and Nitrosomonas (Ns) in Continuous-Flow Culture

Chemical Concentration (mg/g Dry Soil)	DAY											
	0			8[1]			12			16		
	Nl	Np	Ns	Nl	Np	Ns	Nl	Np	Ns	Nl	Np	Ns
Roundup												
0.00	8.02[2] (0.15)[3]	8.36 (0.15)	8.22 (0.15)	5.55 (0.16)	5.08 (0.23)	4.27 (0.25)	5.40 (0.18)	5.01 (0.1)	3.97 (0.15)	5.59 (0.0)	5.02 (0.21)	4.36 (0.10)
0.68							5.37 (0.13)	5.26 (0.11)	4.37 (0.21)	4.99** (0.10)	4.88 (0.15)	4.08 (0.07)
6.8							5.71 (0.10)	5.21 (0.09)	4.34 (0.12)	5.50 (0.10)	5.11 (0.15)	4.14 (0.07)
68							5.44 (0.13)	4.88 (0.11)	4.84* (0.21)	5.40 (0.10)	5.17 (0.15)	4.44 (0.07)

[1] Cultures were treated with Roundup on Day 8.

[2] Data represents mean Log (cells/g) dry soil.

[3] Numbers in parentheses indicate standard error.

* = Significant difference from control ($0.05 > p > 0.01$).

** = Highly significant difference from control ($p < 0.01$).

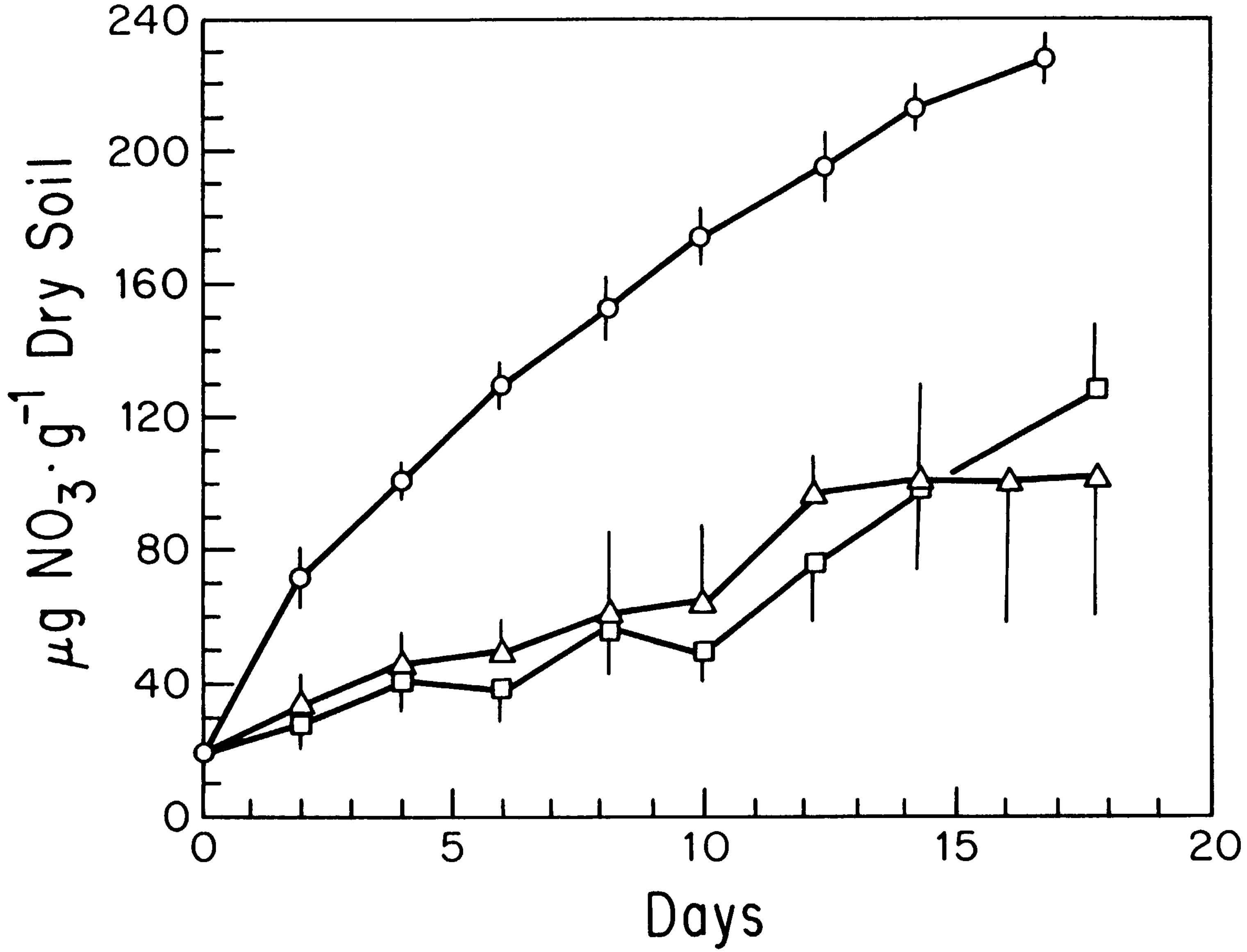

Figure 1. Nitrification in soil using static (Δ), perfusion (□), and continuous-flow (O) culture techniques.

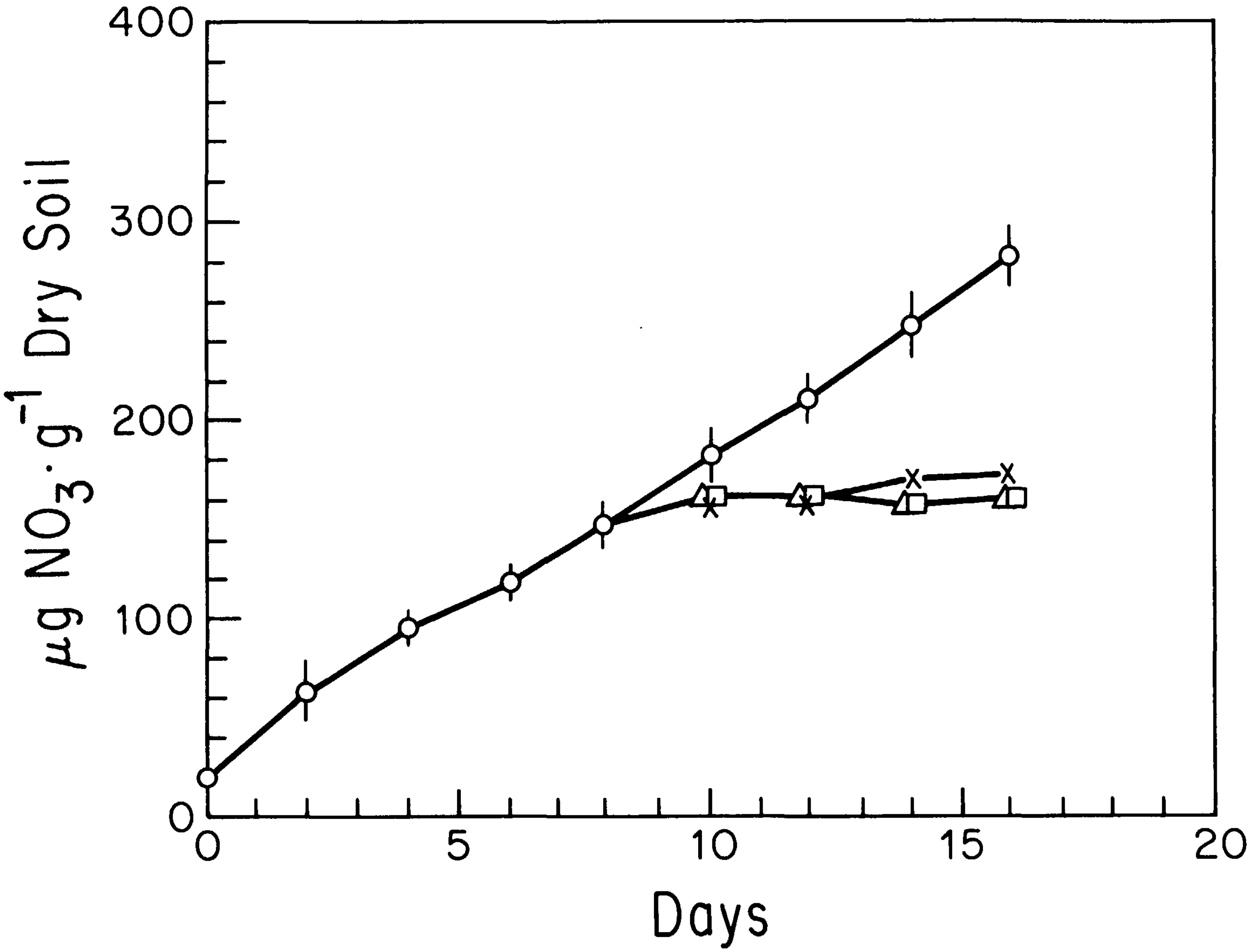

Figure 2. Effects of N-Serve on nitrification in continuous-flow culture. N-Serve concentrations: 0.0 (O), 0.042 (**X**), 0.42 (□), and 4.2 (Δ) mg nitrapyrin g^{-1} dry soil.

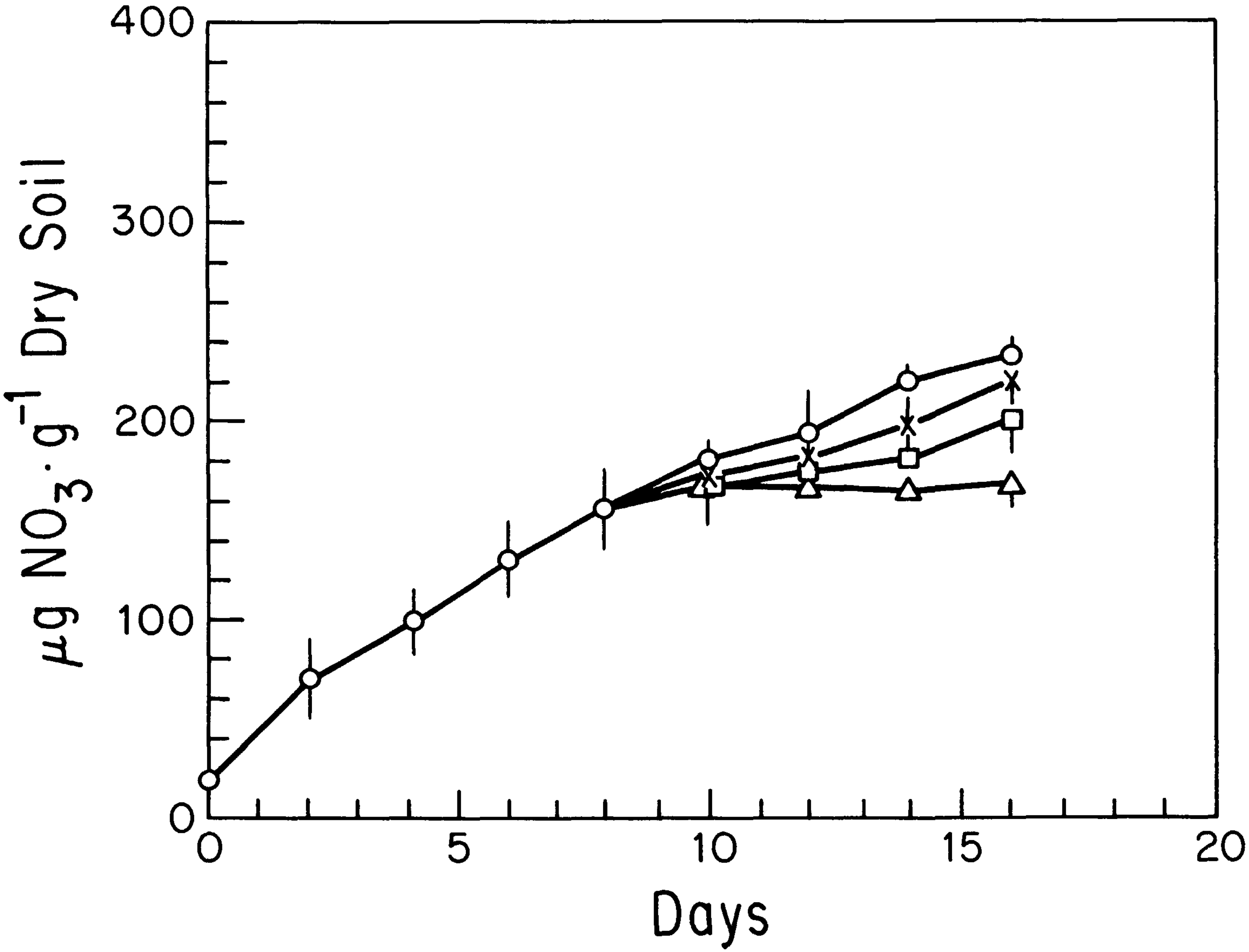

Figure 3. Effects of Roundup on nitrification in continuous-flow culture. Roundup concentrations: 0.0 (O), 0.68 (X), 6.8 (□), and 68 (△) mg glyphosate g^{-1} dry soil.

TOXICITY EVALUATIONS FOR HAZARDOUS WASTE SITES: AN ECOLOGICAL ASSESSMENT PERSPECTIVE

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ABSTRACT

Ecological assessments for hazardous waste sites should include acute toxicity tests as well as short-term tests which measure biological endpoints other than death. Toxicity and field assessment methods may be assembled into "tool boxes" which reflect not only the site-specific demands made by the ecological assessment process, but the continuing progress in methods development. Toxicity assessment tools may yield information regarding acute biological responses elicited by site-samples as well as suggest longer-term biological effects (e.g., genotoxicity or teratogenicity) potentially associated with subacute and chronic exposures to complex chemical mixtures characteristic of hazardous waste sites. Toxicity tests, however, are but one component of an ecological assessment for a hazardous waste site; field components must be given equal regard during the early phases of site evaluation. This becomes particularly important when field sampling is considered, since integration of toxicity assessments (be those in situ or laboratory-generated) and field assessments requires a well-designed sample plan to establish linkages among toxicity, site-sample chemistry and adverse ecological effects, if apparent. Spatial statistic techniques like kriging are finding increased applications in linking toxicity with other elements of site-evaluation (e.g., field-sample chemistry). Through kriging, for example, areal distributions for site-specific toxicity and chemistry data sets may be derived, then "maps" of site-sample toxicity and chemistries overlaid. Patterns of coincidence apparent in these distributions may then suggest linkages among toxicity, site-contaminants, and adverse ecological effects.

INTRODUCTION: Approaches to Ecological Assessment

Ecological assessments for hazardous waste sites have recently gained increased attention after the passage of the Superfund Amendments and Reauthorization Act of 1986 (SARA). As a result, US EPA has drafted numerous guidance documents which suggest approaches to the evaluation of adverse ecological effects which may exist at hazardous waste sites (US EPA 1988a; US EPA 1989; Warren-Hicks, *et al*. 1989); the application of ecological assessment techniques has become an integral part of the remedial investigation/feasibility study process, and in general ecological assessments have assumed a greater role in site assessment.

Ecological assessments at hazardous waste sites may require various methodologies which reflect the site-specific demands required by waste sites. Ecologically based hazard assessments may be considered as integrated evaluations of effects which are attained through site measurements of toxicity and exposure completed in both laboratory and field. As complex functions, toxicity and exposure integrations may yield an estimate of hazard associated with any particular waste site (Figure 1).

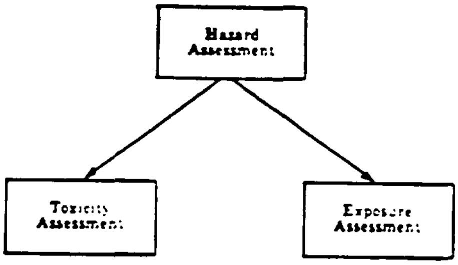

Figure 1. Toxicity and exposure assessments within the hazard evaluation process.

Toxicity assessments are derived from acute tests as well as subacute and chronic tests which measure biological endpoints other than death. Generally, these toxicity assessments are derived from laboratory-generated data. Exposure assessments within an ecological context frequently rely upon field methods which measure ecological endpoints, either on-site or at reference sites, and yield survey data relevant to estimates of adverse ecological effects associated with a waste site.

Both toxicity and field assessment methods may be compiled into "tool boxes" (Kapustka and Linder 1989). Depending upon the environmental matrix being tested, site-specific toxicity assessments may be derived using tests selected from these "tool boxes" (Horning and Weber 1985; Peltier and Weber 1985; Weber, et al. 1988; Greene, et al. 1988), which may include invertebrate and vertebrate, algal, plant, and microbial test systems (Figure 2). These toxicity assessment tools may yield information regarding acute biological responses elicited by site-samples or their derivatives, and may suggest longer-term biological effects (e.g., genotoxicity or teratogenicity) potentially associated with subacute and chronic exposures to complex chemical mixtures characteristic of hazardous waste sites. Potential contaminant migration as well as soil attenuation of contaminant effects may also be evaluated using these toxicity assessment tools, if eluates are prepared and tested in the laboratory. In situ toxicity assessments, while not as well developed as laboratory toxicity tests, are becoming more prominent in the ecological assessment process

(Warren-Hicks, et al. 1989; Murphy and Kapustka 1989), especially since in situ methods infer a linkage between toxicity and exposure functions, and reduce the problems associated with lab-to-field extrapolations of toxicity data.

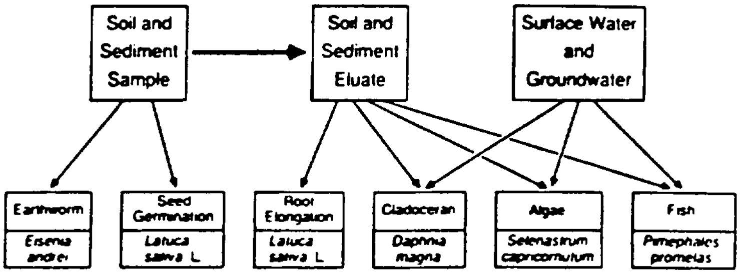

Figure 2. Test profiles useful in toxicity evaluations for ecological assessments may include representative organisms amenable to direct and indirect tests on site-samples.

Toxicity tests, however, are but one component of an ecological assessment for a hazardous waste site; field components must be given equal regard during the early phases of site evaluation. This becomes particularly important when field sampling is considered, since integration of toxicity assessments (be those in situ or laboratory-generated) and field assessments requires a well-designed sample plan to establish linkages among toxicity, site-sample chemistry and adverse ecological effects, if apparent. Ecological methods applicable to hazardous waste site evaluations are varied, and reflect the diversity apparent in waste sites which occur in a variety of geographic settings. Depending upon the environmental setting (aquatic or terrestrial) and the site-specific questions being asked in the evaluation process, methods have been collected into ecological assessment "tool boxes" (e.g., LaPoint and Fairchild 1989; Kapustka 1989; McBee 1989; Bromenshenk 1989) which provide a source of techniques available for ecological site assessments.

Spatial statistic techniques like kriging may be applied to site assessment and help establish linkages between toxicity and other components of site-evaluation (e.g., field-sample chemistry or field surveys). Kriging is a tool borrowed from geostatistics which may help integrate site-specific measures of toxicity and chemistry derived from site-samples. For example, site-soil samples may be evaluated for their toxicity potential through bioassays which evaluate soil eluates (e.g., algal or invertebrate short-term toxicity tests), then eluate chemistries (e.g., routine eluate chemistry) may be completed for these same site-samples. Through kriging, areal distributions for these site-specific toxicity and chemistry data sets may be derived, then "maps" of site-sample toxicity and chemistries developed. Coincidence patterns among these spatial distributions may subsequently suggest linkages among toxicity, contaminants, and adverse ecological effects.

To illustrate these techniques available in the ecological assessment "tool box," a hazardous waste site case study will be outlined briefly and the integration of site-sample chemistry and toxicity data will be summarized spatially.

WASTE SITE CASE STUDY

The Drake Chemical Superfund site[1] in Pennsylvania covers approximately eight acres, and consists of landfills, various lined and unlined treatment lagoons, and a dry unlined "canal" lagoon. Historic records indicate that chemical intermediates for dyes, pharmaceuticals, and cosmetics manufacturing were produced at the site. Also, various intermediates for the herbicide and pesticide industry were produced, including 2,3,6-trichlorophenylacetic acid (and its intermediates), which was the major contaminant found within the site boundaries and at some distance from the source.

Stratigraphically, much of the site consists of an overburden comprised of sludge and contaminated soil lenses, with unconsolidated materials ranging from near-surface sandy silts and clays to near-bedrock coarse sands and gravels. Bedrock is characteristically composed of fractured shales and varies in depth depending upon site location. An "erosional channel" may exist, but has not been clearly delineated. Groundwater occurs in the unconsolidated materials, with the water table being consistently maintained at a depth of 10 to 15 feet. Perched water lenses are not infrequent, and occur in associations with the clays and silts characteristic of near-surface formations. Hydraulic conductivities and flow velocities indicate that movement of groundwater through the unconsolidated materials occurs at 3.5 to 20 feet per year. Surface waters near the site consist of two rivers. The site, however, is bermed by road and railroad embankments. Historically, the site has been inundated by floodwater, but under normal conditions the runoff is contained within the site boundary where it percolates into the soil or directly enters the on-site leachate lagoon as surface runoff. Topographically, the leachate lagoon is the low point on-site. Various landscape constructions have been completed during the site's history, including a French drain and various catch basins designed to direct surface drainage into one of the bordering creeks.

METHODS AND MATERIALS

Site-samples received. Site-samples were obtained through an on-site contractor from locations (surface and below surface sample sites, 40 sites x 3 depths plus eight additional samples) identified in Figure 3. All site-soils were stored

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[1] case study based on waste site assessment completed in conjunction with US EPA regional staff.

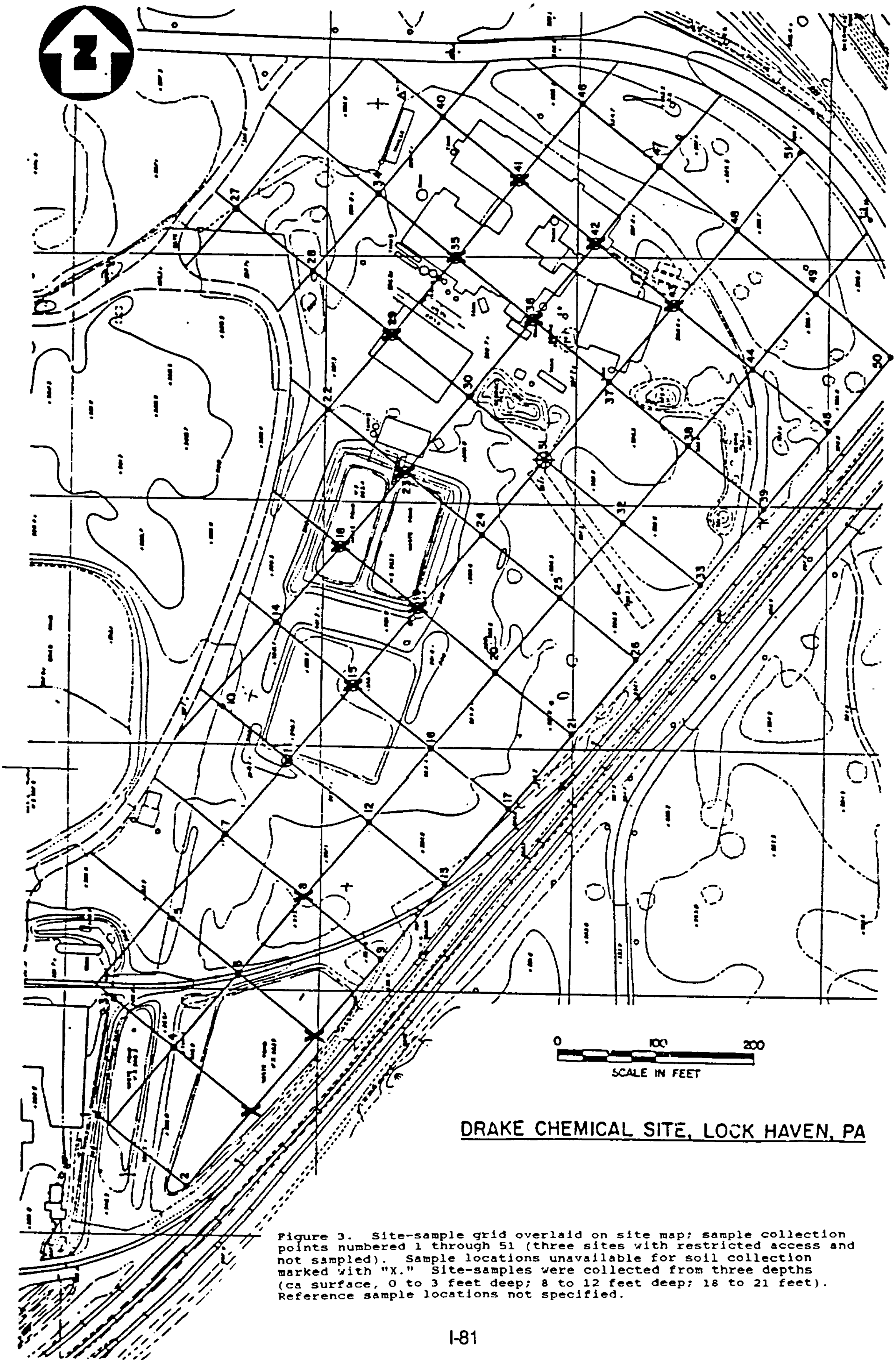

Figure 3. Site-sample grid overlaid on site map; sample collection points numbered 1 through 51 (three sites with restricted access and not sampled). Sample locations unavailable for soil collection marked with "X." Site-samples were collected from three depths (ca surface, 0 to 3 feet deep; 8 to 12 feet deep; 18 to 21 feet). Reference sample locations not specified.

at 4°C until soil processing and in-lab toxicity tests were initiated.

Eluate preparations from site-soils. No direct toxicity tests on soils (see Figure 2) were completed for the samples received from the site, but eluates were prepared from untreated site-soils to evaluate the potential mobility of chemical constituents which were present in the soil samples. Upon receipt, soil samples were screened through a 1/4" soil sieve, then eluted. Screened site-samples were mixed with four volumes eluent (deionized water) per gram dry weight site-soil or sediment. The slurry was then mixed in complete darkness for 48 hours at 20 +/- 2°C. After mixing, the resulting eluate was centrifuged, then filtered through a 0.45 um cellulose acetate or glass fiber filter. Eluate preparation incorporated original sample moisture content into its preparation and hence, a constant "solute/solvent" ratio was assured during the extraction of any site-sample. The filtered eluates were subsequently evaluated with an appropriate aquatic test system such as the algae (Selenastrum capricornutum) or macroinvertebrate (Daphnia magna) toxicity test.

Toxicity assessment tools: Indirect tests on soil eluates. A short-term chronic, Selenastrum capricornutum 96-hour toxicity test was conducted on soil eluates, and yielded toxicity estimates for soil contaminants which were potentially mobile owing to their water solubility. In the algal bioassay, growth in test concentrations which was less than that in controls indicated inhibitory effects during the 96-hour exposure; stimulation was indicated if growth in exposed systems was greater than growth in concurrent controls. Briefly, in the test algae were exposed to known concentrations of soil eluate. Algal cells were inoculated into test flasks which contained known concentrations of soil eluate, then were incubated for 96 hours in environmental chambers held at 24 +/- 2°C and 4304 +/- 430 lux (continuous light). The typical algal bioassay included a range of test concentrations capable of yielding EC_{50} data (effective concentrations which yield 50% reduction in algal growth relative to controls after 96 hours), as well as subculturing information pertinent to the evaluation of lethality. Cell counts performed on electronic particle counters yielded algal biomass estimates based upon cell counts and mean cell volumes. Evaluations of 96-hour EC_{50}s were completed using appropriate statistical methods (Stephan 1977; Stephan and Rogers 1985; Greene, et al. 1988).

Site-soil eluates were also evaluated with a standard Daphnia magna 48-hour static acute toxicity test. Owing to its geographic distribution and relative ease in laboratory culture systems, D. magna was used in these bioassays. As a representative aquatic macroinvertebrate (e.g., role in aquatic food chains), D. magna complemented the algal bioassay component completed as part of the toxicity assessment. Briefly, the bioassay used less than 24-hour old D. magna neonates which were exposed to test sample concentrations diluted (volume:volume) to yield logarithmically spaced exposure concentrations ranging from 100% site sample to 0% site sample (dilution water alone). The bioassays were conducted at 22 +/- 2°C (16:8, light:dark); ten D. magna neonates each were placed into triplicate exposure concentrations when the bioassay was started, and at the end of the 48-hour exposure mortality was assessed. Survivorship data was subsequently evaluated to yield LC_{50} estimates (Hamilton, et al. 1977; Stephan 1977), which are reflected as the percent site sample which is associated with 50% mortality.

For these indirect tests, toxicity categories were applied to the data listed in Appendix 1. As such, a class ranking of short-term toxicity estimates was established for the site samples. For purposes of this toxicity assessment, the following four groups of test results were established on the basis of sample dilutions associated with LC_{50} or EC_{50} estimates:

Group 1 = median effect less than or equal to 20% sample dilution

Group 2 = median effect greater than 20%, but less than or equal to 50%

Group 3 = median effect greater than 50%, but less than or equal to 80%

Group 4 = median effect greater than 80% sample dilution.

Routine eluate chemistries. Hardness, salinity, conductivity, total organic carbon (TOC), and pH were determined for each site-soil eluate (Appendix 2), and contributed to toxicity interpretations derived from preliminary spatial statistic analysis. On the work completed for the site toxicity assessment, sample pH was measured prior to toxicity bioassays, and determined whether adjustments were required before toxicity testing was begun. A second pH was subsequently taken upon completion of the bioassays, since pH effects may be quite pertinent to the toxicity information which was collected over the course of exposure.

Spatial statistic tools for ecological assessment. For the preliminary mapping of site chemistry and toxicity data, Geostatistical Environmental Assessment Software (GEOEAS, US EPA 1988b) was used. Variogram analyses and kriging were performed on sample eluate data (Appendix 1 and Appendix 2) using programs VARIO and KRIGE included in the GEOEAS "tool box" of geostatistical methods; by using program CONREC the resulting data files were used to construct preliminary contour maps for both chemistry and toxicity data generated from soil eluates. Examples of these maps are illustrated in Figures 4, 5, and 6 which summarized representative spatial distribution estimates for selected toxicity and chemical endpoints measured on surface samples.

RESULTS AND DISCUSSION

Toxicity Assessment. Appendix 1 tabulates the comparative toxicity estimates (as LC_{50}s or EC_{50}s) determined for the site-samples. Indirect measures of biological effects were determined on soil eluates and were derived from aquatic toxicity tests (48-hour acute test with D. magna and 96-hour short-term chronic test with S. capricornutum). For the algal and daphnid toxicity tests respectively, Figures 4 and 5 illustrate mappings of site-specific toxicity following variogram analyses and kriging with GEOEAS, while a mapping for a representative soil eluate chemistry (e.g., hardness) is given in Figure 6. Toxicity estimates were based on the toxicity classifications listed above (e.g., Groups 1, 2, 3,and 4) and were derived from the toxicity test results listed in Appendix 1.

Routine Chemistry Support. Appendix 2 lists the results for routine chemical analyses for eluates. In part, these were used for interpreting the biological effects summarized in Appendix 1 (see **Toxicity Assessment**), though the chemistry data routinely included in these toxicity screening tests precludes extensive comments regarding mechanisms of toxicity.

Toxicity evaluation: Correlative Analysis. The sheer number of samples and the heterogeneity in contaminant loads which potentially influence toxicity estimates precludes any definitive statement regarding causality and the toxicity measures derived for the site in these preliminary analyses. The complementary features of the toxicity tests, however, are apparent from a brief overview of the short-term toxicity estimates generated from the work on the site-samples. The 96-hour short-term chronic algal bioassay and the 48-hour acute daphnid toxicity test provided the data base upon which toxicity assessments were developed. For example, when categorized into the toxicity ranks outlined above, the algae and daphnid tests jointly identify 40% of all the site-samples (40 sites x 3 depths plus eight additional soils or 128 samples) as presenting Group 1 endpoints (median effect estimates $\leq$ 20% eluate), which should be considered as potentially highly toxic. These two single-species toxicity tests are quite complementary. Ten samples (10 of 128, or 8%) were jointly flagged by these tests as being highly toxic; the algal and daphnid bioassays respectively identified 27% (35 of 128) and 5% (6 of 128) of site-samples as being in Group 1. "No effect" samples were jointly identified by the algal and daphnid tests in 60% (77 of 128) of the soil eluates evaluated for short-term toxicity. Alone, the 96-hour algal bioassay identified 35% (44 of 128) of all the samples as being in Group 1, while the daphnid test identified 10%, or 13 of 128 samples as being in this highly toxic category. If one extends this clustering approach to toxicity assessment and includes Groups 1 and 2 as particularly relevant toxicity categories, the algal and daphnid tests respectively identified 50% and 23% of all sample eluates as being highly to moderately toxic. Both identified only 9% of the samples as being in Group 3, while Group 4 (low toxicity, median effect estimates >80%) samples were identified in algal and daphnid tests at 41% and 68%, respectively.

Toxicity evaluation: Spatial distributions. Summary correlative analyses could be drawn for the toxicity assessments at various depths, but Figures 4 and 5 amply illustrate a preliminary toxicity mapping which considers the spatial distribution of toxicity within two surface dimensions for both algae and daphnid. Figure 6 illustrates two distribution maps for surface soil-eluates tested with algae

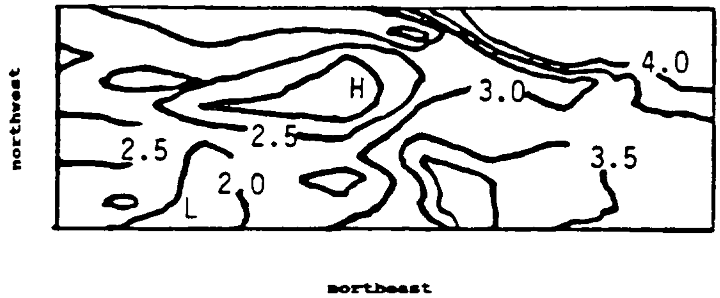

Figure 4. Spatial distribution of toxicity indicated by the short-term algal test and illustrated on toxicity contour map generated by CONREC program in GEOEAS for surface samples [Group 4 toxicity category (EC_{50}s > 80%); Group 3 toxicity category (50% < EC_{50}s $\leq$ 80%); Group 2 toxicity category (20% < EC_{50}s $\leq$ 50%); Group 1 toxicity category (0% < EC_{50}s $\leq$ 20%)]. H = highest toxicity location; L = lowest toxicity location. Reference area unspecified.

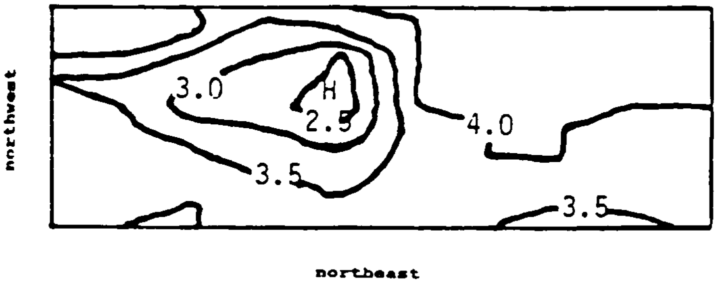

Figure 5. Spatial distribution of toxicity indicated by the daphnid toxicity test and illustrated on toxicity contour map generated by CONREC program in GEOEAS for surface samples [Group 4 toxicity category (LC_{50}s > 80%); Group 3 toxicity category (50% < LC_{50}s $\leq$ 80%); Group 2 toxicity category (20% < LC_{50}s $\leq$ 50%); Group 1 toxicity category (0% < LC_{50}s $\leq$ 20%)]. H = highest toxicity location; L = lowest toxicity location. Reference area unspecified.

and daphnia. From routine eluate chemistry results (Appendix 2), mappings for each chemistry data set (e.g., eluate hardness and salinity in Figure 6) could be plotted, again using the programs of GEOEAS. The preliminary assessment for spatial correlations between site-chemistry and toxicity data could then be achieved through simple "overlay" techniques, and the linkage between toxicity and eluate chemistry inferred from the coincidence patterns noted between the two mappings. The significance of overlay techniques, however, must be viewed in the context of potential bias associated with the mappings generated through GEOEAS. For example, variogram analysis in GEOEAS relies heavily upon interpretation and "trial and error" computations to derive a variogram model used in kriging (US EPA 1988b); more generally, map overlay techniques present a variety of problems when independently derived maps are compared in a spatial context (Bailey 1988).

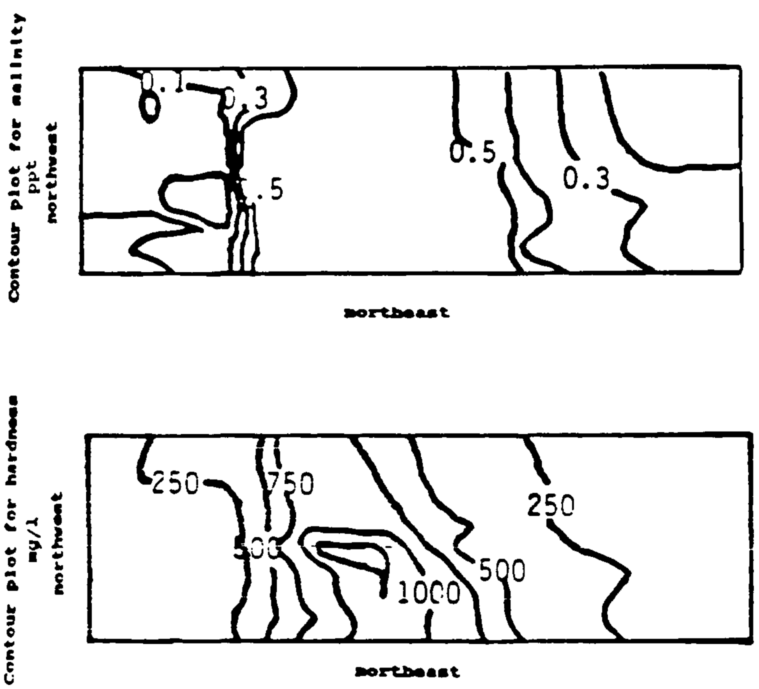

Figure 6. Spatial distribution of eluate chemistry data, e.g., hardness and salinity, illustrated on toxicity contour map generated by CONREC program in GEOEAS for surface samples. Reference area unspecified.

Even without using overlay techniques, distribution maps may be beneficial to toxicity data interpretation nonetheless. For Drake Chemical, even a cursory review of the toxicity data at the various depths presented patterns of toxicity as identified by algae and daphnia toxicity maps. For example, surface point estimators of highly toxic soils (EC_{50}s $\leq$ 20%) were identified by nine algal short-term endpoints which, depending upon closest-neighbor toxicity characteristics, resolves into contour mappings (Figure 4) similar to those illustrated for daphnid toxic responses in Figure 5. The daphnid toxicity rankings derived from the acute tests suggest fewer highly toxic point estimators but the mapping presents a highly coincident toxicity distribution.

Though exploratory by design, these preliminary mappings and toxicity interpretations may bear more relevance to site evaluation than methods related to hypothesis testing in a strictly statistical sense. More rigorous analytical techniques could be applied if additional site information were gathered, and if greater resolution were indicated beyond these short-term screening tests. Reference sites should be critically defined in order to weight toxicity endpoints within the overall site evaluation. Considering the influence that sample integrity bears on toxicity assessment, well-designed field studies should be emphasized regardless of whether laboratory-based or in situ toxicity assessments are integral components in the ecological assessment of a site. Through these correlative analyses, preliminary toxicity evaluations may yield information pertinent to site assessments and identify potential topics relevant to site management, e.g., site characterization and effectiveness of remediation efforts (Athey, et al. 1987).

SUMMARY: Toxicity evaluations for ecological assessments

As part of the overall ecological assessment for hazardous waste sites, toxicity assessments contribute significantly to site evaluation. These expectations should be clearly defined in the development of the site-specific data quality objectives. Both laboratory and field studies are critical, if the ecological assessment is intended to be an integral part of site evaluation. The following summary points illustrate the value of toxicity assessments in the evaluation process for site:

(1) the waste site presented a characteristically widespread spatial toxicity distribution, though its significance must be evaluated relative to a site-specific reference; the role of well-defined reference sites becomes invaluable in interpreting the extent to which the potential toxicity is expressed in the field;

(2) the algal and daphnid toxicity tests indicated that quantitatively different biological responses occurred at various sampling points (surface and below surface) on the site; the toxicity assessment clearly indicated the potential for high toxicity to occur within ecological contexts, if water soluble constituents from the chemical mixtures in soils were mobilized;

(3) the algal 96-hour short-term chronic test presented EC_{50}s of less than 20% site-sample dilution (Group 1) in 27% of the site-sample eluates; the 48-hour daphnid acute test presented Group 1 responses to 5% of the site-samples; the algal and daphnid tests were complementary and together identified 40% of the site-samples as potentially highly toxic (EC_{50}s of less than 20% site-sample);

(4) vertical migration of toxicity was apparent from the preliminary mapping completed for each of the depths tested, but the significance of the biological responses requires more familiarity with the site reference;

(5) mechanisms of toxicity and causality should not be inferred from preliminary correlative or spatial distribution analyses, nor should toxicity distributions based upon associations between site locations and screening test results infer chemical specific migration without the supporting analytical results.

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Appendix 1. Short-term toxicity estimates (EC_{50}s and LC_{50}s) derived from tests (algal and daphnid) completed on site-sample eluates (sorted by site locations, see also Figure 3).

SAMPLE SITE #	ALGAL EC_{50} (95% C.I.)	DAPHNIA EC_{50} (95% C.I.)
1 surface	NE	NE
middle	1.51 (0.70-3.3)	67.1 (58.4-77.1)
deepest	18.0 (9.2-31.6)	91.2 (87.3-95.3)
2 surface	NE	NE
middle	NE	NE
deepest	NE	NE
3 surface	NE	NE
middle	NE	42.8 (38.0-48.1)
deepest	NE	8.3 (3.7-18.9)
4 surface	1.5 (0.7-3.3)	55.2 (46.7-65.2)
middle	15.1 (9.6-24.6)	66.2 (62.6-70.0)
5 surface	71.7 (17.0-80.0)	NE
middle	NE	NE
deepest	NE	-50.0
6 surface	NE	84.3 (80.4-88.4)
middle	NE	NE
deepest	5.6 (4.2-7.6)	49.0 (37.2-64.6)
7 surface	NE	NE
middle	NE	NE
deepest	67.1 (64.3-69.8)	NE
8 NO SAMPLES COLLECTED		
9 surface	-40.0	16.6 (10.4-26.40
middle	1.1 (0.3-3.9)	43.9 (36.5-52.9)
deepest	32.7 (22.9-47.9)	80.5 (76.0-85.3)
10 surface	17.88 (0.0-74.1)	NE
middle	NE	NE
deepest	NE	NE
11 surface	NE	NE
middle	NE	NE
deepest	5.5 (1.0-39.8)	-30.0
12 surface	NE	NE
middle	20.8 (4.5-80.0)	-16.7
deepest	16.7 (6.3-80.0)	NE
13 surface	NE	NE
middle	21.6 (11.0-42.2)	NE
deepest	15.9 (4.0-63.0)	95.9 (90.2-100.0)
14 surface	NE	NE
middle	43.8 (23.1-80.0)	NE
deepest	NE	NE
15 NO SAMPLES COLLECTED		
16 surface	NE	NE
middle	6.3 (1.1-35.5)	-20.0
deepest	NE	NE
17 surface	NE	NE
middle	37.0 (0.7-80.0)	NE
deepest	NE	NE
18 NO SAMPLES COLLECTED		
19 NO SAMPLES COLLECTED		
20 surface	NE	50.7 (45.3-55.3)
middle	NE	NE
deepest	NE	NE
21 surface	1.0 (0.03-39.8)	89.8 (88.6-91.1)
middle	8.0 (1.6-39.8)	92.8 (89.6-96.1)
deepest	0.4 (0.01-20.0)	87.4 (82.7-92.4)
22 surface	32.9 (23.4-46.0)	72.9 (63.8-83.2)
middle	18.0 (10.7-31.6)	2.2 (1.8-2.8)
deepest	66.2 (25.1-80.0)	NE
23 NO SAMPLES COLLECTED		
24 surface	0.7 (0.2-3.2)	22.0 (18.9-25.4)
middle	50.4 (16.2-80.0)	-53.0
deepest	NE	-40.0
25 surface	NE	NE
middle	NE	NE
deepest	NE	NE
26 surface	4.5 (0.01-80.0)	NE
middle	31.1 (5.0-80.0)	46.6 (41.1-52.8)
deepest	NE	NE
27 surface	14.2 (5.6-22.4)	91.4 (89.4-93.5)
middle	1.6 (0.6-4.4)	45.0 (30.6-66.1)
deepest	5.8 1.7-19.7)	NE
28 surface	NE	NE
middle	8.1 (2.6-25.1)	NE
deepest	NE	NE
29 NO SAMPLES COLLECTED		
30 surface	33.9 (0.0-80.0)	39.3 (33.9-45.4)
middle	41.9 (28.5-61.7)	67.9 (64.4-71.7)
deepest	7.6 (2.9-18.2)	21.7 (17.9-26.2)
31 surface	10.2 (3.9-26.3)	22.0 (18.1-26.7)
middle	11.4 (3.2-39.8)	2.2 (1.8-2.7)
deepest	2.4 (0.3-20.0)	6.8 (5.6-8.4)
32 surface	NE	NE
middle	6.6 (2.3-19.1)	4.4 (3.4-5.7)
deepest	0.7 (0.04-14.1)	2.9 (2.0-4.2)
33 surface	72.1 (43.6-80.0)	93.9 (90.0-97.3)
middle	NE	NE
deepest	8.8 (2.5-30.2)	43.0 (39.9-46.4)
34 surface	NE	NE
middle	NE	NE
deepest	NE	NE
35 NO SAMPLES COLLECTED		
36 NO SAMPLES COLLECTED		
37 surface	71.7 (66.8-76.9)	NE
middle	NE	NE
deepest	4.3 (1.5-12.6)	8.6 (7.2-10.3)
38 surface	NE	97.1 (97.1-100)
middle	11.1 (5.8-20.9)	21.4 (17.0-26.8)
deepest	43.8 (30.3-61.7)	5.4 (4.1-7.1)
39 surface	NE	NE
middle	7.2 (1.0-51.9)	-10.0
deepest	7.9 (2.5-21.9)	NE

SAMPLE SITE #	ALGAL EC_{50} (95% C.I.)	DAPHNIA EC_{50} (95% C.I.)
40 surface	34.2 (5.2-80.0)	NE
middle	74.8 (9.9-80.0)	NE
deepest	NE	NE
41 NO SAMPLES COLLECTED		
42 NO SAMPLES COLLECTED		
43 NO SAMPLES COLLECTED		
44 surface	NE	NE
middle	77.9 (18.2-80.0)	-47.0
deepest	46.5 (0.0-80.0)	NE
45 surface	37.9 (3.7-80.0)	NE
middle	73.5 (60.6-80.0)	92.8 (86.4-99.7)
deepest	65.3 (20.8-80.0)	55.0 (47.7-63.3)
46 surface	NE	NE
middle	NE	79.6 (74.3-85.2)
deepest	NE	75.3 (67.5-84.1)
47 surface	29.0 (0.0-80.0)	NE
middle	12.0 (2.9-50.0)	51.7 (42.6-62.7)
deepest	56.1 (1.9-80.0)	72.8 (58.8-90.1)
48 surface	8.6 (2.5-29.5)	71.2 (50.0-100.0)
middle	19.9 (7.6-52.5)	33.7 (27.8-40.8)
deepest	-50.0	90.2 (84.9-95.8)
49 surface	7.5 (3.1-17.4)	-40.0
middle	50.3 (29.0-87.1)	71.1 (63.5-79.5)
deepest	5.0 (2.5-10.0)	87.8 (85.0-90.7)
50 surface	NE	NE
middle	17.0 (4.3-67.6)	NE
deepest	11.7 (6.5-20.4)	NE
51 surface	NE	NE
middle	-40.0	NE
deepest	NE	-20.0

[1] Reports listed as negative percents reflect mortality or extent of inhibition observed at highest concentration tested (algae, 80%; <u>Daphnia</u>, 100%). 95 % C.I. = 95% confidence interval about point estimate.

[2] If EC_{50} estimates are extrapolations and not interpolations, projections exceed highest (or lowest) concentrations tested and no precision estimates are possible; median effect estimates should be evaluated as relative measures.

[3] NE = no effect.

Appendix 2. Chemical analysis completed for site-samples received from the Drake Chemical site. Water quality characteristics (conductivity, uS/cm; salinity, ppt; TOC (=total organic carbon), mg/l; hardness, mg/L) completed on eluates prepared from site-soils. Samples sorted by laboratory identification number; sample location listed in Final Technical Report for Drake Chemical site available from NSI Technology Services Corporation, U.S. EPA, ERL-Corvallis, Oregon.

CHEMISTRY NUMBER	SOURCE CODE	COND. (uS)	SALINITY (ppt)	TOC (ppm)	HARD-NESS	INIT. pH	FINAL pH
44000	LE	1925.0	1.271	256.40	759.85	9.5	9.4
44001	LE	475.0	0.314	8.10	94.60	4.50	6.50
44002	LE	860.0	0.568	24.40	110.55	5.40	6.50
44100	DE	2475.0	1.634	31.20	918.70	9.90	9.80
44101	DE	2550.0	1.683	116.00	1581.85	6.90	7.00
44102	DE	2470.0	1.630	105.60	1301.04	7.50	7.50
44103	DE	3150.0	2.079	19.70	1623.25	4.80	6.10
44104	DE	2900.0	1.914	88.20	1487.64	4.70	6.30
44105	DE	2770.0	1.828	53.40	1039.75	7.10	7.20
44106	DE	2650.0	1.749	49.90	1704.18	10.00	9.00
44107	DE	2900.0	1.914	135.70	2392.87	8.40	8.30
44108	DE	3350.0	2.211	186.80	1141.41	7.10	7.50
45101	DE	978.0	0.645	81.20	503.21	6.9	7
45113	DE	630.0	0.415	51.90	145.59	6.00	6.90
45114	DE	1890.0	1.247	37.30	222.91	5.40	6.10
45119	DE	862.0	0.569	19.10	340.16	7.20	7.30
46000	LE	338.0	0.223	9.10	170.54	7.80	7.80
46001	LE	1115.0	0.736	10.00	404.93	4.60	6.20
46002	LE	448.0	0.296	8.19	202.78	8.30	8.20
46003	LE	800.0	0.528	24.60	284.38	7.10	7.10
46004	LE	372.0	0.246	12.70	63.70	5.70	6.20
46005	LE	448.0	0.296	11.80	247.40	7.30	7.60
46007	LE	130.5	0.086	6.40	15.12	5.20	6.50
46008	LE	207.0	0.137	11.80	104.40	8.00	8.00
46009	LE	103.5	0.068	6.40	34.66	6.60	6.50
46010	LE	124.5	0.082	2.70	46.55	7.10	7.20
46011	LE	705.0	0.465	23.70	161.21	3.30	6.20
46012	LE	272.0	0.180	4.60	18.18	4.80	6.30
46013	LE	538.0	0.355	11.80	82.15	5.00	6.40
46014	LE	520.0	0.343	10.30	212.42	5.00	6.30
46015	LE	324.0	0.214	11.30	17.19	5.60	6.50
46016	LE	478.0	0.315	20.90	45.94	4.60	6.20
46017	LE	148.0	0.098	6.40	55.71	6.60	7.10
46018	LE	630.0	0.416	30.90	193.82	4.50	6.40
46019	LE	375.0	0.248	24.60	108.59	4.70	6.20
46020	LE	1900.0	1.254	5.60	605.17	4.10	7.30
46021	LE	1370.0	0.904	14.70	231.60	4.00	6.50
46022	LE	219.0	0.145	4.20	110.05	7.40	7.90
46023	LE	144.0	0.095	4.20	15.81	5.80	6.20
46024	LE	376.0	0.248	2.10	112.51	6.40	6.60
46026	LE	1860.0	1.228	86.10	1060.97	5.50	6.60
46027	LE	875.0	0.578	16.10	304.56	6.60	6.80
46028	LE	1285.0	0.848	6.30	877.14	5.30	6.60
46030	LE	1375.0	0.908	9.10	842.33	5.20	6.40
46100	DE	374.0	0.247	10.90	66.96	6.30	6.50
47000	LE	439.0	0.290	14.70	245.45	7.70	7.80
47002	LE	740.0	0.488	4.90	316.17	6.30	6.40
47006	LE	497.0	0.328	11.90	266.94	7.40	8.00

CHEMISTRY NUMBER	SOURCE CODE	COND. (uS)	SALINITY (ppt)	TOC (ppm)	HARD-NESS	INIT. pH	FINAL pH
47007	LE	363.0	0.240	3.50	162.71	7.60	7.50
47008	LE	1233.0	0.814	25.20	627.20	6.90	7.70
47009	LE	730.0	0.482	10.50	109.70	5.80	6.90
47010	LE	630.0	0.416	9.80	331.82	7.40	8.10
47011	LE	1720.0	1.135	18.90	1302.57	6.90	7.60
47012	LE	1080.0	0.713	14.70	335.60	5.10	5.40
47013	LE	1080.0	0.713	23.10	667.47	7.30	8.10
47014	LE	930.0	0.614	95.90	404.03	6.60	7.00
47015	LE	770.0	0.508	4.90	361.36	8	7.2
47016	LE	290.0	0.191	28.70	35.60	5.5	6.2
47017	LE	302.0	0.199	4.90	43.63	6	6.2
47020	LE	471.0	0.311	12.80	113.04	7.8	7.6
47022	LE	540.0	0.356	12.80	284.85	7.9	7.6
47023	LE	1055.0	0.696	22.30	688.16	6.7	7.4
47024	LE	970.0	0.640	12.80	379.95	5.4	6
47025	LE	800.0	0.528	15.50	129.21	8	7.5
47026	LE	142.0	0.094	14.20	53.46	5.9	6.3
47028	LE	459.0	0.303	3.40	244.76	7.1	7.9
47029	LE	481.0	0.317	8.80	210.02	5.5	6.3
47030	LE	550.0	0.363	11.50	262.51	6.5	7.1
47031	LE	525.0	0.347	8.10	277.54	6.2	7.4
47032	LE	104.0	0.069	8.10	37.04	6.8	6.8
47033	LE	110.0	0.073	15.50	36.89	7.00	6.20
47034	LE	402.0	0.265	12.80	23.01	6.70	6.60
47035	LE	300.0	0.198	7.40	158.25	7.80	8.10
47036	LE	94.0	0.062	2.00	28.46	4.90	6.30
47037	LE	89.8	0.059	2.00	25.33	5.00	6.20
47100	LE	990.0	0.653	59.40	394.38	7.50	7.70
47101	DE	385.0	0.254	83.00	152.50	7.10	7.00
47102	DE	462.0	0.305	40.50	189.74	7.10	7.00
47104	DE	1170.0	0.772	15.50	624.54	7.50	7.70
47107	LE	740.0	0.488	14.20	325.76	5.80	7.10
47108	LE	478.0	0.315	0.00	213.10	7.90	7.30
47109	LE	638.0	0.421	0.00	126.46	6.20	6.50
47110	DE	82.0	0.054	0.00	24.87	7.00	6.90
47111	DE	57.0	0.038	0.00	11.22	6.70	6.30
47112	LE	550.0	0.363	34.40	85.30	6.40	6.20
47113	LE	141.0	0.093	0.00	29.99	5.50	6.60
47114	LE	223.0	0.147	14.20	48.04	5.70	6.70
48000	LE	345.0	0.229	21.30	174.48	8.00	7.90
48001	LE	142.0	0.094	5.46	33.32	6.30	6.40
48002	LE	145.0	0.096	6.40	50.72	6.70	6.70
48003	LE	244.0	0.161	11.60	109.57	6.90	7.70
48004	LE	168.0	0.111	0.20	62.65	6.20	6.60
48005	LE	363.0	0.240	8.19	176.87	7.60	7.70
48006	LE	321.0	0.212	10.00	145.66	7.70	7.80
48007	LE	425.0	0.281	11.80	201.35	7.50	7.70
48100	DE	195.0	0.129	0.00	35.24	5.10	6.20

APPLICATION OF MICROBIAL TOXICITY AND MUTAGENICITY ASSAYS FOR IDENTIFICATION AND EVALUATION OF TOXIC CONSTITUENTS IN FRACTIONATED HAZARDOUS WASTES.

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Current monitoring methods for hazardous waste site chemicals present numerous analytical problems due to (1) matrix interferences and (2) the complexity of the chemical mixtures present. We have employed microbial toxicity and mutagenicity assays to rapidly identify toxic fractions and components of hazardous wastes and individual chemical constituents representing the predominant toxic species in each mixture. In this approach, extracts of environmental samples are fractionated via normal-phase or gel permeation chromatography and coincubated in microbial bioassays (the Salmonella/microsome assay). The resulting toxic or mutagenic responses (produced in 24-48 hours) are used to define the toxicity of whole or fractionated waste samples. This approach was utilized for the analysis of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polychlorinated dioxins (PCDDs) in three waste environments: municipal fly ash, estuary effluents, and soil amended with wood-preserving waste. Fly ash samples were extracted with dichloromethane for 24 hours using Soxhlet extraction, and the isolated organics were evaporated to dryness and reconstituted in dimethyl sulfoxide. Estuary samples were air dried and extracted at room temperature with acetonitrile; exchanged into pentane and fractionated on a silica gel column. Fractions were evaporated to dryness with N_2 and dissolved in DMSO. In all three case studies, close correlation was found between the identification of known classes of toxic chemicals and the toxic and mutagenic potency of these wastes. Microbes were found to be sensitive to all major classes of toxicants when tester bacteria were exposed to mixed wastes in the presence of a rodent liver preparation (S-9) competent to biotransform polycyclic compounds to toxic/mutagenic intermediates. Fly ash-associated mutagens, predominantly benzo(a)pyrene, fluoranthene and phenanthrene, elicited toxic and mutagenic effects in the presence and absence of rodent S-9 fractions. Estuary and wood-preserving wastes, containing polycyclic aromatic and chlorinated hydrocarbons, exhibited toxic effects only in cultures supplemented with rodent S-9. Data to be presented supports this approach as an improved method for rapid identification of toxic constituents in uncharacterized wastes as well as prioritization of wastes sites for remediation.

APPLICATION OF MAMMALIAN CELL CULTURE SYSTEMS TO EVALUATE AND MONITOR HAZARDOUS WASTES AND WASTE SITES.

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Current strategies targeted to evaluate hazardous wastes and design hazardous waste site remediation strategies have traditionally focussed on ecotoxicological effects in the absence of methods to determine the fate and effects of waste site mixtures on human populations. While microbial methods have been advanced to assess the genotoxicity of waste site chemicals, methods have not been applied to monitor other human toxic endpoints, such as prenatal toxicity, neurotoxicity, and reproductive toxicity, characteristic of hazardous wastes constituents. We have adapted mammalian cell culture systems to monitor these toxic effects for uncharacterized chemical waste mixtures, direct hazardous wastes, and direct environmental samples (soil, water, air particulates) from hazardous waste sites; these include: (i) prenatal toxicity (via postimplantation rodent embryo culture (ii) neurotoxicity (via continuous glial cell cultures), (iii) reproductive toxicity (via rodent blastocyst culture), as well as (iv) carcinogenicity (via clastogenic analysis of primary human and rodent cell cultures) of samples from hazardous waste sites. Using this approach, we have characterized the toxic effects of complex waste mixtures (petroleum creosote, phenolic wood-preserving wastes, aromatic and chlorinated hydrocarbon solvent mixtures) to prioritize waste sites in terms of acute and chronic health effects. In addition, we have also employed these assays to evaluate various hazardous waste clean-up strategies (e.g. extraction, biodegradation) to identify conditions which optimize the removal of the key toxic constituents of waste site chemical mixtures.

SCREENING FOR POLYCHLORINATED DIOXINS AND FURANS BY IMMUNOASSAY

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ABSTRACT. We have reported (Toxicology 45:229) a set of monoclonal antibodies that bind preferentially to polychlorinated dioxins and furans having chorines in the lateral positions. Mice were immunized with a 1-adipamino-3,7,8-trichlorodibenzodioxin, and the resulting monoclonal antibodies recognize the highly toxic 2,3,7,8-tetrachloro-dioxin (TCDD) and 1,2,3,7,8-pentachloro-dioxin and furans, and a limited number of other intermediately chlorinated congeners. With this binding selectivity the antibodies are suitable for screening samples for the presence of a subset of the recognized congeners, but GC/MS analysis is needed to confirm the exact congeners present in positive samples. An enzyme linked immunosorbant assay (ELISA) incorporating one of these antibodies has been developed, with a detection limit of about 100 pg of 2,3,7,8-TCDD. This assay has been successfully applied to the analysis of industrial chemicals, PCBs, fly ash, and soil samples contaminated with TCDD at 1 ppb and above. While samples extraction and preparation was required for the immunoassay, the sample clean-up was less extensive than that needed for GC/MS analysis. Immunoassay results correlated with GC/MS analysis of the same samples, encouraging us to pursue the use of immunoassays as a screen for contamination. Work is currently in progress to expand the range of matrices tested to include eggs, milk, and animal fats.

There is regulatory concern about the presence of hexa- and hepta- chlorinated dioxins, which are not recognized by the current set of antibodies. As such, we are developing a new set of monoclonal antibodies directed to these more chlorinated congeners. We have synthesized 2-carboxymethyl-3,6(9),7,8-tetrachlorodibenzo-dioxin for use as a hapten, mice have been immunized, and production of new monoclonal antibodies is now in progress. It is anticipated that these new antibodies will show preference for more highly chlorinated congeners. It is also expected that the new hapten should produce antibodies with higher affinity for all laterally substituted dioxins. Data on the binding selectivity of the new monoclonal antibodies should be available within the next few months to confirm or refute these expectations. When used in conjunction with the existing antibodies these new monoclonal antibodies should provide a screen that recognizes all of the most toxic congeners of dioxins and furans.

THE USE OF SCREENING PROTOCOLS TO EVALUATE BIOREMEDIATION TECHNOLOGY FOR SITE CLEANUP

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The selection of suitable technology for hazardous waste site cleanup is complicated by the lack of objective performance criteria for many treatment options. Where there has been an extended period of development activity, the technology is recognized for its more advanced state. Consequently, the treatment technologies identified as having less development activity are regarded as incomplete and do not receive recognition as competitive technology.

Bioremediation technology has not been left unscathed in this comparison. In spite of its promise and recognized beneficial effects it has been generally avoided as a remediation technology. A major issue for the acceptance of bioremediation is the establishment of an objective means whereby prospective users can differentiate between competitive and conflicting claims. This paper presents the first of a proposed series of protocols devoted to the formulation of an objective criterion to measure biological treatment. The initial protocol is devoted to the assessment of aerobic biological treatment of contaminated soils. The protocol has been organized to permit the adaptation of the testing to configurations closely mimicing large scale operations.

ENFORCEMENT

COMPUTERS IN THE DECISION PROCESS: LEGAL IMPLICATIONS OF ELECTRONIC DATA TRANSFER AND DATA MANAGEMENT SYSTEMS

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ABSTRACT.

The use of computers and electronic information poses a complex problem for potential litigation. The problem currently manifests itself in at least two ways.

First, the EPA enforcement of CERCLA/SARA statutes is moving quickly towards site clean-up activities that will require responsible decisions based on quick turn-around analytical data. Site managers increasingly rely on direct data transfer or FAX information while making crucial decisions concerning both the scope (and expense) of clean-up activity and potential liability for the site owners or operators.

Second, many laboratories in both the public and private sectors are either developing their own data management tracking systems or purchasing data management software packages. These trends are likely to continue.

Insufficient documentation of electronic transfers may render any action or decision "non-defensible." While draft data in an electronic system may enable the end-user (i.e., On-Scene Coordinator) to make a necessary decision quickly, that information may later be lost as documented support for the decision because it is deleted as a "final" version of the data is prepared. Hard copies of some data transfers may never be produced. Some laboratory personnel are using their data management tracking systems as replacements for hand-written records of laboratory activities.

Also at issue are the evidentiary considerations related to computer-generated data. How does the best evidence rule apply to electronically transferred data? How is the issue of admissability, more specifically authenticity, dealt with for computer-generated data?

A solution to these considerations requires constant monitoring by quality assurance personnel for successful implementation. Documentation of data transfers is essential; hard-copies of all data should be produced and filed by the data-generator. Computer usage in the laboratory in lieu of hand-written documents requires that a record be computer-generated in a timely manner (i.e., the same day) and signed and dated by the individual involved. All users of field and laboratory data systems should develop and maintain accurate Standard Operating Procedures (SOPs) for this quality assurance procedure.

A PLANNING TOOL FOR SITE MANAGERS: HISTORICAL PERSPECTIVE ON LITIGATION USES OF SAMPLE DATA FOR EPA CERCLA/SARA CASES

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ABSTRACT.

Data quality objectives are defined in terms of completeness, precision, accuracy, representativeness, and comparibility. The "usability" of data has been traditionally expressed in terms of the end-users responsible for conducting a site study. A second end-user may be a local, state, or Federal litigation team. This second end-user is often not considered in planning for individual site studies or in the management of large analytical programs.

The needs of this second end-user go beyond custody and document control considerations. Data quality and implementation of written protocols by both field and laboratory personnel are being attacked more frequently during settlement negotiations and in the courtroom. Site owners and operators are employing highly sophisticated defense stratagies, sometimes based on criticism of non-conformance by government agencies when following their own procedures.

A review of the uses of data in the litigation process during the last eight years can be a valuable planning tool for both site managers and program managers. An awareness of this secondary use could facilitate future litigation and substantially reduce government costs. The authors will present a review of the historical uses of data in CERCLA/SARA cases during the last 8 years. Each component of the sampling and analytical process will be reviewed. This review will enable managers to accurately assesss their data quality objectives as well as determine the sampling and analytical protocols that have been most useful to this second end-user.

EXAMPLES OF THE USE OF AN ADVANCED MASS SPECTROMETRIC DATA PROCESSING ENVIRONMENT FOR THE DETERMINATION OF SOURCES OF WASTES

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ABSTRACT

One of the most important and complex issues facing the cleanup of Superfund Sites is "who is responsible for site contamination and what percentage of the cleanup costs should be prorated among the Potentially Responsible Parties (PRPs)". This paper describes one approach which has recently been used to answer these questions. This method uses a state-of-the-art mass spectrometric data processing environment to produce visual and quantitative comparisons of chromatographic and mass spectrometric patterns in an attempt to determine the origin of wastes present that produced these patterns.

INTRODUCTION

Routine capillary GC/MS instrumentation and analytical methods using this instrumentation has resulted in the collection of orders of magnitude more data than can easily be processed. The Priority Pollutant analysis protocols are, in effect, efforts to simplify and summarize complex mixture information by searching for specific target compounds. However, for many Superfund Sites, Priority Pollutant characterization gives an incomplete picture of the site, because Priority Pollutants may not be present. The present paper describes a general approach that requires: 1) the waste components are chromatographable, and 2) suspected sources of these wastes are available for analysis.

SUMMARY OF THE APPROACH

One important element in the comparison of chromatograms and mass spectra is that, while these two types of data are quite different, they can be treated in analogous ways. In the present paper, examples are given which show how chromatograms can be compared using the same software and approaches that have been developed for the comparison of mass spectra. Just as histograms of mass intensities (mass spectra) can be used to identify what molecule is present in a complex mixture, so can histograms of chromatographic peak areas (reduced chromatograms) be used to identify the likely source from which the mixture of compounds originated. The following sections show three examples where this approach has been used to determine: 1) the types of wastes at a Superfund Site, 2) the types of wastes in environmental samples adjacent to the site, and 3) the similarity of different gasolines which may be present from leaking underground storage tanks.

This approach could often be used in the place of Priority Pollutant analyses, when samples of suspected sources of wastes are available and when rigid protocols are not required for the quantification and identification of certain target compounds. Significant cost savings can be gained using this approach since **the unequivocal identification of all components is not required** to identify a waste source with high certainty. Indirect cost savings are also realized, since the extraction and analysis

Mass Spectral/Gas Chromatographic Analogies

Analogue		Analogue
Mass Spectrum	< = >	Chromatogram
Mass Spectrum	< = >	Reduced Chromatogram
Compound Producing the Mass Spectrum	< = >	Formulation Producing Reduced Chromatogram

methods are rapid, and interpretation depends upon computer generated graphical output. Field operations can be supported overnight with these extraction, analysis and interpretation protocols.

INSTRUMENTATION AND ANALYTICAL SYSTEMS

All data shown in the present paper were obtained using Hewlett-Packard's RTE-VI mass spectrometric data processing environment. This data processing environment is in effect an array processing system. This system allows for arrays of mass spectrometric and/or gas chromatographic data to be added, subtracted, multiplied, and divided in much the same way as single numbers are manipulated using a hand calculator. One important advantage of this environment is that individual commands or programs which are to be executed can be combined in an ASCII file and executed in much the same way as batch or macro files can be processed in personal computers. Several batch procedure files were developed to produce the various displays shown in the present paper. These procedure files were also written to create HPGL-compatible files that could be transferred to a PC-compatible personal computer which was used to produce the various graphic displays on a 300 dots-per-inch laser printer.

The compatibility of these mass spectrometric data reduction programs with the file structure of Hewlett-Packard's Laboratory Automation System GC/FID and GC/EC raw data files, results in the use of the same batch procedure files for comparing chromatographic data not obtained using a mass spectrometer detector system. This capability allows for PCB formulations and other complex formulations to be easily identified in much the same way as sources of wastes are determined.

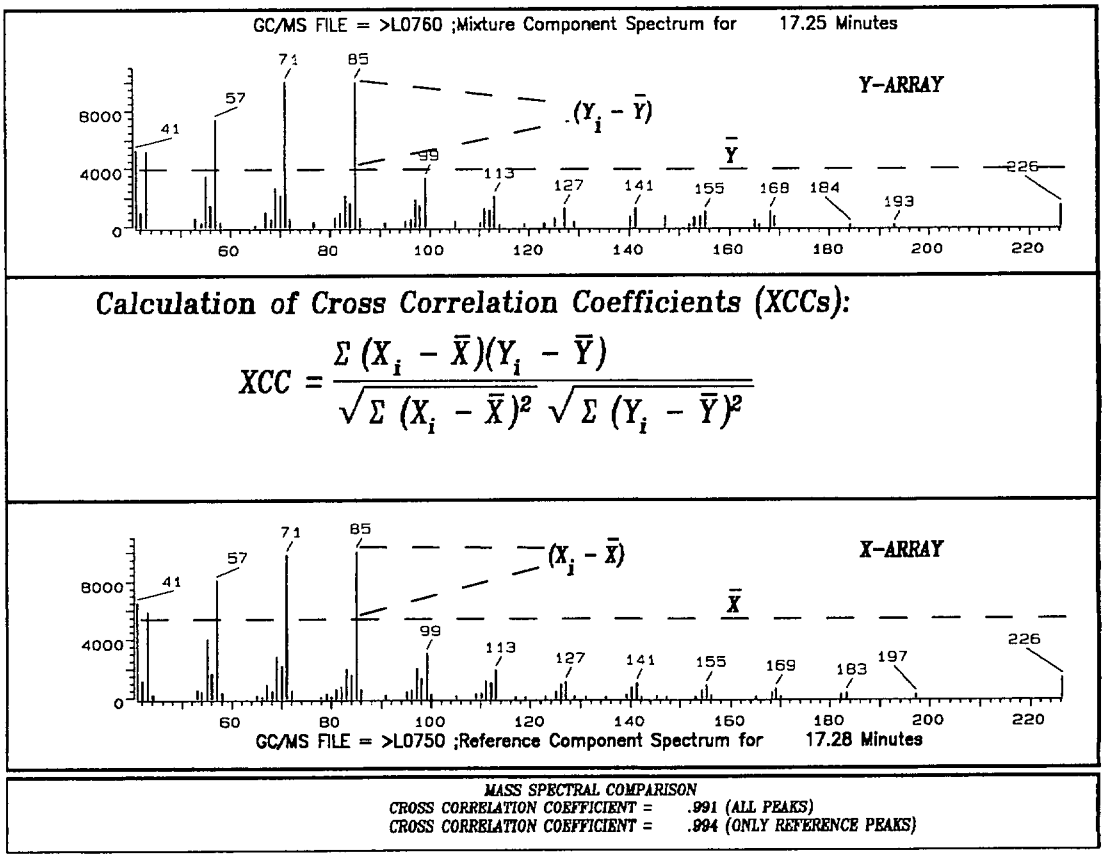
SAMPLE EXTRACTION

The present analysis protocol was designed so that chromatographic patterns could be used as important indications as to the source of unknown wastes. Therefore great care was used so that sample manipulation would not greatly modify the pattern of organics present. In addition, these methods were developed for the relatively high level analysis of organic components present in wastes and environmental samples adjacent to waste sites. Samples in these studies contained total organic concentrations from 0.01 to 100%. Therefore a very simple extraction protocol was required. Sample extraction involved placing a known amount of the waste or contaminated soil in a 14-mL glass vial with teflon-lined lid, adding 10 mLs methylene chloride, and ultrasonically agitating for one-half hour. In most cases, the concentration of individual chromatographable components were in the 1 - 500 μg/mL concentration range of the resulting extract. Since very little sample manipulation was required, no surrogate standards were used. This resulted in the simplification of the chromatographic patterns. Further simplification occurred with the use of only one internal standard (anthracene-d_{10}) for extractable component analysis, and three volatile internal standards for the purgeables analysis.

THE CROSS CORRELATION COEFFICIENT

One of the early ways of comparing two mass spectra which may contain between 10 and >100 mass/intensity pairs of information, was to calculate a cross correlation coefficient (XCC). This was one of the early ways of comparing unknown spectra with a library of spectra. However, this calculation, by itself, did not contain enough information nor could it reliably be used for mass spectra generated on various mass spectrometers. Figure 1 shows the XCC formula and how it can be used to compare two mass spectra of a n-C16-alkane present in two different samples. X_i and Y_i are the individual intensities of the i-th masses in the X- and Y-arrays, and X and Y are the average of the intensities in these two arrays. Note that when the differences between the individual intensities and the average intensity of the two arrays approach each other, the value of the XCC approaches 1.000. Therefore, to a first approximation, the deviation of the XCC from 1.000 can be used as a simple way of determining the deviation of one spectrum from another.

This approach is particularly useful because both spectra are taken under almost identical conditions. Furthermore, the retention times of the two components producing the mass spectra can also be used as an additional parameter in evaluating whether the spectra are being produced



$$XCC = \frac{\Sigma (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\Sigma (X_i - \bar{X})^2}\,\sqrt{\Sigma (Y_i - \bar{Y})^2}}$$

MASS SPECTRAL COMPARISON
CROSS CORRELATION COEFFICIENT = .991 (ALL PEAKS)
CROSS CORRELATION COEFFICIENT = .994 (ONLY REFERENCE PEAKS)

Figure 1. The Cross Correlation Coefficient Calculation Applied to Mass Spectra.

from the same compound. In Figure 1, it can be seen that the Y-array spectrum was obtained for a component having a retention time of 17.25 minutes and the X-array spectrum was obtained from a component having a retention time of 17.28 minutes. Therefore, the similarity of compounds as judged from the XCC being 0.991, and from almost identical retention times, results in the conclusion that the two compounds are identical.

One important property of the XCC calculation is that the correlation can be calculated in a number of ways. As is shown in Figure 1, the XCC is calculated for "all peaks" and for "only reference peaks". This is done by being able to identify a window that is applied to all the data in the X- and Y-array. In the present case, a window of ±0.3 amu is used to determine whether the masses in the two arrays should be treated as the same feature. All mass/intensity information is included in the XCC for "all peaks". However, just those masses in the Y-array which are within the windows of the masses in the X-array are included in the XCC calculated for "only reference peaks". These two calculations are used to determine whether the reference component spectrum (shown in the X-array) may be imbedded in the mixture component spectrum (shown in the Y-array). In the present example, since both XCCs are almost identical and almost 1.000, it can be concluded that over 95% of the mixture component spectrum is produced from the reference component. Examples will be shown later where this distinction is important in searching for spectra of reference components which may be imbedded in spectra in a mixture of components.

APPLYING THE XCC TO CHROMATOGRAPHIC DATA

In order to use the XCC calculation as a way of comparing chromatographic data, the chromatographic data must be presented in much the same way as mass spectrometric data. This is done in Hewlett-Packard's data processing environment by converting the analogue chromatogram to a reduced chromatogram. This reduced chromatogram is no more than a histogram display of the chromatographic (retention time)/(peak area) pairs which is exactly analogous to the mass spectrum histogram display of mass/intensity pairs. Figure 2 shows how the XCC is calculated for reduced chromatograms produced from chromatographic data. One important difference between the reduced chromatograms and mass spectra is that mass spectra have built-in digitizing features since the x-axis is composed of integer masses. This feature simplifies identifying the features in the X- and Y-arrays which are the same and which should be included in the XCC calculation. However, as mentioned above, since a mass window can be defined which is used to determine which mass features are the same, so can the retention time window be used for exactly the same purpose. For the present study, a retention time range of ±4.8 seconds was used. This is very important since for chromatographic data, there are no integral parameters such as mass for the x-axis parameter. The continuous property of chromatographic retention times means that comparisons can be properly made only when the mixture and reference chromatograms are obtained under identical conditions. Approaches have been reported in the literature which involves converting chromatographic retention times to indices, which may help when comparing data obtained under different conditions or from different laboratories. The strength of the present approach is that there is no need for this conversion since the XCC calculation of chromatographic data includes the windowing feature for determining whether chromatographic peaks in two different samples are the same feature.

In Figure 2, the reduced chromatogram features identified as X_1 and Y_1 are the two features for which mass spectra are com-

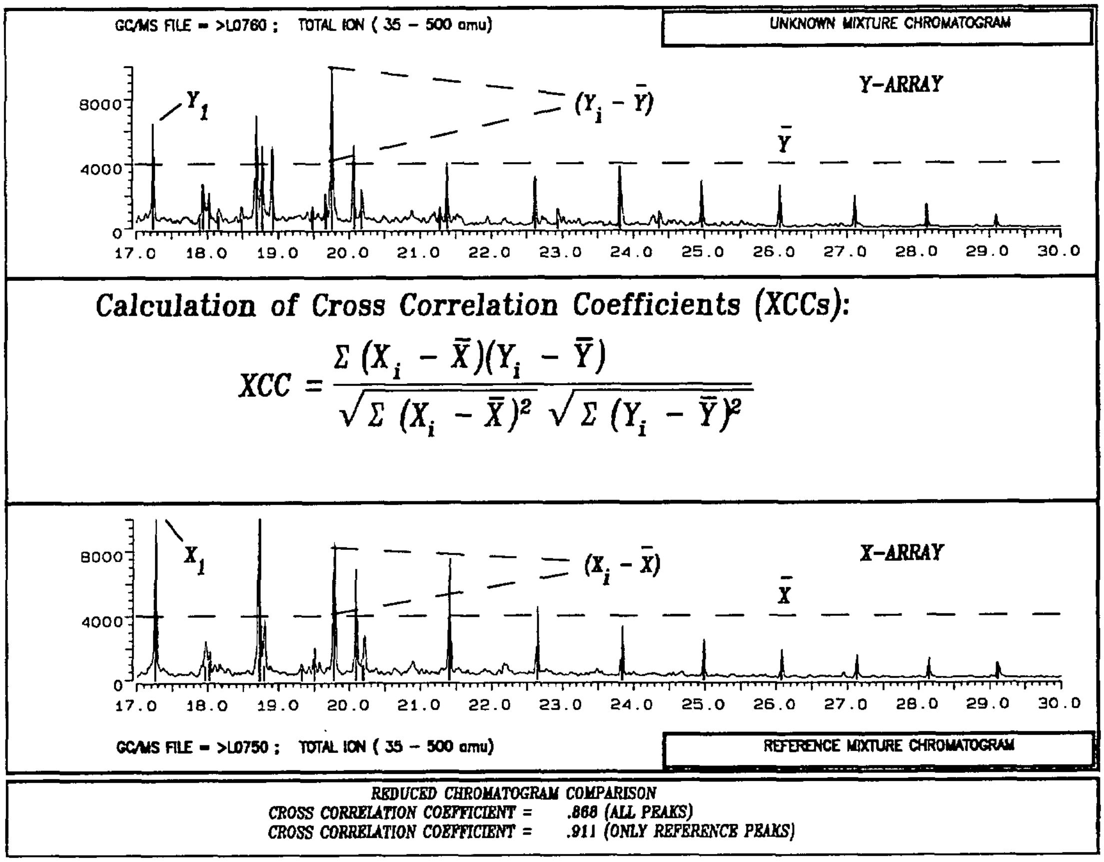


Figure 2. The Cross Correlation Coefficient Calculation Applied to Reduced Chromatograms.

pared in Figure 1. The comparison of chromatograms in combination with the comparison of mass spectra of each of the chromatographic features, is the basis for a very complete and highly reliable comparison of two samples. The following sections show how these comparisons can be used to efficiently and cost effectively answer some difficult questions concerning complex mixtures.

IDENTIFYING SOURCES OF WASTES AT A SUPERFUND SITE

The application of this approach to the study of wastes present at a Superfund Site can be seen in Figures 3 - 8. Figure 3 shows the range of compounds eluting between n-C9-alkanes and n-C26-alkanes. Figure 6 shows the n-C16-alkane through n-C18-alkane region and Figure 8 shows the n-C11-alkane through n-C17-alkane region. The reduced chromatogram XCC calculation for "all peaks" shows that a large number of Crude Oil Sample components are present in the Waste Sample. Detailed comparisons of mass spectra of the major and minor crude oil components give mass spectral XCCs on the order of 1.000. Figure 8 shows an example where an imbeded chromatographic pattern of the Styrene Waste Sample is also present in the Waste Sample chromatogram. The reduced chromatogram XCCs of 0.305 for "all peaks" and 0.874 for "only reference peaks" shows that the Styrene Waste Sample pattern is present in minor quantities. XCC comparisons of mass spectra of the major and minor Styrene Waste Components are on the order of 1.000. Figures

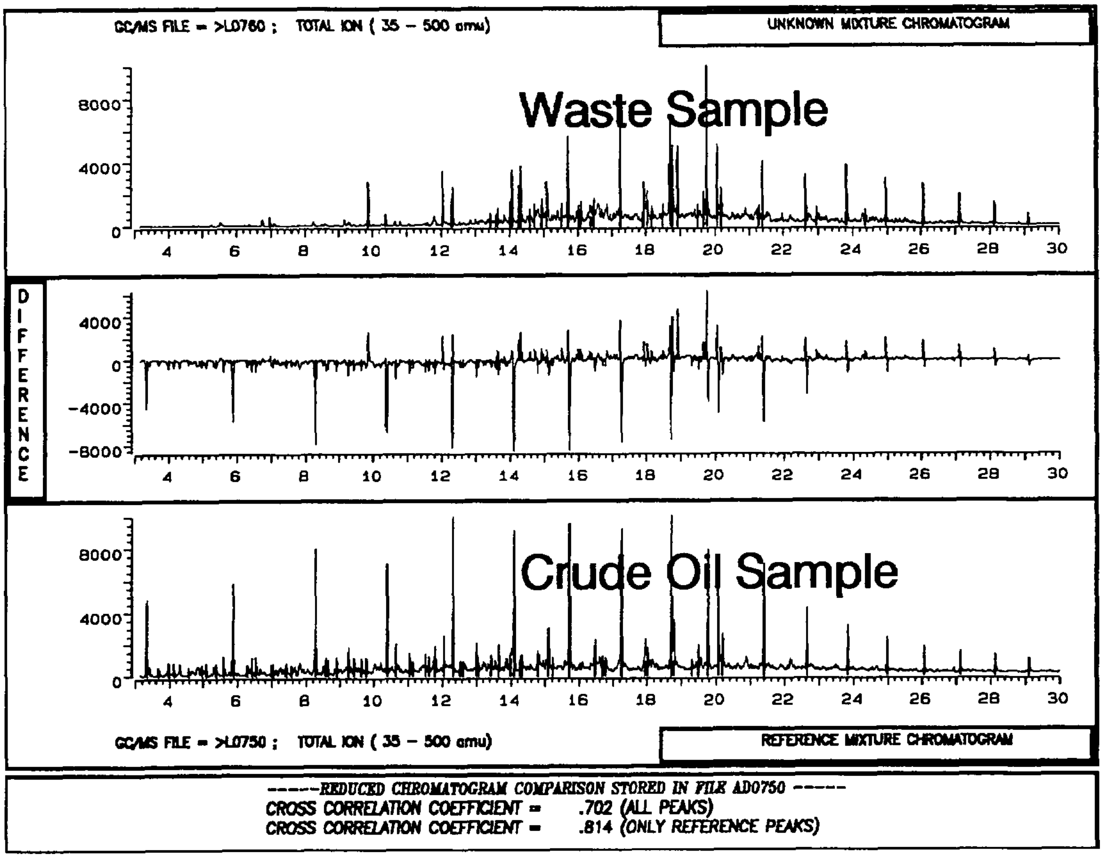


Figure 3. Comparison of Chromatographic Patterns of a Superfund Site Waste Sample and a Crude Oil Sample.

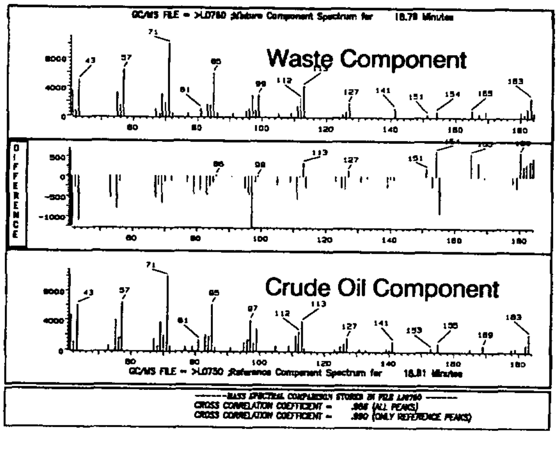


Figure 4. Comparison of Pristane Mass Spectra in Superfund Site Waste and in Crude Oil.

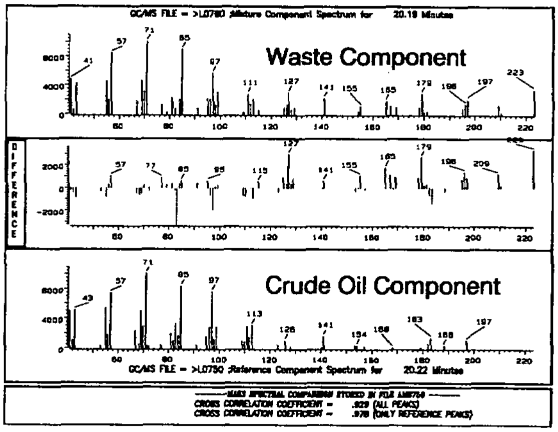


Figure 5. Comparison of Phytane Mass Spectra in Superfund Site Waste and in Crude Oil.

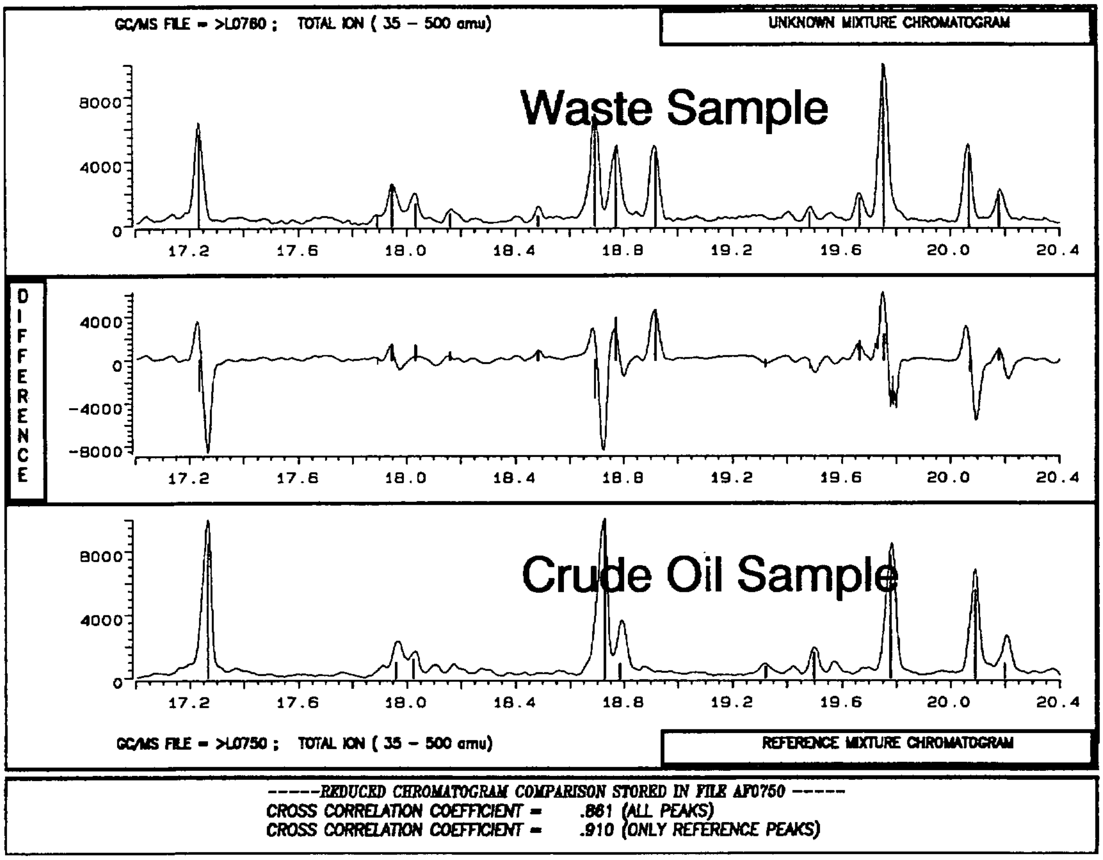


Figure 6. Comparison of a Narrow Region of Chromatographic Patterns of a Superfund Site Waste Sample and a Crude Oil Sample.

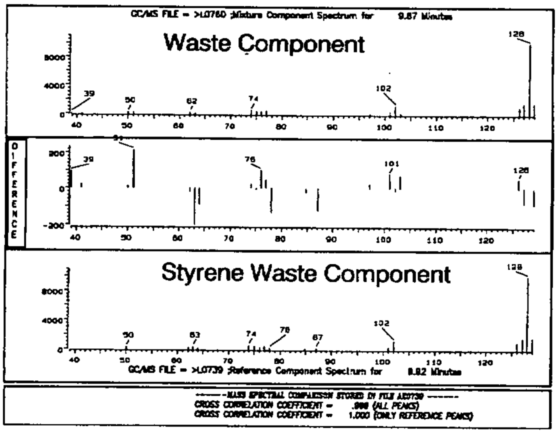
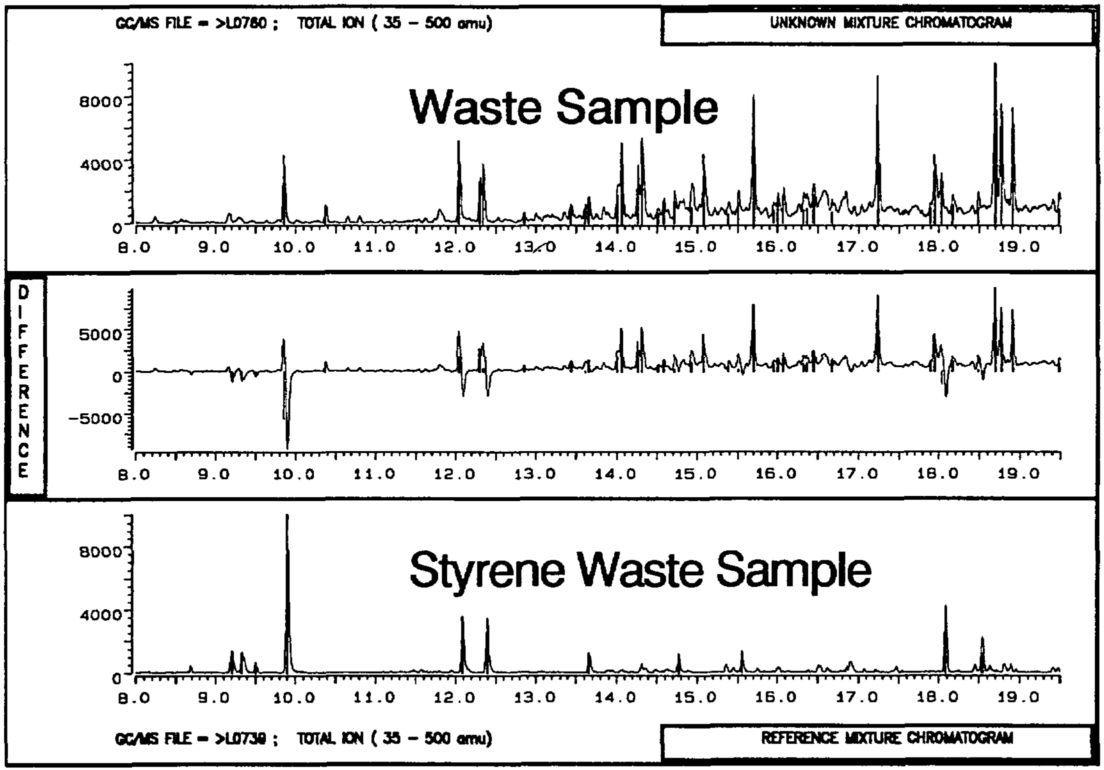


Figure 7. Comparison of Naphthalene Mass Spectra in Superfund Site Waste and in Styrene Waste.

4 and 5 show the comparison of mass spectra of pristane and phytane which are crude oil biomarkers and Figure 7 shows the comparison of naphthalene which is the major chromatographable component present in the Styrene Waste Sample.

Conclusions: A major source of contamination at this Superfund Site has its origins from the petroleum industry. As a result of this conclusion, extensive interviews with waste haulers in the region confirmed this fact. Ultimately, Clean Sites Incorporated reviewed this data and confirmed our findings which resulted in a portion of the remediation costs being paid by Petroleum Industry PRPs.



-----*REDUCED CHROMATOGRAM COMPARISON STORED IN FILE AB0739* -----
CROSS CORRELATION COEFFICIENT = .305 (ALL PEAKS)
CROSS CORRELATION COEFFICIENT = .874 (ONLY REFERENCE PEAKS)

Figure 8. Comparison of Chromatographic Patterns of a Superfund Site Waste Sample and a Styrene Waste Sample.

IDENTIFICATION OF SOURCES OF CONTAMINATION ADJACENT TO A SUPERFUND SITE

Figures 9 and 12 summarize chromatographic data obtained from an Adjacent Soil Sample Extract, a #6 Fuel Oil Sample, and a Styrene Waste Sample obtained from the Superfund Site. Comparison of the XCCs calculated from these comparisons indicates that the #6 Fuel Oil pattern is more similar to the Soil Extract than the Styrene Waste Sample. In the comparison with the Styrene Waste Sample shown in Figure 12, the XCC for "all peaks" is 0.286 and the XCC for "only reference peaks" is 0.563. In this case, the higher XCC for "only reference peaks" does not indicate that the Styrene Waste Sample pattern is imbedded in the Soil Extract pattern. This higher value is due to the fact that some of the major components in the Soil Extract are also present in the Styrene Waste Sample. However, none of the minor components present in the Styrene Waste Sample are detected in the Soil Extract, although they should have been detected if the Styrene Waste pattern had been present in the Soil Extract pattern. Figures 10 and 11 compare mass spectra of methyl and dimethyl naphthalene isomers in the Soil Extract and in #6 Fuel Oil.

Conclusions: The likely source of contamination in this area adjacent to the Superfund Site was from fuel spills rather than waste migration from the site. The actual site from which the contaminated soil was obtained was from an area which had been filled with off-site soil prior to commercial development.

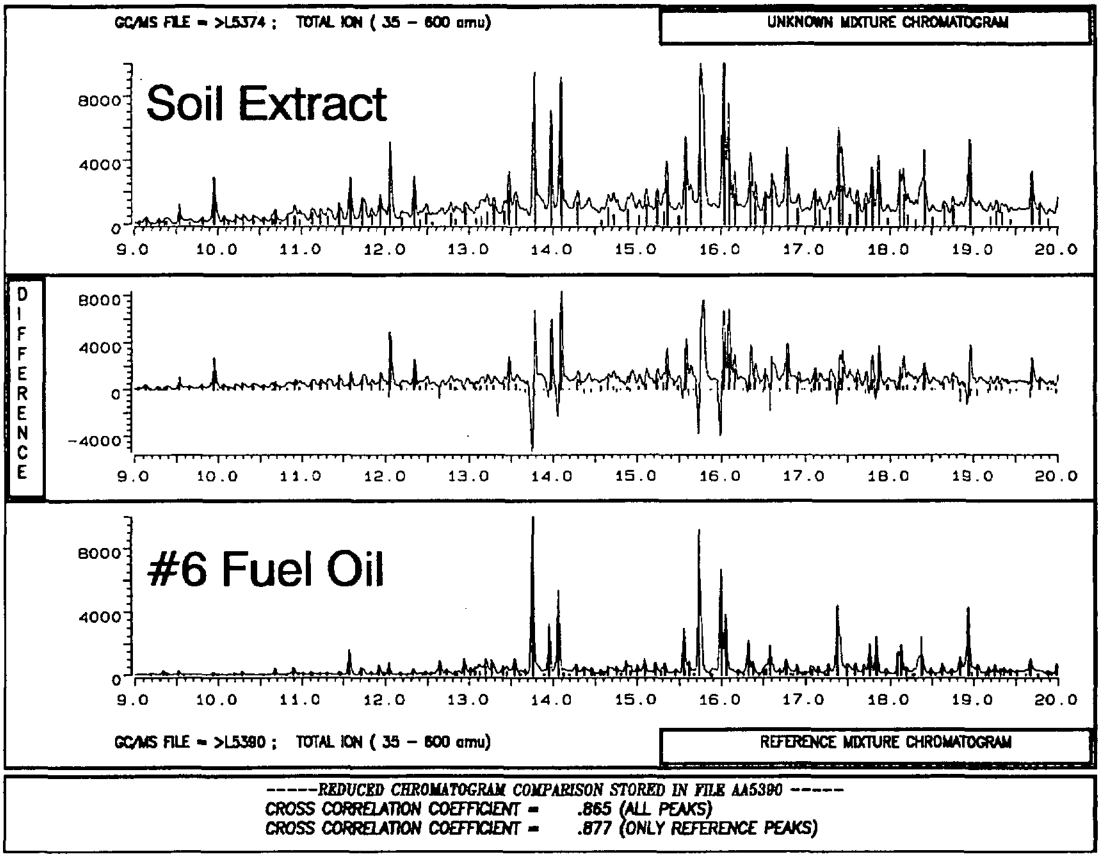
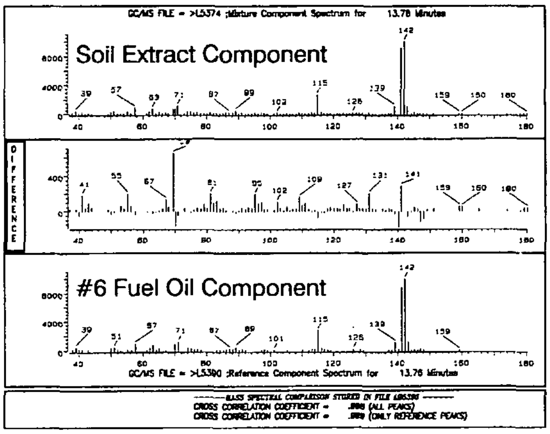


Figure 9. Comparison of Chromatographic Patterns of a Site Adjacent to a Superfund Site and #6 Fuel Oil.



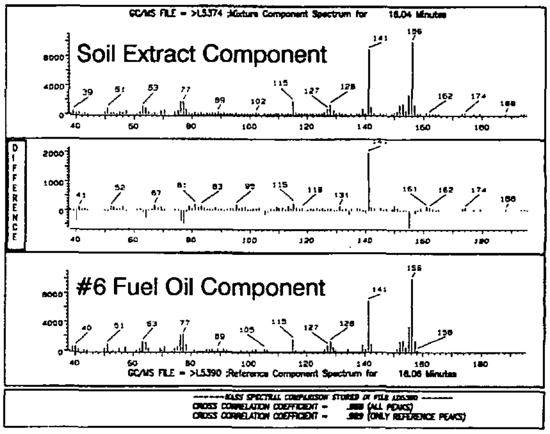


Figure 10. Comparison of Methyl Naphthalene Isomer Mass Spectra in an Adjacent Site and in #6 Fuel Oil.

Figure 11. Comparison of Dimethyl Naphthalene Isomer Mass Spectra in an Adjacent Site and in #6 Fuel Oil.

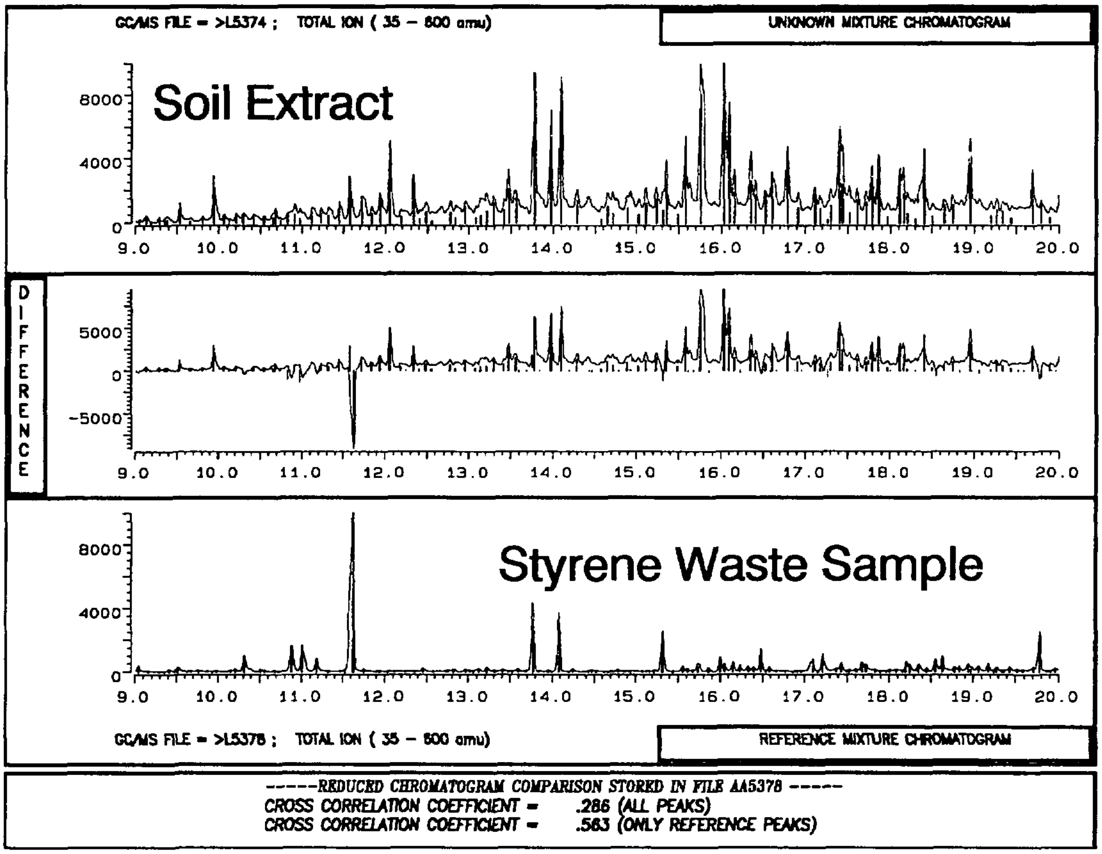
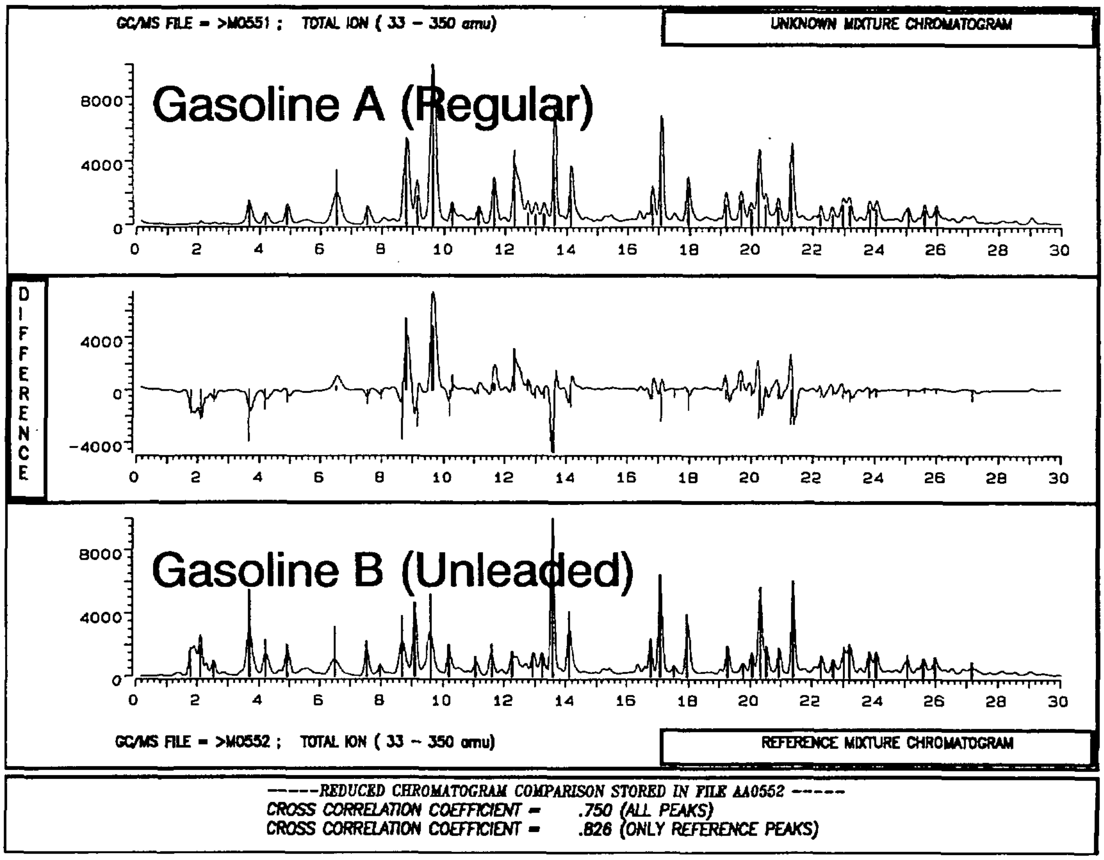


Figure 12. Comparison of Chromatographic Patterns of a Site Adjacent to a Superfund Site and a Styrene Waste Sample.

COMPARISON OF GASOLINE SAMPLES

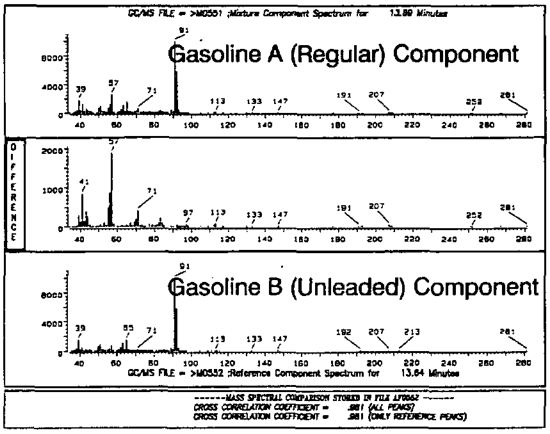
One potentially important source of environmental contamination is from leaking underground storage tanks. When these tanks contain petroleum distillates such as different grades of gasoline or diesel fuel, it is very difficult to determine the sources of this contamination, using standard EPA protocols. This difficulty arises since many of these components are not present in the volatile priority pollutant list and standard EPA analysis protocols would overlook some of the major features of these formulations. Figures 13, 16, and 19 compare chromatographic patterns of Gasoline A (Regular) with Gasoline B (Unleaded), Gasoline C (Diesel), and a Volatile Priority Pollutant Standard, respectively. The comparisons of Gasolines A and B show that Regular and Unleaded are very similar, while Gasoline C (Diesel) and the Volatile Priority Pollutant Standard are very different.

Figures 14 and 15 show the high similarity of mass spectra of toluene and a trimethyl benzene isomer in Gasolines A and B. Figures 17 and 18 compare the mass spectra of 1,4-dichlorobutane internal standard and a trimethyl benzene isomer in Gasolines A and C. Note in Figure 18 that Gasoline C also contains a significant amount of n-hydrocarbon spectrum in the Gasoline C feature mass spectrum. This fact is reflected in the low XCC (0.579) and the large positive and negative mass intensities shown in the difference spectrum.



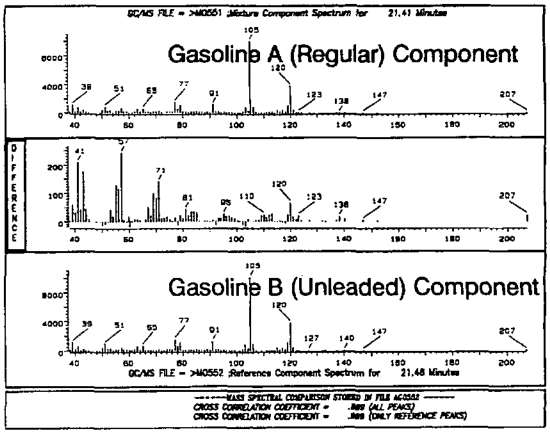
-----REDUCED CHROMATOGRAM COMPARISON STORED IN FILE AA0552 -----
CROSS CORRELATION COEFFICIENT = .750 (ALL PEAKS)
CROSS CORRELATION COEFFICIENT = .826 (ONLY REFERENCE PEAKS)

Figure 13. Comparison of Chromatographic Patterns of Gasoline A (Regular) and Gasoline B (Unleaded).



------MASS SPECTRAL COMPARISON STORED IN FILE AF0662 ------
CROSS CORRELATION COEFFICIENT = .981 (ALL PEAKS)
CROSS CORRELATION COEFFICIENT = .981 (ONLY REFERENCE PEAKS)

Figure 14. Comparison of Toluene Mass Spectra in Gasolines A (Regular) and B (Unleaded).



------MASS SPECTRAL COMPARISON STORED IN FILE AC0552 ------
CROSS CORRELATION COEFFICIENT = [illegible] (ALL PEAKS)
CROSS CORRELATION COEFFICIENT = [illegible] (ONLY REFERENCE PEAKS)

Figure 15. Comparison of Trimethyl Benzene Isomer Mass Spectra in Gasolines A (Regular) and B (Unleaded).

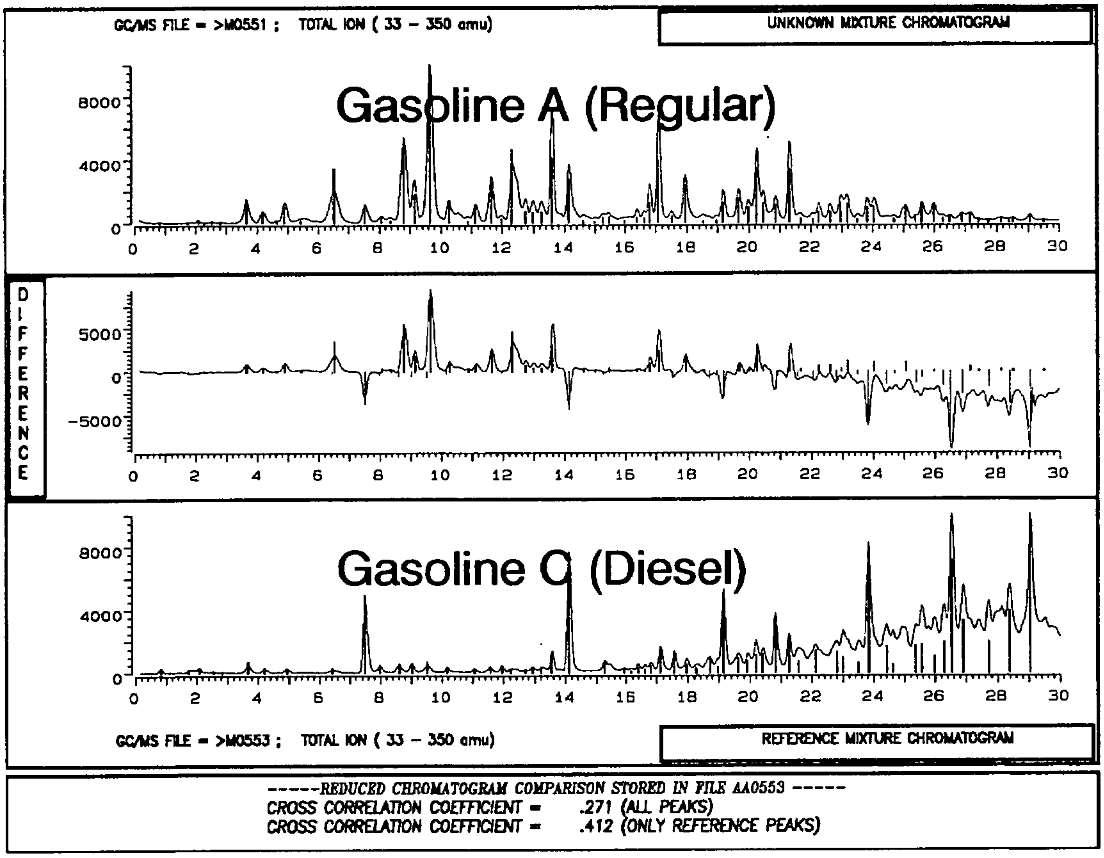


Figure 16. Comparison of Chromatographic Patterns of Gasoline A(Regular) and Gasoline C (Diesel).

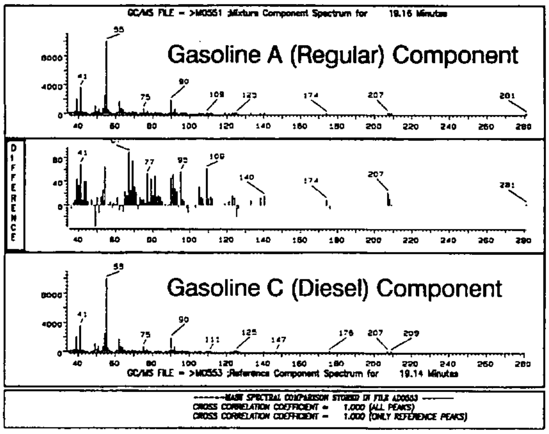


Figure 17. Comparison of 1,4-Dichlorobutane Internal Standard Spectra in Gasolines A (Regular) and C (Diesel).

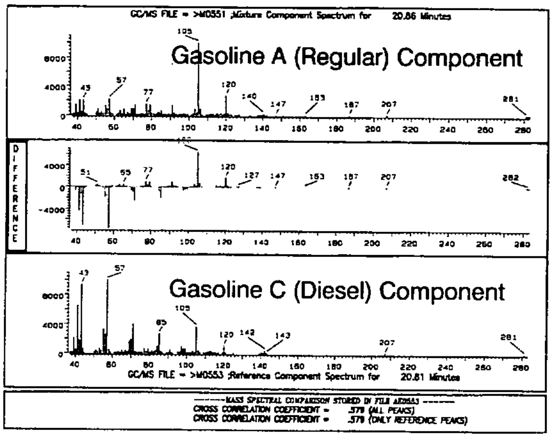


Figure 18. Comparison of Trimethyl Benzene Spectra in Gasolines A (Regular) and C (Diesel).

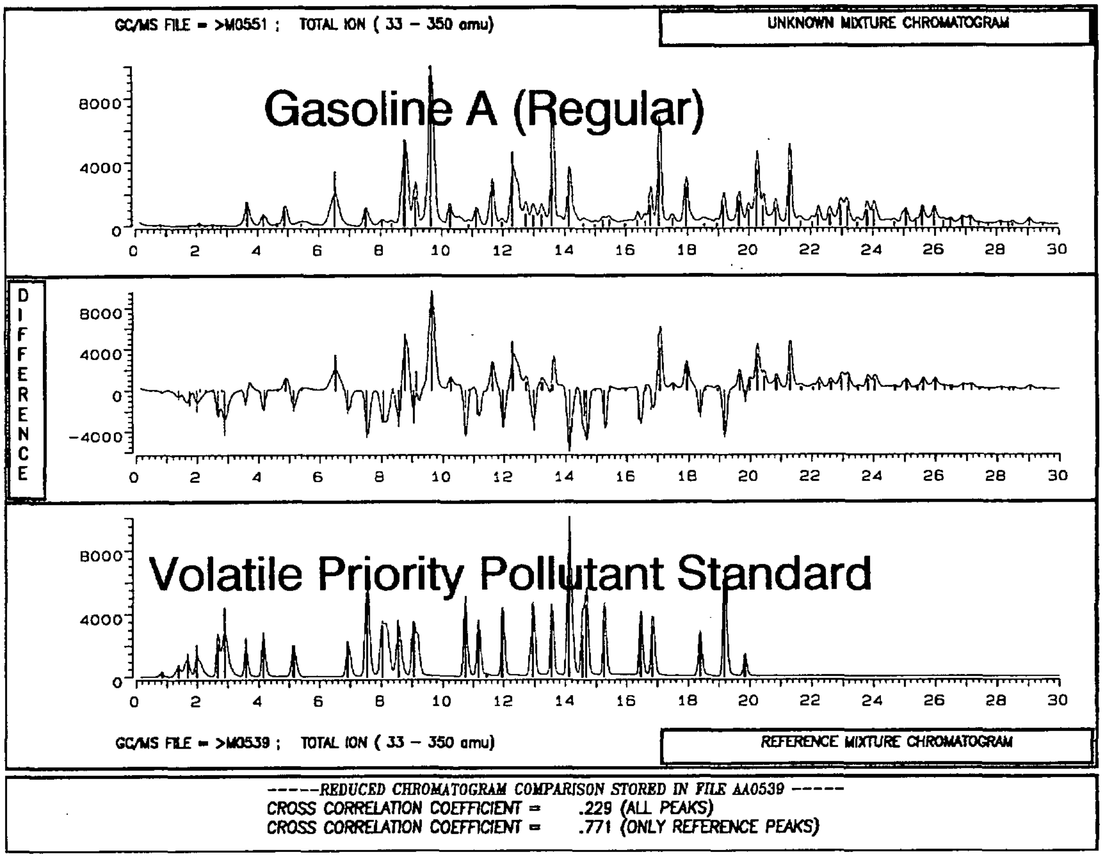
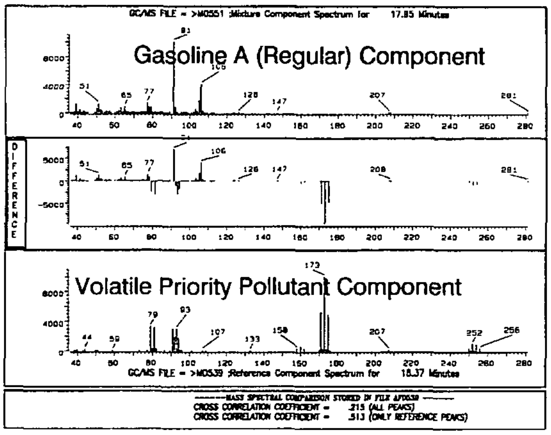


Figure 19. Comparison of Chromatographic Patterns of Gasoline A (Regular) and an 80 μg/L Volatile Priority Pollutant Standard.



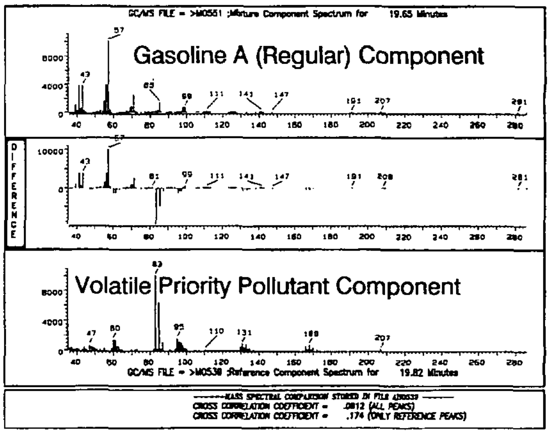


Figure 20. Comparison of Dimethl Benzene and Bromoform Spectra in Gasoline A and Priority Pollutant Standard.

Figure 21. Comparison of Hydrocarbon and Cl_4-ethane Spectra in Gasoline A and Priority Pollutant Standard.

Figures 20 and 21 compare mass spectra of two features present in Gasoline A and an 80 μg/L Volatile Priority Pollutant Standard. Low XCCs and large positive and negative intensities in the difference spectra show that these Gasoline A features are not present in the Volatile Priority Pollutant Standard.

The comparison of gasoline samples highlights an important limitation of this approach. While the first two examples of this approach for Superfund Site wastes were for fairly high molecular weight compounds which were present in highly contaminated organic wastes, contamination of water by highly volatile organic compounds presents several problems when chromatographic pattern comparisons are used. Patterns can be changed due to component volatility and due to partitioning between soil and rock with which the water samples may come in contact. Therefore it may be very difficult to obtain a pattern of the suspected waste source which has been subjected to exactly the same weathering processes as the actual sample in question. However, the presence of many of the same components in an unknown mixture which are also present in gasoline samples, may be a strong indication of the source of these components.

SUMMARY

The calculation of Cross Correlation Coefficients for reduced chromatographic and mass spectrometric data is a very powerful way of comparing complex chemical data. This approach allows for the very rapid evaluation of differences and similarities of samples which may contain a large number of discrete chromatographable components. The major strength of this method lies in the fact that specific, unequivocal identification of unknown compounds is not required in order to make very important, fundamental decisions concerning complex mixtures. In addition, this method can be extended to any data which has been acquired on compatible computer systems. This latter strength makes this processing approach available to HPLC/MS, pyrolysis/GC/MS, GC/FID, GC/EC, and any GC/detector data which has been acquired on HP-1000 systems which have compatible file structures with Hewlett-Packard's present RTE-VI mass spectrometer operating system.

CALIFORNIA'S PROPOSITION 65, A VOTER APPROVED ENVIRONMENTAL LAW

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ABSTRACT. California's Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986, became law through the initiative process. It is voter-passed legislation designed to reduce public exposure to toxic chemicals. Under the Act, the Governor's Scientific Advisory Panel is mandated to develop a list of chemicals "known to cause cancer or reproductive toxicity"; the list included 269 materials in January, 1989. Individuals and businesses are prohibited from knowingly discharging a significant amount of these chemicals into drinking water or from exposing individuals to these chemicals without prior warning. The Act defines a "significant amount" as any detectable amount of a chemical, as long as that concentration (1) conveys with it an excess risk of cancer of 1 in 100,000 (10^{-5}), or (2) exceeds 1/1000 the no-observable-effect-level (NOEL) for reproductive toxicants. Because standardized measurement methods are not available for all 269 chemicals, the Air and Industrial Hygiene Laboratory of the California Departments of Health Services (CDHS) has been made responsible for the evaluation of suitable collection and analysis methods. While the state does not have a specific monitoring program for Proposition 65 analytes, these methods may be required when individuals attempt to recover damages from businesses under the provisions of the Act. The authors will discuss how California is developing the mandated list of chemicals, is setting their lawful limits, and is evaluating methods for sampling and analysis.

INTRODUCTION

In 1986 the voters of the State of California manifested their concern for hazardous chemicals by passing into law "the Safe Drinking Water and Toxic Enforcement Act" (Health and Safety Code section 25249.5 et seq.). This act became law by a direct vote of the people under the initiative process of the California constitution. The Act prohibits persons in the course of doing business from knowingly contaminating drinking water with chemicals known to the State to cause cancer or reproductive toxicity or from knowingly exposing individuals to such chemicals without prior warnings. The Governor is required to name and consult with a Scientific Advisory Panel (SAP) in order to establish a list of such chemicals. Businesses are required to issue warnings before any listed chemicals are discharged into the environment (water, air, food, or soil), incorporated into consumer products, or used in a fashion that will result in occupational exposure.

The Act is aimed at limiting public exposure to these toxic substances by requiring companies to restrict discharges of the listed chemicals and to alert workers and customers whenever any of the listed chemicals are discharged. Under the penalty provisions of the act, businesses may be brought to trial by the California Attorney General or local Districts Attorney's. for violating the Act. Individuals may initiate such proceedings and may be awarded portions of any fines if they intervene in a case on an ex-parte basis.

TARGET COMPOUNDS AND ACTION LEVELS

The first 29 chemicals were listed under the Act on February 27, 1987; those chemicals included the 26 suspect human carcinogens listed by the International Agency for Research on Cancer (IARC) and three reproductive toxicants. As of January 1, 1989, the state had increased the number of chemicals to 269 (238 carcinogens and 31 reproductive toxicants). Roughly half (137 of 269) of the listed material are included in U.S. EPA's Appendix VIII (47 Federal Register 32296 [July 26, 1982]). Annual updates of the Proposition 65 list of chemicals are required under the terms of the Act. Once a chemical is listed, warnings are required 12 months after the listed date, and discharge prohibitions are required 20 months after listing.

The state must establish what constitutes a significant amount of each listed material, that is, the quantity that may exist before a warning must be issued or an illegal discharge reported. The Act (section 25249.11, subdivision (c) of the Health and Safety Code) defines "significant amount" as any detectable amount of a chemical, unless the chemical concentration in question conveys with it no significant risk of cancer or does not exceed one one-thousandth of the no observable effect level (NOEL) for reproductive toxicants (section 25249.10 (c)). The California State Health and Welfare Agency performs quantitative risk assessments to determine those concentrations and to establish the lawful levels for the materials listed under the Act. As of January 1, 1989, lawful levels have been established for 50 carcinogens (sections 12709 and 12711) and two reproductive toxicants (section 12805). One chemical, ethylene oxide, has lawful levels for both carcinogenicity and reproductive toxicity.

The detection limits for measurement methods suitable for this application are calulated using the lawful levels and exposure scenarios for environmental, occupational, and dietary sources. To date, the exposure scenarios for drinking water and breathing air have been established. Section 12721 of the Act assumes that a person consumes two liters of water a day. The target detection limit (TDL, µg/L) for drinking water methods are determined by dividing the lawful level (µg/day) by 2 L/day. Section 12707 of the Act assumes that a person respires 20 m^3 of air per day. The target detection limit (TDL, µg/L) for air methods are determined by dividing the lawful level (µg/day) by $20m^3$/day).

In order to implement the Act, it is critical for businesses and enforcement agencies to have standardized sampling and analysis methods which are capable of measuring the listed chemicals at their lawful levels. In most cases, standard methods are not available to measure the target chemicals at the low concentations required. CDHS, through the Air and Industrial Hygiene Laboratory and its contractor S-Cubed, initiated a project to conduct a comprehensive survey and evaluation of sampling and analysis methods that can provide low detection limits. The U.S. EPA, through the Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) and Region 9, is cooperating in this effort. This article describes the progress in evaluating methods for the analysis of the 51 compounds with established lawful levels.

METHODS

There are three possible scenarios to be expected in the evaluation of methods of detection for the listed chemicals as follows: For some chemicals, there exists a validated, standardized method that includes a comprehensive quality assurance (QA) program with detailed quality control (QC) requirements; methods for these compounds need only be compiled, evaluated and reported. For other chemicals, a scientifically acceptable method has been developed but it lacks validation or comprehensive QC procedures; these will require single-laboratory validation. For a third group of chemicals, there is no acceptable method available, and method development efforts will be needed. In the initial phase of this project, methods for chemicals in the first category are evaluated and compiled.

For listed chemicals in the first category, there are standardized methods that have already been published by federal or state agencies or professional organizations such as the U.S. Environmental Protection Agency (U.S. EPA), U.S. National Institute of Occupational Safety and Health (NIOSH), U.S. Food and Drug Administration (FDA), CDHS, California Department of Food and Agriculture (CDFA), California Air Resources Board (CARB), California State Water Resources Control Board (CWRCB), California Regional Water Quality Control Board (CRWQCB), local air pollution control districts (APCDs), Association of Official Analytical Chemists (AOAC), and American Society of Testing and Materials (ASTM). In the initial phase of this project, the following publications have been used to compile and evaluate the standardized methods. Several method compendia published by EPA include the "Test Methods for Evaluating Solid Waste (SW-846)" organized by the Office of Solid Waste, and the "Analytical Methods for CERCLA Hazardous Substances" prepared for the Office of Emergengy and Remedial Response by the EMSL-LV. The "Recommended Methods of Analyses for the Organic Components Required for AB 1803" published by CDHS includes a number of EPA and CDHS water methods. CDHS's Environmental Laboratory Accreditation Program is in the process of assembling a collection of validated methods for drinking water and hazardous waste. Method detection limits (MDLs) and analytical methods are available from these publications and other literature for a number of the chemicals listed.

During the first phase of this project, federal and state methods for these 51 chemicals are being evaluated to find methods which can detect chemicals in water at levels as close as possible to the lawful levels. A critical factor in the evaluation of methods is the MDL. MDL was chosen as a basis of comparison because the term is recognized within the analytical community as the smallest reliably detectable quantity of an analyte (40 CFR Part 136, Appendix B, Vol.49, No. 209, October 26, 1984). Most authorities in the field agree that this quantity is related to the standard deviation (SD) of replicated standard analyses at near-zero analyte concentrations. The detection signals must be at least three times larger than the noise of the system. The MDL is a basic performance characteristic of an analytical method and is matrix-sensitive. The following equation is used to calculate the MDL from seven replicate analytical determinations:

$$MDL = (t_{.99})(SD)$$

where SD is the standard deviation of the average analyte recovery from the seven determinations, and $t_{.99}$ is the Student's t value (one-tailed) for n-1 determinations at the 99% confidence level. Generally, it is possible to estimate closely the MDL for matrices with which the analyst has had some experience.

Methods examined under this project are intended for regulatory purposes. In order to provide a routine procedure for evaluating and comparing the methods, a risk-detection ratio (RDR) is obtained by dividing the TDL by the MDL. Values for RDR that are one or greater indicate that the method will detect analytes a concentrations equal to the TDL. In general, RDR values of five to ten or greater are preferred for regulatory purposes. This value was chosen because analytical methods should not be used to produce regulatory quality data a the MDL; action levels should be greater than the limit of quantitation (LOQ) of a method. The U.S. EPA defines this concentration as the practical quantitation limit (PQL) of a method and CDHS defines it as "detection limits for the purpose of data reporting" (DLR).

All methods that are acceptable for monitoring and enforcement provisions of the act will be accumulated in a database by CDHS. The database will be developed using the program Q and A. This database will contain method performance data (precision, accuracy, method detection limit, linear concentration range, and suitability for specific matrices), the level of method validation, specific QC requirements, and compatible cleanup procedures.

RESULTS

Table I includes the lawful levels (μg/day) for chemicals that have been established under the Act as of January 1, 1989; these chemicals have been given higher priority for method evaluation. Tables II and III list CDHS and EPA methods in water and compare the MDL or DLR with the TDL. Table II lists chemicals with at least one water test method which has a RDR equal or greater than 1; Table III lists those with a RDR less than 1. Table IV shows chemicals which do not require water methods because they are listed as inhalation hazards only. Table V lists chemicals for which no appropriate methods are currently available.

The information presented in Table II indicates that there are methods suitable for measuring 21 of the analytes. The most sensitive organic methods (those with the lowest MDL or DLR) use gas chromatography (GC) with selective detectors (EPA methods 502.2, 603, 607, 8081 and 8141) or high performance liquid chromatography (HPLC) (EPA methods 605 and 8310). Analytical methods that use GC/mass spectrometry (GC/MS, EPA Methods 524.2, 8270, 8280 and 8290) provide better identification of analytes but have higher MDL's. In contrast, the most sensitive method for arsenic, the only inorganic analyte listed in Table II, is an inductively coupled plasma/MS technique. It is anticipated that routine EPA water sampling methods will be suitable for all 21 of these analytes. It is hoped that the same measurement methods can be used for the analysis of water, soil, air, and other matrices once appropriate sample collection and preparation methods are identified.

At the present time there are no accepted EPA or CDHS methods with the sensitivity to measure the lawful levels in water for nine of the analytes (Table III). Methods that may be suitable for hexachlorobenzene (draft 8080.1) and for lead (preconcentration) are under development at EMSL-LV and are expected to be submitted for review in October. Potential HPLC method(s) for the six nitrogen containing analytes (benzidine, dinitrotoluene, and the nitroso compounds) are being investigated at EMSL-Cincinnati (EMSL-Ci). While a more sensitive method for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD, Method 8290) has been submitted for U.S.EPA review by EMSL-LV, its RDR value is still less than one. Once the most suitable method is obtained for any of these analytes, it will be added to the CDHS data base.

Among the 51 analytes listed in Table I, according to section 12707 of the Regulations, six materials have been designated as inhalation hazard only (Table IV). They are asbestos, beryllium, beryllium oxide, beryllium sulfate, cadmium, and hexavalent chromium compounds. These analytes may require no methods for analysis in water; the air matrix will be dealt with in a later report.

Those materials for which no appropriate method is available are listed in Table V. Methods for three of these analytes are being developed by the EMSL-Ci in support of the RCRA program. The remaining 14 analytes pose particular analytical problems in water or are not clearly defined. As a result, it is unlikely that suitable methods will be located for this group. A brief paragraph describing the problems and a recommended solution is provided for each of the 14 analytes.

1,3-Butadiene. The initial literature search did not provide any analytical methods with low MDL. Since it is a gas at room temperature with low water solubility, it may be determined in air only. 1,3-Butadiene reacts with hydroxy radicals in air to form acetaldehyde and acrolein.

Bis(chloromethyl)ether. Analytical measurement of this analyte in water at low MDLs is extremely difficult. This is primarily due to decomposition of the analyte by water (half-life 10-38 seconds at pH 7). This analyte may be determined in air only.

Chlordane. Technical chlordane consists primarily of heptachlor and two chlordane isomers with the remainder being hexa-, hepta-, and nonachlor and other related dicyclopentadienes. Chlordane itself has two structural isomers, alpha and gamma chlordane. The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample matrix and its history, almost any combination of the 11 major and 30 minor components in the technical mixture can be found. Because of the inability to predict a chlordane residue pattern for GC, a simple method cannot be specified. If alpha and gamma chlordane were specified under the Act, the ambiguity from the analytical determination could be removed. Method 8081 is suitable for the determination of the major chlordane isomers and heptachlor.

Coke oven emissions. This is a complex mixture which requires definition. Coke oven emissions are known to contain polyaromatic hydrocarbons (PAH's) which could be analyzed by EPA Method 8270 (GC/MS) or Method 8310 (HPLC).

Epichlorohydrin. This analyte does not purge well and decomposes in water (half-life 29 days). It is currently not on any EPA water or soil method list. It may be determined in air only.

Ethylene oxide. Epoxide compounds in general are reactive and water-sensitive. This analyte does not purge well and decomposes in water (half-life 9-14 days). It may be determined in air only.

Hexachlorocyclohexane (technical grade). This analyte is a mixture of chemicals also known, and improperly named, as benzene hexachlorides (BHC's). The name arises from the industrial production of technical hexachlorocyclohexane by the chlorination of benzene. Technical-grade BHC or hexachlorocyclohexane consists of a mixture of six hexachlorocyclohexane isomers and several isomers of heptachloro- and octachlorocyclohexane. The most toxic isomer, gamma-BHC, is also called lindane. EPA Method 8081 will measure the four major components (alpha-, beta-, gamma- and delta-BHC) of the technical mixture.

Nickel Refinery Dust from the pyrometallurgical process. Further definition is needed for this analyte. Its toxicity may be caused by the fact either that it is a dust or that it is a metal. If its toxicity is due to the physical properties as a dust, then air is an appropriate matrix to sample. If the toxicity is due to the chemical properties as a metal, then Method 6020 should be suitable.

Nickel subsulfide. This analyte presents a particularly difficult analytical problem. It is a complex mixture of two oxidation states of nickel. Because it is a sulfide chelate of a metal, it is virtually insoluble in water, and thus is an inappropriate analyte for that matrix. An exhaustive literature search is currently in progress to locate an analytical method specific for nickel subsulfide.

N-Nitrosodiphenylamine. Determination of this analyte is ambiguous because it decomposes in the inlet of GC and GC/MS systems to diphenylamine and is then quantitated as such. While the EMSL-Ci has recently published an HPLC/MS method for N-nitrosodiphenylamine, it has a significantly higher MDL than Method 8270.

N-Nitroso-N-ethylurea and N-Nitroso-N-methylurea. No suitable methods have been found for these analytes yet.

Methods for most of the N-nitroso compounds researched thus far have fallen short of the TDL by significant margins. Based on the chemistry of these analytes, it is probable that validated methods for their determination at the low lawful levels specified under the Act cannot be found.

Polychlorinated biphenyls (60% or greater chlorination). Polychlorinated biphenyls are normally found in complex mixtures(i.e., Aroclors). The most sensitive methods for Aroclors employ GC/electron capture detector (GC/ECD), and the identification is almost always done by recognition of the characteristic Aroclor pattern. These methods are not congener- specific so they are inappropriate due to the Regulation's stipulation for biphenyls with 60% or greater chlorination. More appropriate methodology (Method 680) employs GC/MS and software that allows the analyst to determine level of chlorination for the biphenyls. Unfortunately, Method 680 may not be suitable for this application because congeners with different levels of chlorination are not always resolved by GC and the GC/MS hardware responds better to biphenyls with less than 60% chlorination. If low-level detection of polychlorinated biphenyls is required, a GC/ECD pattern recognition method for determining Aroclors may be required. Improvements in Method 8081 being developed at the EMSL-LV should provide better PCB isomer identification than existing methods.

Toxaphene. The analyte is a complex mixture of chlorinated camphenes. A determination of toxaphene is normally done by using GC/ECD and pattern recognition. Pattern recognition is difficult, however, in the presence of interfering GC/ECD peaks.

CONCLUSIONS

California's Safe Drinking Water and Toxic Enforcement Act of 1986 is the first environmental law in which the risk assessment values of health effect evaluation have regulatory impact. The state has listed 269 chemicals as carcinogens or reproductive toxicants; lawful levels for discharge or exposure for 51 of these compounds have been established. Preliminary evaluations of analytical methods for the 51 analytes have been completed and methods are available for 21 of the analytes with sufficient sensitivity for regulatory purposes. The limitations of standard methods to measure these analytes at toxicologically relevant concentrations is apparent. Equally apparent is the need for those responsible for generating lists of new toxicants to recognize the relevance of the environmental stability of chemicals and the difficulty of measuring poorly defined parameters. Successful interaction of analytical chemists, toxicologists, and regulatory specialists is required to craft laws that will effectively reduce risks associated with exposure to chemicals.

Table I. Lawful levels of Proposition 65 chemicals as of January 1, 1989.

Chemical	CAS Number	Listed Date	Lawful Level (µg/day)
CHEMICALS KNOWN TO THE STATE TO CAUSE CANCER			
Acetaldehyde	75070	April 1, 1988	90
Acrylonitrile	107131	July 1, 1987	3
Aldrin	309002	July 1, 1988	0.04
Arsenic (inorganic compounds)	---	February 27, 1987	10
Asbestos* (inhalation only)	1332214	February 27, 1987	100Fibers/day
Benzene	71432	February 27, 1987	20
Benzidine [and its salt]	92875	February 27, 1987	0.003
Benzo[a]pyrene	50328	July 1, 1987	0.06
Beryllium (inhalation only)	---	October 1, 1987	0.1
Beryllium oxide (inhalation only)	---	October 1, 1987	0.1
Beryllium sulfate (inhalation only)	---	October 1, 1987	0.0002
Bis(chloromethyl)ether (bis(Chloromethyl)ether)	542881	February 27, 1987	0.6
1,3-Butadiene	106990	April 1, 1988	0.4
Cadmium (inhalation only)	---	October 1, 1987	1
Carbon tetrachloride	56235	October 1, 1987	5
Chlordane	57749	July 1, 1988	0.5
Chloroform	67663	October 1, 1987	9
Chromium (hexavalent) (inhalation only)	---	February 27, 1987	0.001
Coke oven emissions	---	February 27, 1987	0.3
DDT(1,1,1-Trichloro-2,2-bis(p-chloropheyl)ethane)	50293	October 1, 1987	2
3-3'-Dichlorobenzidine (3,3'-Dichlorobenzidine)	91941	October 1, 1987	0.4
Dichloromethane (Methylene chloride)	75092	April 1, 1988	50
Dieldrin	60571	July 1, 1988	0.04
Di(2-ethylhexyl)phthalate (bis(2-Ethylhexyl)phthalate)	117817	January 1, 1988	80
2,4-Dinitrotoluene	121142	July 1, 1988	2
Epichlorohydrin	106898	October 1, 1987	70
Ethylene dibromide (1,2-Dibromoethane) (EDB)	106934	July 1, 1987	3
Ethylene dichloride (1,2-Dichloroethane) (EDC)	107062	October 1, 1987	9
Ethylene oxide	75218	July 1, 1987	2
Formaldehyde (gas)	50000	January 1, 1988	15
Heptachlor	76448	July 1, 1988	0.2
Heptachlor epoxide	1024573	July 1, 1988	0.08
Hexachlorobenzene	118741	October 1, 1987	0.4
Hexachlorocyclohexane (technical grade)	---	October 1, 1987	0.4
Nickel refinery dust/pyrometallurgical process	---	October 1, 1987	0.8
Nickel subsulfide	12035722	October 1, 1987	0.4
N-Nitrosodi-n-butylamine	924163	October 1, 1987	0.1
N-Nitrosodiethylamine	55185	October 1, 1987	0.02
N-Nitrosodimethylamine	62759	October 1, 1987	0.03
N-Nitroso-diphenylamine	86306	April 1, 1988	140
N-Nitroso-N-ethylurea	759739	October 1, 1987	0.02
N-Nitroso-N-methylurea	684935	October 1, 1987	0.002
N-Nitrosopyrrolidine	930552	October 1, 1987	0.3
Polychlorinated biphenyls (>60% chlorine)	---	January 1, 1988	0.09
2,3,7,8-Tetrachlorodibenzo-para-dioxin (TCDD)	1746016	January 1, 1988	0.000005
Tetrachloroethylene	127184	April 1, 1988	14
Toxaphene (polychlorinated camphenes)	8001352	January 1, 1988	0.6
Trichloroethylene (Trichloroethene)	79016	April 1, 1988	60
2,4,6-Trichlorophenol	88062	January 1, 1988	40
Vinyl chloride	75014	February 27, 1987	0.3

Table I. Lawful levels of Proposition 65 chemicals as of January 1, 1989. (continued)

CHEMICALS KNOWN TO THE STATE TO CAUSE REPRODUCTIVE TOXICITY

Developmental toxicity			
Lead	---	February 27, 1987	0.5
Female reproductive toxicity			
Ethylene oxide	75218	February 27, 1987	20
Lead	---	February 27, 1987	0.5
Male reproductive toxicity			
Lead	---	February 27, 1987	0.5

*Fibers equal to or greater than 5 micrometers in length and 0.3 micrometers in width, with a length/width ratio of greater than or equal to 3:1 as measured by phase contrast microscopy.

NOTE:The lawful level under the Act is established by the California State Health and Welfare Agency, 1600 Ninth Street, Room 450, Sacramento, CA 95814.

Table II. Validated water methods with risk-detection ratios* equal to or greater than 1

Chemical	Lawful Level µg/day	TDL* (µg/L)	Method	MDL/DLR (µg/L)	RDR*
		VOLATILES IN WATER			
Acrylonitrile	3	1.5	EPA 603	0.5	3
Benzene	20	10	EPA 502.2	0.01	1,000
			DHS/AB1803	0.5	100
			EPA 524.2	0.5	20
Carbon tetrachloride	5	2.5	EPA 502.2	0.01	250
			DHS/AB1803	0.5	25
			EPA 524.2	0.5	5
Chloroform	9	4.5	EPA 502.2	0.02	225
			DHS/AB1803	0.5	45
			EPA 524.2	0.5	9
Dichloromethane (Methylene chloride)	50	25	EPA 502.2	0.02	1,250
			EPA 524.2	0.09	278
			DHS/AB1803	0.5	250
Ethylene dibromide (1,2-Dibromoethane) (EDB)	3	1.5	DHS/AB1803	0.02	375
			EPA 504	0.02	75
			EPA 524.2	0.06	5
Ethylene dichloride (1,2-Dichloroethane) (EDC)	9	4.5	EPA 502.2	0.03	150
			EPA 524.2	0.06	75
			DHS/AB1803	0.5	45
Tetrachloroethylene (Perchloroethylene) (Tetrachloroethene)	14	7	EPA 502.2	0.04	175
			EPA 524.2	0.05	140
			DHS/AB1803	0.5	70

Table II. Validated Water Methods with risk-detection ratios* equal to or greater than 1 (continued)

Chemical	Lawful Level (µg/day)	TDL* (µg/L)	Method	MDL* (µg/L)	RDR*
			VOLATILES IN WATER (continued)		
Trichloroethylene (Trichloroethene)	60	30	EPA 502.2	0.01	3,000
			EPA 524.2	0.02	1,500
			DHS/AB1803	0.5	300
Vinyl chloride	0.3	0.15	EPA 502.2	0.04	4
			DHS/EPA 524	0.1	10
			EPA 524.2	0.17	1
			DHS/EPA 502	0.3	2.5
			EXTRACTABLES IN WATER		
Benzo[a]pyrene	0.06	0.03	EPA 8310	0.001	30
			DHS/AB1803	10	0.015
			EPA 8270	10	0.003
3,3'-Dichlorobenzidine	0.4	0.2	EPA 605	0.13	2
			EPA 8270	10	0.1
			DHS/AB1803	20	0.01
Di(2-ethylhexyl)phthalate (bis(2-Ethylhexyl)phthalate)	80	40	DHS/AB1803	5	40
			EPA 8270	10	4
N-Nitroso-diphenylamine	140	70	DHS/AB1803	5	70
2,4,6-Trichlorophenol	40	20	DHS/AB1803	5	20
			EPA 8270	20	1
			PESTICIDES IN WATER		
Aldrin	0.04	0.02	DHS/AB1803	0.01	10
			EPA 8080.1	0.01	2
DDT (1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane)	2	1	DHS/AB1803	0.02	250
			EPA 8080.1	0.1	10
Dieldrin	0.04	0.02	EPA 8080.1	0.02	1
			DHS/AB1803	0.05	2
Heptachlor	0.2	0.1	EPA 8080.1	0.01	10
			DHS/AB1803	0.02	20
Heptachlor epoxide	0.08	0.04	EPA 8080.1	0.02	2
			DHS/AB1803	0.1	2
			METALS IN WATER		
Arsenic	10	5	EPA 206.2	1	5
			EPA 7061	2	3
			d-EPA 6020	2	3

*Risk-detection ratio (RDR) is the ratio of the target detection limit (TDL) versus the method detection limit (MDL). RDR = TDL/DLR X 5, RDR = TDL/MDL

Table III.
Water methods with risk-detection ratios* less than one (continued)

Chemical	Lawful Level (µg/day)	TDL* (µg/L)	Method	MDL* (µg/L)	RDR*
		EXTRACTABLES IN WATER			
Benzidine [and its salt]	0.003	0.0015	EPA 605	0.08	0.02
			DHS/AB1803	5	0.0015
2,4-Dinitrotoluene	2	1	DHS/AB1803	5	1
			EPA 625	5	0.2
N-Nitrosodi-n-butylamine	0.1	0.05	EPA 8270	10	0.005
N-Nitrosodiethylamine	0.02	0.01	EPA 8270	10	0.001
N-Nitrosodimethylamine	0.03	0.015	EPA 607	0.15	0.1
			DHS/AB1803	5	0.015
			EPA 8270	10	0.002
N-Nitrosopyrrolidine	0.3	0.15	EPA 8270	10	0.02
2,3,7,8-Tetrachloro-dibenzo-para-dioxin (TCDD)	0.000005	0.0000025	EPA 8280	0.00044	0.006
		PESTICIDES IN WATER			
Hexachlorobenzene	0.4	0.2	DHS/AB1803	5	0.2
			EPA 625	5	0.04
			EPA 8080.1	0.1	2**
		METALS IN WATER			
Lead	0.5	0.25	EPA 239.2	1	0.25
			draft	>0.1	5**

* Risk-detection ratio, (RDR) is the ratio of the target detection limit (TDL) versus the method detection limit (MDL). RDR = TDL/DLR X 5 and RDR = TDL/MDL

** Draft method

Table IV. Chemicals that do not require methods in water

Chemical (inhalation hazard only)	Lawful Level (µg/day)
Asbestos	100 Fibers/day
Beryllium	0.1
Beryllium oxide	0.1
Beryllium sulfate	0.0002
Cadmium	1
Chromium (hexavalent)	0.001

Table V. Problem Analytes

Chemical	Lawful Level (ug/day)
COMPLEX MIXTURES	
Chlordane	0.5
Coke oven emissions	0.3
Hexachlorocyclohexane (technical grade)	0.4
Nickel refinery dust from the pyrometallurgical process	0.8
Nickel subsulfide	0.4
Polychlorinated biphenyls (containing 60 or more percent chlorine by molecular weight)	0.09
Toxaphene (polychlorinated camphenes)	0.6
DECOMPOSE IN WATER	
Bis(chloromethyl)ether	0.6
Epichlorohydrin	70
Ethylene oxide (Cancer)	2
INSOLUBLE AT PH 8	
Nickel subsulfide	0.4
DRAFT METHODS - EMSL-Ci	
Acetaldehyde	90
Acrylonitrile	3
Formaldehyde	15
SENSITIVITY PROBLEMS	
1,3-Butadiene	0.4
N-Nitroso-N-ethylurea	0.02
N-Nitroso-N-methylurea	0.002

ENFORCEMENT OF RCRA AT RADIOACTIVE MIXED WASTE FACILITIES

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Radioactive mixed wastes (mixed wastes) are wastes that contain hazardous wastes subject to RCRA and radioactive wastes subject to the Atomic Energy Act (AEA). It is clear that source, special nuclear and byproduct material are exempt from RCRA. On July 3 1986 EPA published a Federal Register Notice which clarifies that wastes containing both hazardous wastes and radioactive wastes are subject to dual regulation. Due to unique technical and regulatory aspects concerning mixed wastes, special enforcement considerations and issues arise. This paper will focus on EPA's enforcement involvement for mixed wastes. Special mixed waste considerations that will be addressed include sampling, testing and analysis, documentation and safety.

HAZARDOUS GROUND-WATER TASK FORCE DATA BASE/ IMPLEMENTATION OF FIELD QA/QC

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In the Fall of 1984, EPA established the Hazardous Waste Ground-Water Task Force to evaluate the level of compliance and identify the causes of poor compliance with ground-water monitoring regulations at hazardous waste disposal facilities. As a part of this effort an evaluation team was formed to determine the status of ground-water monitoring programs at existing hazardous waste treatment, storage and land disposal facilities. The inspection team evaluated 58 commercial and private land disposal facilities. To assist the members of the Task Force in executing thorough investigations and collecting representative samples, a protocol was developed to provide detailed guidance and procedures. This protocol has been made available to the EPA regional and state personnel. Throughout the conduct of the Task Force investigations, an intensive field quality control program was utilized for ground-water sample collection to ensure that the data was of high quality.

Analytical data obtained from the field inspections were compiled and input into a data base. EPA intends to utilize this data base to gain a better understanding of ground-water contamination problems identified at facilities subject to RCRA. Efforts are currently ongoing to develop a second data base to house pertinent field information such as well construction materials, screen lengths, well diameter, sampling devices, sampling procedures, and well development techniques. The EPA hopes to use this data base to study the impacts of field components on the quality of the analytical data generated and to apply the findings to enforcement and permitting decisions.

INORGANICS

VALIDATION OF A METHOD FOR DETERMINING ELEMENTS IN SOLID WASTE BY MICROWAVE DIGESTION

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ABSTRACT

The techniques which are typically used to prepare RCRA wastes for analysis for metals and other elements are generally relatively time consuming, requiring several hours to several days to complete. They also often involve the use of acid digestions and thermal decomposition steps which may result in analyte losses, incomplete recoveries, or sample contamination. These limitations are well known to the analytical community and to the end users of this data in EPA, States, and industry. The resulting inefficiency of these techniques reduces laboratory sample throughput, drives up the cost of analytical testing and impedes decisionmaking. Given these concerns, the OSW Methods Section is interested in developing cost effective sample preparation techniques for metals and other elements in environmental and process waste samples. Once developed, these techniques can then be written as methods for inclusion in "Test Methods for Evaluation of Solid Waste SW-846" and made available to the user community.

A microwave assisted sample preparation method for determining elements in solid waste has been developed (Method 30XX). This paper reports on the validation of this method by a collaborative study to determine its precision and accuracy. Both qualitative and quantitative aspects of the method were assessed. Qualitative factors evaluated were ease of use and time requirements. Quantitative factors evaluated were the precision of the method both within a single laboratory and the total method precision, and the bias of the method.

The method was compared with Method 3050, an open vessel hot plate digestion method.

INTRODUCTION

Microwave assisted sample dissolution is now receiving considerable attention and use in the laboratory. The procedure generally involves placing a sample in an acid solution in a closed vessel equipped with a pressure relief valve. The vessel is then subjected to microwave energy in a modified microwave oven. The conditions of high pressure generated in the container, coupled with the rapid heating of the sample via direct microwave energization of the acid molecules, can result in significantly reduced preparation time; from several hours in a conventional convection oven, hot plate, or steam bath, to several minutes in the microwave oven.

Based on in-vessel temperature and pressure profile studies conducted by the National Institute of Standards and Technology (NIST), formerly known as the National Bureau of Standards (NBS), microwave oven preparation conditions for oils and soils have been determined and written as a draft method. This involves the use of concentrated nitric acid as the digestion medium. The intent is not to completely solubilize all elements in the sample; rather, it is to solubilize those elements most likely to be made environmentally available.

Previous work has reported on the evaluation in a single laboratory of the draft method using NIST Standard Reference Material (SRM) representative of oils and soils[1]. It was reported that this method should prove a suitable alternative for SW-846 Method 3050 with a substantial time/cost savings. Based on these results, a collaborative study was conducted for final method validation.

This paper reports on results of the collaborative study for validation of the microwave method. Four NIST SRMs and one solvent recovery waste were digested by 15 laboratories using the microwave draft method. Analysis of these digests was carried out by RTI using Inductively Coupled Plasma (ICP) Spectrometry and Graphite Furnace Atomic Absorption (GFAA). In addition, laboratories digested the samples by SW-846 Method 3050 with results using the microwave draft method compared to SW-846 Method 3050.

EXPERIMENTAL METHODS

Microwave Oven

The MDS-81D Microwave system (CEM Corporation, Indian Trail, NC) was used for this study. The oven resembles a standard microwave oven, but is equipped with additional features to facilitate sample preparation. For example, the Teflon-coated microwave cavity has a variable speed corrosion resistant exhaust system. The main element of the system couples a precise microwave variable power system with a programmable micro-processor digital computer. Other elements include a rotating turntable, Teflon vessels with caps, a patented pressure relief valve, and a capping system.

The Teflon sample vessels and caps are designed to withstand pressures up to 100 psi and temperatures up to 200°C.

Collaborative Study Materials

The collaborative study was carried out using the following materials:

- NIST SRM 2704 - Buffalo River Sediment
- NIST SRM 4355 - Peruvian Soil
- NIST SRM 1085 - Wear Metals in Oil

- NIST SRM 1634b - Trace Elements in Fuel Oil
- Solvent recovery waste

To simulate a contaminated soil, a 1:1 mixture of 1634b and 2704 was prepared and analyzed.

Microwave Test Method

The method described below was developed for only two vessels placed in the microwave oven and is optimized for temperatures and pressures that would produce efficient chemical decomposition of the sample. Essentially the same conditions with an increased power setting are utilized for six vessels.

Two vessels, each containing up to 0.5 g of sample in 10 mL concentrated HNO_3 are heated in the microwave oven for ten minutes at a power setting of 344 watts. These vessels are placed in the microwave oven carousel with accompanying vapor trap vessels. For six vessels, a power setting of 574 watts is used.

To reduce the likelihood of analyte loss when decomposing samples producing significant gas on decomposition, a configuration is employed using a second vessel to trap the hot acid vapor and any aerosol expelled when the pressure relief valve of the first vessel opens. A PFA Teflon tube connects the digestion vessel to a second vessel with a double-ported cap. The second port on the catch vessel is connected to the center well of the carousel to capture potential venting from this overflow vessel. The acid and any sample condensed in the second vessel is washed back into the sample digestion vessel at the end of the microwave procedure. The vessel contents are filtered into an acid-cleaned 50 mL volumetric flask.

Collaborative Study Design

The objective of the collaborative study was to validate the draft microwave method. This involved determination of the precision of the method both within a single laboratory and the total precision (within and between laboratory) of the method. In addition, the bias of the method was evaluated for those samples where the method results in a sample digest such that a compositional analysis of the original sample can be made.

A total of 15 laboratories participated in the study. Each laboratory was sent aliquots of the four NIST SRMs and the Solvent Waste along with instructions and a copy of the draft method.

A scheme was developed where each laboratory digested two replicates, one replicate was digested under two vessel conditions and the other replicate digested under six vessel conditions.

In addition, each laboratory was requested to perform duplicate digestions using SW-846 Method 3050, an open vessel hot plate acid digestion.

All digests were forwarded to Research Triangle Institute (RTI) where ICP and GFAA analyses were performed.

RESULTS

ICP results for the microwave draft method 30XX and SW-846 Method 3050 are shown in Tables 1 and 2. Buffalo River Sediment, Peruvian Soil, the 1:1 mixture of Buffalo River Sediment/Trace Elements in Fuel Oil, and the Solvent Recovery Waste were analyzed for 19 elements. SRM 1085, Wear Metals in Oil, was analyzed for the nine elements that are certified by NIST. The number of observations varies from the ideal of 30 due to exclusion of outliers and non-digested samples.

GFAA results for the microwave draft method for arsenic and selenium in Buffalo River Sediment and Peruvian Soil are shown in Table 3. Digests from the first six laboratories to return samples were analyzed. Precision for arsenic is excellent whereas selenium is only fair, probably reflecting the extremely low concentration of selenium present in the two samples. A comparison of mean concentrations with the certified values reveals generally poor recovery, ranging from a percent bias of 12 for selenium in Peruvian Soil to 39 for selenium in Buffalo River Sediment.

A closer look at the ICP data is shown in Table 4. Values obtained using the draft microwave method for SRM 1085, Wear Metals in Oil, are compared to the NIST certified levels. Of the nine certified elements, seven exhibit excellent recovery with 0 to 9% bias. Silver and molybdenum are low, but are generally regarded as "problem" elements. The precision ranges from 8 to 15% RSD, which is quite good.

A comparison of the draft microwave method versus SW-846 Method 3050 is extremely interesting (Tables 5 and 6). Because HCl and H_2O_2 are used in addition to HNO_3, it would be expected to see higher recoveries for Method 3050 and this is generally true, but the differences between the two methods are slight. In the case of SRM 2704, Buffalo River Sediment (Table 5), with the exception of boron, recoveries are very similar. Recovery differences range from a low of 2% for chromium and zinc to a high of 18% for beryllium. In the case of the Solvent Recovery Waste (Table 6), with the exception of silver, which disappears in the presence of HCl and calcium, recoveries are again very similar. Recovery differences range from 0 to 8%.

Of further interest is a comparison of method precision. For SRM 2704, Buffalo River Sediment, the microwave method is more precise than Method 3050 in 15 out of 17 elements (Table 5). The two exceptions are calcium and cadmium. For the Solvent Recovery Waste, the microwave method exhibits better precision for 14 out of the 18 elements (Table 6).

An additional observation is the variation of method precision with sample heterogeneity. An SRM such as Buffalo River Sediment provides much better overall precision than a non-homogeneous "real" sample (Tables 5 and 6) such as the Solvent Recovery Waste.

CONCLUSIONS

Evaluation of the draft microwave digestion method by a collaborative study indicates that this method should prove a suitable alternative for SW-846 Method 3050 with a substantial time/cost savings.

Comparison of the draft method with Method 3050 reveals similar numbers with overall better precision. For the one sample where the bias of the method can be evaluated, it is excellent.

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TABLE 1 -- ICP Analysis Using Method 30XX (μg/g)

	Sample				
Element	1 Mean ± S.D.(n)[a]	2 Mean ± S.D.(n)	3 Mean ± S.D.(n)	4 Mean ± S.D.(n)	5 Mean ± S.D.(n)
Ag	<1.0	2.05 ± 0.908(18)	234 ± 35.9(22)	<1.0	3.28 ± 1.90(9)
Al	1.18 ± 0.137%(30)	1.92 ± 0.223%(30)	295 ± 31.1(28)	0.685 ± 0.145%(21)	0.148 ± 0.027%(28)
B	34.6 ± 9.31(30)	35.5 ± 7.47(30)		20.7 ± 7.65(22)	37.4 ± 7.01(25)
Ba	77.7 ± 5.90(30)	135 ± 10.8(30)		43.5 ± 7.86(22)	538 ± 110 (28)
Be	0.562 ± 0.068(30)	0.493 ± 0.069(30)		0.297 ± 0.064(23)	<0.25
Ca	2.00 ± 0.383%(30)	1.09 ± 0.275%(30)		1.13 ± 0.260%(23)	0.219 ± 0.093%(28)
Cd	3.19 ± 0.613(29)	0.901 ± 0.227(27)		1.50 ± 0.219(21)	4.90 ± 1.04(27)
Co	10.7 ± 1.46(30)	10.4 ± 1.24(30)		5.89 ± 1.27(23)	21.9 ± 5.04(26)
Cr	81.7 ± 5.33(30)	13.8 ± 1.18(28)	293 ± 26.6(30)	43.1 ± 4.90(21)	161 ± 23.8(26)
Cu	80.3 ± 6.92(30)	53.4 ± 5.74(30)	289 ± 23.8(30)	41.4 ± 5.03(23)	208 ± 32.6(26)
Fe	2.96 ± 0.214%(30)	2.50 ± 0.392%(30)	311 ± 34.7(27)	1.58 ± 0.180%(19)	0.316 ± 0.052%(26)
Mg	0.810 ± 0.047%(30)	0.705 ± 0.041%(30)	270 ± 29.1(28)	0.410 ± 0.064%(23)	0.038 ± 0.009%(26)
Mn	460 ± 25.7(30)	541 ± 29.1(30)		238 ± 30.0(21)	31.7 ± 5.05(26)
Mo	<2.5	<2.5	238 ± 30.3(30)	<2.5	19.1 ± 3.36(28)
Ni	36.4 ± 2.52(27)	9.59 ± 1.10(28)	293 ± 25.0(30)	30.5 ± 5.08(23)	50.9 ± 9.96(26)
Pb	143 ± 9.46(30)	121 ± 8.28(30)	279 ± 22.1(30)	74.5 ± 8.88(20)	437 ± 70.3(26)
Sr	33.0 ± 2.05(30)	81.0 ± 7.04(30)		17.5 ± 2.05(19)	71.1 ± 13.5(26)

TABLE 1 -- ICP Analysis Using Method 30XX (µg/g)
(Continued)

	Sample				
	1	2	3	4	5
Element	Mean ± S.D.(n)[a]	Mean ± S.D.(n)	Mean ± S.D.(n)	Mean ± S.D.(n)	Mean ± S.D.(n)
V	21.0 ± 2.46(30)	61.2 ± 5.85(30)		34.2 ± 6.46(23)	9.92 ± 1.76(26)
Zn	383 ± 26.5(30)	366 ± 26.8(30)		195 ± 29.9(23)	748 ± 108(28)

[a] n = number of observations.

Sample: 1 = NIST 2704, Buffalo River Sediment
2 = NIST 4355, Peruvian Soil
3 = NIST 1085, Wear Metals in Oil
4 = 1:1 mixture - 2704 and 1634b, Trace Elements in Fuel Oil
5 = Solvent Recovery Waste

TABLE 2 -- ICP Analysis Using SW-846 Method 3050 (μg/g)

	Sample				
	1	2	3	4	5
Element	Mean ± S.D.(n)a	Mean ± S.D.(n)	Mean ± S.D.(n)	Mean ± S.D.(n)	Mean ± S.D.(n)
Ag	<1.0	1.66 ± 0.297(17)	172 ± 52.4(24)	<1.0	1.25 ± 0.253(6)
Al	1.31 ± 0.367%(24)	2.55 ± 0.689%(27)	277 ± 25.5(26)	0.638 ± 0.170%(18)	0.141 ± 0.030%(27)
B	55.4 ± 25.8(27)	56.8 ± 21.7(27)		23.8 ± 7.81(19)	39.6 ± 10.8(27)
Ba	85.3 ± 17.9(27)	160 ± 28.5(27)		45.8 ± 8.60(19)	513 ± 132 (27)
Be	0.682 ± 0.209(25)	0.608 ± 0.115(27)		0.335 ± 0.097(20	< 0.25
Ca	1.83 ± 0.200%(27)	1.02 ± 0.119%(27)		0.932 ± 0.075%(20)	0.190 ± 0.077%(27)
Cd	3.32 ± 0.436(27)	1.03 ± 0.202(23)		1.67 ± 0.196(21)	4.96 ± 0.861(27)
Co	11.1 ± 2.75(27)	13.7 ± 2.83(27)		5.89 ± 1.43(20)	21.6 ± 8.30(27)
Cr	83.3 ± 14.0(27)	17.1 ± 2.37(25)	274 ± 33.7(26)	42.3 ± 6.04(18)	157 ± 34.7(27)
Cu	83.2 ± 11.0(24)	57.0 ± 9.03(27)	274 ± 24.0(26)	39.0 ± 5.40(18)	206 ± 35.1(25)
Fe	3.06 ± 0.308%(27)	2.98 ± 0.342%(25)	288 ± 26.3(24)	1.52 ± 0.195%(20)	0.345 ± 0.074%(23)
Mg	0.850 ± 0.120%(27)	0.785 ± 0.097%(27)	244 ± 25.0(25)	0.419 ± 0.050%(20)	0.038 ± 0.007%(25)
Mn	472 ± 57.2(27)	606 ± 75.9(27)		238 ± 23.2(20)	31.5 ± 4.95(25)
Mo	2.95 ± 0.902(23)	<2.5	258 ± 29.3(26)	<2.5	20.0 ± 4.18(27)
Ni	37.7 ± 5.15(27)	9.93 ± 1.46(24)	282 ± 26.1(26)	31.4 ± 5.56(19)	51.2 ± 11.7(25)
Pb	147 ± 16.6(27)	131 ± 14.2(27)	279 ± 20.5(26)	76.4 ± 8.17(18)	463 ± 82.9(25)
Sr	35.0 ± 7.04(26)	98.9 ± 19.0(27)		17.7 ± 3.32(20)	71.0 ± 16.8(27)

TABLE 2 -- ICP Analysis Using SW-846 Method 3050 ($\mu g/g$)
(Continued)

	Sample				
Element	1 Mean ± S.D.(n)[a]	2 Mean ± S.D.(n)	3 Mean ± S.D.(n)	4 Mean ± S.D.(n)	5 Mean ± S.D.(n)
V	24.2 ± 7.21(25)	81.4 ± 17.3(27)		37.4 ± 10.2(19)	9.73 ± 1.86(26)
Zn	393 ± 60.7(27)	401 ± 49.2(27)		207 ± 24.3(20)	747 ± 120(27)

[a] n = number of observations.

Sample: 1 = NIST 2704, Buffalo River Sediment
2 = NIST 4355, Peruvian Soil
3 = NIST 1085, Wear Metals in Oil
4 = 1:1 mixture - 2704 and 1634b, Trace Elements in Fuel Oil
5 = Solvent Recovery Waste

TABLE 3 -- GFAA Analysis Using Method 30XX ($\mu g/g$).

	Sample							
	SRM 2704				SRM 4355			
Element	Mean ± S.D.(n)[a]	% RSD	NIST Value	% Bias	Mean ± S.D.(n)	% RSD	NIST Value	% Bias
As	18.3 ± 1.04 (12)	6	23.4	-22	63.9 ± 3.19 (12)	5	90	-29
Se	0.668 ± 0.127 (10)	19	(1.1)	-39	1.12 ± 0.192 (12)	17	1	+12

( ) Not certified.

[a] n = number of observations.

TABLE 4 -- ICP Analysis of SRM 1085 Wear Metals in Oil
Using Method 30XX (μg/g)

Element	Mean ± S.D.	% RSD	NIST Value	% Bias
Ag	234 ± 35.9	15	(291)	-20
Al	295 ± 31.1	10	296	0
Cr	293 ± 26.6	9	298	- 2
Cu	289 ± 23.8	8	295	- 2
Fe	311 ± 34.7	11	300	+ 4
Mg	270 ± 29.1	11	297	- 9
Mo	238 ± 30.3	13	292	-18
Ni	293 ± 25.0	8	303	- 3
Pb	279 ± 22.1	8	(305)	- 8

( ) Not certified.

TABLE 5 -- ICP Analysis of SRM 2704 Buffalo River Sediment -- Comparison of Methods 30XX and 3050 (μg/g)

Element	3050		30XX		
	Mean ± S.D.	% RSD	Mean ± S.D.	% RSD	% Diff.
Al(%)	1.31 ± 0.367	28	1.18 ± 0.137	12	-10
B	55.4 ± 25.8	46	34.6 ± 9.31	27	-38
Ba	85.3 ± 17.9	21	77.7 ± 5.90	8	- 9
Be	0.682 ± 0.209	31	0.562 ± 0.068	12	-18
Ca(%)	1.83 ± 0.200	11	2.00 ± 0.383	19	+ 9
Cd	3.32 ± 0.436	13	3.19 ± 0.613	19	- 4
Co	11.1 ± 2.75	25	10.7 ± 1.46	14	- 4
Cr	83.3 ± 14.0	17	81.7 ± 5.33	7	- 2
Cu	83.2 ± 11.0	13	80.3 ± 6.92	9	- 3
Fe(%)	3.06 ± 0.308	10	2.96 ± 0.214	7	- 3
Mg(%)	0.850 ± 0.120	14	0.810 ± 0.047	6	- 5
Mn	472 ± 57.2	12	460 ± 25.7	6	- 2
Ni	37.7 ± 5.15	14	36.4 ± 2.52	7	- 3
Pb	147 ± 16.6	11	143 ± 9.46	7	- 3
Sr	35.0 ± 7.04	20	33.0 ± 2.05	6	- 6
V	24.2 ± 7.21	30	21.0 ± 2.46	12	-13
Zn	393 ± 60.7	15	383 ± 26.5	7	- 2

TABLE 6 -- ICP Analysis of Solvent Recovery Waste --
Comparison of Methods 30XX and 3050 (µg/g)

	3050		30XX		
Element	Mean ± S.D.	% RSD	Mean ± S.D.	% RSD	% Diff.
Ag	1.25 ± 0.253	20	3.28 ± 1.90	58	162
Al	0.141 ± 0.030	21	0.148 ± 0.027	18	+ 5
B	39.6 ± 10.8	27	37.4 ± 7.01	19	- 6
Ba	513 ± 132	26	538 ± 110	20	+ 5
Be	<0.25	...	<0.25	...	...
Ca	0.190 ± 0.077	40	0.219 ± 0.093	42	+15
Cd	4.96 ± 0.861	17	4.90 ± 1.04	21	- 1
Co	21.6 ± 8.30	38	21.9 ± 5.04	23	+ 1
Cr	157 ± 34.7	22	161 ± 23.8	15	+ 2
Cu	206 ± 35.1	17	208 ± 32.6	16	+ 1
Fe	0.345 ± 0.074	21	0.316 ± 0.052	16	- 8
Mg	0.038 ± 0.007	18	0.038 ± 0.009	24	0
Mn	31.5 ± 4.95	16	31.7 ± 5.05	16	+ 1
Mo	20.0 ± 4.18	21	19.1 ± 3.36	18	- 4
Ni	51.2 ± 11.7	23	50.9 ± 9.96	20	- 1
Pb	463 ± 82.9	18	437 ± 70.3	16	- 6
Sr	71.0 ± 16.8	24	71.1 ± 13.5	19	0
V	9.73 ± 1.86	19	9.92 ± 1.76	18	+ 2
Zn	747 ± 120	16	748 ± 108	14	0

MICROWAVE DIGESTION FOR ICP ANALYSIS
REGION V ALTERNATE TEST PROCEDURE

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ABSTRACT

The microwave oven in conjunction with pressurized teflon digestion vessels has reduced our sample preparation time significantly. The Alternate Test Procedure process, or other verification depending upon the program requirements, are necessary for new technology to enter our laboratory. The application process and data necessary are briefly described. There are several factors to consider when choosing operating conditions and methodology. The operation of the pressure vessel has an effect on whether the volume remains constant. Pressure and temperature profiles have a pronounced effect on the effectiveness of the digestion on various waters. The method currently in use in Region V contains several assumptions about sample retention and temperatures achieved. The assumptions about temperature have been validated. Some experiments were carried out concerning the retention of metals in the walls of the teflon vessels. There is some retention but it is well below our current detection limits. The method detection limits have not changed much even though there is now dilution from the acid added. (Dilution factor 1.22) This seems to imply better precision. The data gathered to support the Alternate Test Procedure application will be available for examination.

INTRODUCTION

There has been a great deal of interest in using microwave ovens as a heating source for sample preparation. In our experience this interest is justified; a significant time reduction in sample preparation accompanied our adoption of the microwave oven method. The time savings did not cause any loss in detection limits or accuracy.

In the EPA Central Regional Laboratory of Region V, where this work was done, the methodology must be defensible in court. Under different EPA programs there are different requirements for method validation. The NPDES validation is more formal than some of the others. Approval for use in NPDES work requires an Alternate Test Procedure approval. This approval requires statistical validation of the test. My inquiries determined that sample preparation, while not a testing method, has such a great effect on the analysis results that the stringent statistical requirements also applied to it.

The validation required that five samples from six different industries be analyzed. Each of these samples was prepared for analysis in quadruplicate by each of the methods of digestion. Each sample had eight digestions done and analyzed. This made a total of two hundred and forty separate analyses.

In the planning stages of the validation study we considered the possibility of validating the digestion for atomic absorption analysis as well as the inductively coupled plasma. An estimate of a man year of time for atomic absorption validation alone made us reject this option. Thus our Alternate Test Procedure Approval is only for preparation of samples for ICP not for AA. The ICP work took about three months to complete.

A value less than detection limit would tell us little about the similarities or differences of the two methods. All samples were analyzed prior to use in the validation study. Any element not present at detectable levels was spiked into the sample at a level about five to ten times the detection limit. The sample was then digested by both methods and analyzed. We tried to analyze the digestions associated with one sample as close together as possible to minimize the instrument variation in the analysis. The analysis was accompanied by digested blanks and our usual instrument check samples. The controls on the analyses were as stringent as those for our usual work.

The samples were analyzed on a Jarrell Ash Model 1160 Inductively Coupled Plasma. Our instrument reports twenty five elements. The data was sorted by element and entered into a spreadsheet. A floppy disk with the spreadsheet as well as printed copies of the data were sent for statistical analysis at EMSL Cincinnati. They found twelve outliers. Upon investigation six of these were found to be typing errors. That left six thousand pieces of data with only six outliers. In April of 1988 the data was approved as supporting an Alternate Test Procedure Approval and we began using the method on a regular basis.

The conditions for the digestion are not as severe as are now being recommended. The conditions used were ten minutes at 100% power. The term 100% power is somewhat ambiguous. We have found that there has been significant losses in the wattage in our microwave since this study was done. The initial wattage found when the oven was a year old was 560; the most recent wattage was 540. The wattage varies slightly with the position of the beaker in the microwave cavity. An average of several values is recommended to get a reliable number.

The milder conditions were chosen to avoid the venting of the vessel. The information on the pressure and temperature profiles was not as extensive as it is now. Through trial and error we determined that there was no venting at these settings. Our preliminary experiments indicated that the digestion was as complete as the hot plate digestion. The data gathered to for the Alternate Test Procedure Application supports this conclusion.

Venting was undesirable because of questions about the composition of the vented material and the problem of correcting for the lost volume if it were only steam. Currently a specially designed vessel can be used to catch and condense overflow, but they were not widely publicized three years ago.

The temperature profile as shown in the graph plotted from CEM data shows that the solution reaches about 95° under the conditions of the digestion. This is about the same as the tempertures recommended for the hot plate digestion. The hot plate/beaker digestion does not digest oily waters well and neither does this microwave digestion. Other papers have demonstrated that a temperature of 160 to 165° C must be attained to digest oils. As you can see this digestion does not approach this temperature.

Recently there was some discussion about retention of metals in the walls of the Teflon digestion vessels. In fact this retention probably occurs but not at a level that interferes with our analysis. Some experiments were conducted with well used vessels. The normally washed and rinsed vessels were heated with the digestion acids only. Some were at 10 ml and some at 20ml. The 20 ml volumes showed nothing upon ICP analysis. The 10 ml volumes showed a little iron and copper. This contamination was well below our detection limit if the acid had been diluted with 50 or even 25 ml of sample. There has been much less difficulty with contamination in the digestion blanks since we started using the Teflon microwave vessels instead of glass beakers. Filter paper has been a much larger source of contamination than the vessels or even acid washed beakers.

Although there is a dilution factor of 1.22 of each sample, remarkably the method detection limits for the ICP elements have not changed. This indicates the greater stability and reproduction of the microwave digestion.

Unfortunately, the permission to use this method for official analytical work is currently limited to our laboratory. Other laboratories may use our data to support their application for test procedure approval. They will need to supply some data to confirm that the method works as well in their laboratory as it did in ours to the Reagional Quality Assurance Branch. The local Quality Assurance Branch can supply you with further information. The last I heard the microwave digestion was to be included in the next Statement of Work for the CLP program.

SUMMARY

The microwave digestion has much to recommend it. The microwave oven is quicker, more reproducable than the hot plate and less easily contaminated. At the mild conditions of this digestion there is no venting or loss of sample. The data support the conclusion that the digestion does as well as the beaker hotplate digestion. There have been no contamination problems with the repeated use of the vessels with only washing between uses. We have certainly been pleased with the microwave oven digestion in our laboratory.

A COMPARISON STUDY OF QUALITY CONTROL PERFORMANCE BETWEEN ICP-MS METHOD 6020 AND THE ICP-AES AND GFAA SPECTROSCOPY METHODS

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ABSTRACT. A multi-laboratory study has been conducted to measure the comparability of the Inductively Coupled Plasma - Mass Spectrometry (ICP/MS) method 6020 with the present inorganic methods used by the Contract Laboratory Program (CLP) of the U.S. Environmental Protection Agency. Performance Evaluation (PE) samples made up of solid and water matrices were split and sent to a group of CLP laboratories for analysis by routine methods and to another group of laboratories for analysis of the same elements by ICP/MS. The results of this study were used to determine the comparability of ICP/MS to the Inductively Coupled Plasma - Atomic Emission (ICP-AES) and Graphite Furnace Atomic Absorption (GFAA) spectroscopy methods. The purpose of the presentation is to compare the performance of the quality control (QC) analyzed by the ICP/MS method with that of the routine methods. The following QC parameters have been reviewed and compared: spikes, duplicates, interference check sample results, as well as the linear range and detection limit data. The spike and duplicate QC comparison supply accuracy and precision performance, respectively, for both methods. The QC results for the Interference Check Solutions have been evaluated for each method's potential for spectral interference. Comparison of the instrument detection limits and linear ranges will provide an evaluation of the overall sensitivity and operating range for each method. The results of this QC study will then be compared with similar QC data for the CLP from the past year. This presentation will provide information on the expected QC performance of the method with comparison to other well characterized methods to the users of the ICP/MS method.

CTIVELY COUPLED PLASMA MASS
ETRY METHOD 6020

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ABSTRACT

Inductively coupled plasma mass spectrometry (ICP-MS) offers detection limits below a part per billion for multi-elemental analysis with the convenience and speed of nebulizer sample introduction. Digestion using hydrobromic acid (HBr) instead of hydrochloric acid (HCl) avoids adding chloride interferences to the ICP-MS measurements for arsenic and vanadium, but gives reduced recoveries for silver compared with HCl. An interlaboratory study has been completed comparing several digestion procedures as well as analyses by atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and ICP-MS for water, fly ash, sediment, industrial sludge and soil samples. The study required nearly 36,000 analyses. Analytical precision using ICP-MS is more variable than with ICP-AES for several elements. This lack of precision may have resulted from the need to perform additional dilutions of samples for ICP-MS analysis. Since results of the analysis of standard reference materials by ICP-MS for selenium exceeded the reference values provided by the National Institute of Standards and Technology [formerly the National Bureau of Standards (NBS)], more appropriate corrections for this element are still required. The preliminary results from this study indicate that it is suitable for many elements in solid wastes, but do not support using ICP-MS for the determination of potassium, selenium, silver, sodium or vanadium in solid wastes. Silver data from ICP-AES also showed wide variability.

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

INTRODUCTION

To evaluate the performance of inductively coupled plasma mass spectrometry (ICP-MS) Method 6020 for waste analysis, an interlaboratory study was conducted by the Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV) for the Analytical Operations Branch of the Office of Emergency and Remedial Response. The participants in this interlaboratory study included ICP-MS manufacturers, private laboratories, and government facilities. The participating laboratories received both digested and undigested samples. Consequently, performance data were obtained with and without sample preparation as a variable. Variations in the sample preparation were investigated because the Contract Laboratory Program specifies different procedures for furnace AAS and non-furnace AAS analyses and because the amount of hydrochloric acid added in sample preparation affects the amount of ICP-MS interference for arsenic and vanadium.

While it was not part of the interlaboratory study, an alternate HBr digestion procedure was tested as a means to minimize ICP-MS chloride interferences. Hydrochloric acid (HCl) is used in many digestion procedures for its solubilizing benefits. However, chloride contributes interferences to the ICP-MS measurements for the environmentally important elements arsenic and vanadium. Substituting hydrobromic (HBr) or hydroiodic (HI) acid for HCl in the digestion of samples might provide the solubilizing benefit of a halide without adding to the chloride interference on arsenic and vanadium. Silver is one element that is especially sensitive to the chloride level because of its solubility (Figure 1). According to the literature, HBr and HI solubilize more of the corresponding silver halides than HCl on an equal-molar basis (Table 1).

Figures 2 and 3 show that HBr and HI produce less interfering halo-oxide and halo-argon species than does HCl. But, more importantly, these bromide and iodide species do not interfere with arsenic or vanadium measurements. In the case of bromide, molybdenum isotopes at mass-to-charge ratio (m/z) 95 and 97 are affected by BrO^+ ions, but the most abundant isotope of molybdenum is measured at m/z 98. Bromide ions combined with argon affect the antimony isotope at 121 m/z but not the 123-m/z isotope. HI produces interferences on only one neodymium and one erbium isotope. Unfortunately, in testing the HI, it was found that iodide is converted to iodine even by dilute nitric acid. Consequently, the use of HI was discontinued and HBr was used in place of HCl in the digestion of 4 samples spiked with silver and antimony. The results of this feasibility testing with single portions of the 4 samples are shown in Table 2. Although the HBr and HCl recoveries are similar for antimony, silver recoveries with HBr are much lower than with HCl for 3 of the 4 wastes analyzed. Therefore, while HBr does provide lower background levels than HCl for arsenic and vanadium, it does not seem to provide equivalent performance for other elements. The use of HBr instead of HCl could be useful for samples containing arsenic or vanadium where silver is not present. When HBr is used, selenium measurements at m/z 82 are affected by HBr^+ ions, but selenium can be measured at m/z 77 or 78 without any contribute from bromide-containing ions.

Preliminary examination of the interlaboratory data reveals more variability in the ICP-MS data than in the ICP-AES data for several of the major elements including aluminum, calcium, potassium, magnesium, sodium, and zinc. This lack of precision (by ICP-MS in comparison to ICP-AES) may have been, in part, the indirest result of the high sensitivity of ICP-MS; laboratories were required to dilute samples extensively or to use signal suppression for concentrations above a couple of mg/L. This additional sample handling or signal alteration may have increased the measurement variability. Vanadium ICP-MS results are particularly variable, possibly because the correction for CLO^+ ions is inconsistent. Most of the selenium values by ICP-MS exceed those obtained using furnace atomic absorption spectroscopy. ICP-MS analysis of River Sediment (NBS 1645) and Estaurine Sediment (NBS 1646) gave selenium values exceeding those provided by NBS. Clearly, there is a need for appropriate corrections for selenium determinations by ICP-MS.

The preliminary results from this interlaboratory study indicate that ICP-MS Method 6020 is suitable for many elements, but do not support the use of ICP-MS for the determination of potassium, selenium, silver, sodium or vanadium in solid wastes. The interlaboratory relative standard deviation values for these 5 elements (Table 3) exceed 30% by ICP-MS for one or more of the tested samples and are freguently several times higher than the standard deviations obtained by the reference techniques. With proper corrections applied, this ICP-MS database may provide data comparable to furnace AAS for selenium and to ICP-AES for vanadium.

TABLE 1. Silver halide solubilities[a]

compound	solution silver concentration (mg/L) water	HX (1N)
AgCl	1.45	11
AgBr	0.077	115
AgI	0.0012	29,400

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[a] Published data (no standard deviations provided) by Linke and Seidell, <u>Solubilities of Inorganic and Metal Organic Compounds</u>, American Chemical Society, Washington, D.C., 1958.

TABLE 2. Comparison of HCL and HBr digests spiked with 500 ug/L silver and antimony

sample	concentration (ug/L) silver HCl	HBr	antimony HCl	HBr
electroplating sludge	415	51	162	150
EPA waste soil	447	31	105	100
mixed waste sludge	445	78	91	80
river sediment (NBS 1645)	453	442	189	205

TABLE 3. Comparison of relative standard deviations between the tested methods

	percent relative standard deviation			
	potassium		selenium	
Sample	ICP-AES	ICP-MS	GFAAS	ICP-MS
QC Standard #1	13	8.0	12	16
QC Standard #2	11	7.6	9.6	15
electroplating sludge	4.7	36	78	130
EPA waste soil	5.7	23	31	36
mixed waste sludge	13	53	40	240
river sediment (NBS 1645)	17	24	38	200
estuarine sediment (NBS 1646)	6.2	25	31	260
fly ash (NBS 1633a)	5.7	37	17	29
spiked soil	7.7	33	19	110

ICP-AES is inductively coupled plasma atomic emission spectroscopy.
ICP-MS is inductively coupled plasma mass spectrometry.
GFAAS is graphite furnace atomic absorption spectroscopy.
QC is quality control, and BD is below detection.

TABLE 3. (Continued)

	percent relative standard deviation			
	silver		sodium	
sample	ICP-AES	ICP-MS	ICP-AES	ICP-MS
QC Standard #1	69	51	12	20
QC Standard #2	43	9.0	5.1	20
electroplating sludge	29	29	7.7	23
EPA waste soil	60	39	14	28
mixed waste sludge	30	16	9.5	31
river sediment (NBS 1645)	38	17	9.2	26
estuarine sediment (NBS 1646)	33	10	3.5	24
fly ash (NBS 1633a)	BD	9.0	8.6	22
spiked soil	33	19	5.1	27

ICP-AES is inductively coupled plasma atomic emission spectroscopy.
ICP-MS is inductively coupled plasma mass spectrometry.
GFAAS is graphite furnace atomic absorption spectroscopy.
QC is quality control, and BD is below detection.

TABLE 3. (Continued)

	percent relative standard deviation	
	vanadium	
sample	ICP-AES	ICP-MS
QC Standard #1	6.3	9.5
QC Standard #2	10	14
electroplating sludge	28	33
EPA waste soil	12	24
mixed waste sludge	16	19
river sediment (NBS 1645)	11	44
estuarine sediment (NBS 1646)	7.2	25
fly ash (NBS 1633a)	4.3	21
spiked soil	7.4	26

ICP-AES is inductively coupled plasma atomic emission spectroscopy.
ICP-MS is inductively coupled plasma mass spectrometry.
GFAAS is graphite furnace atomic absorption spectroscopy.
QC is quality control, and BD is below detection.

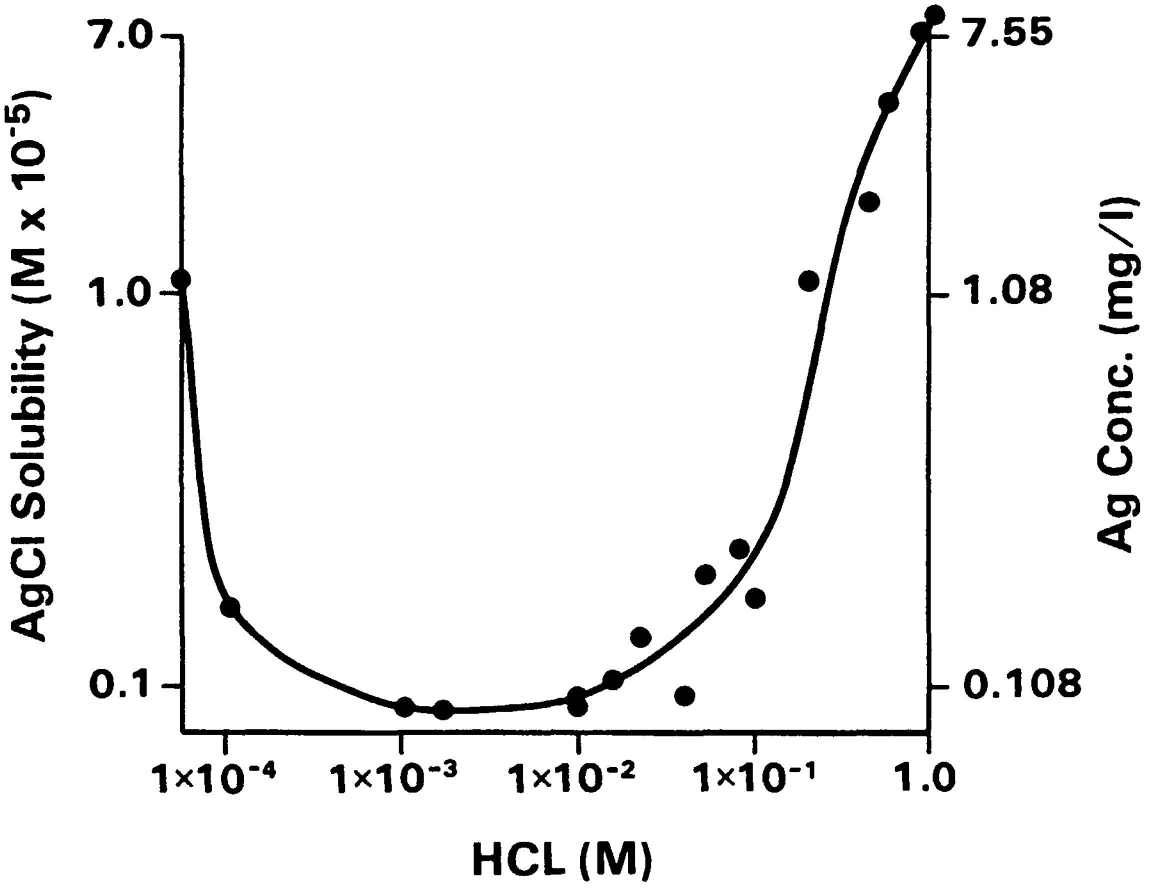

Figure 1. Solubility of silver chloride in HCL at 25°C.

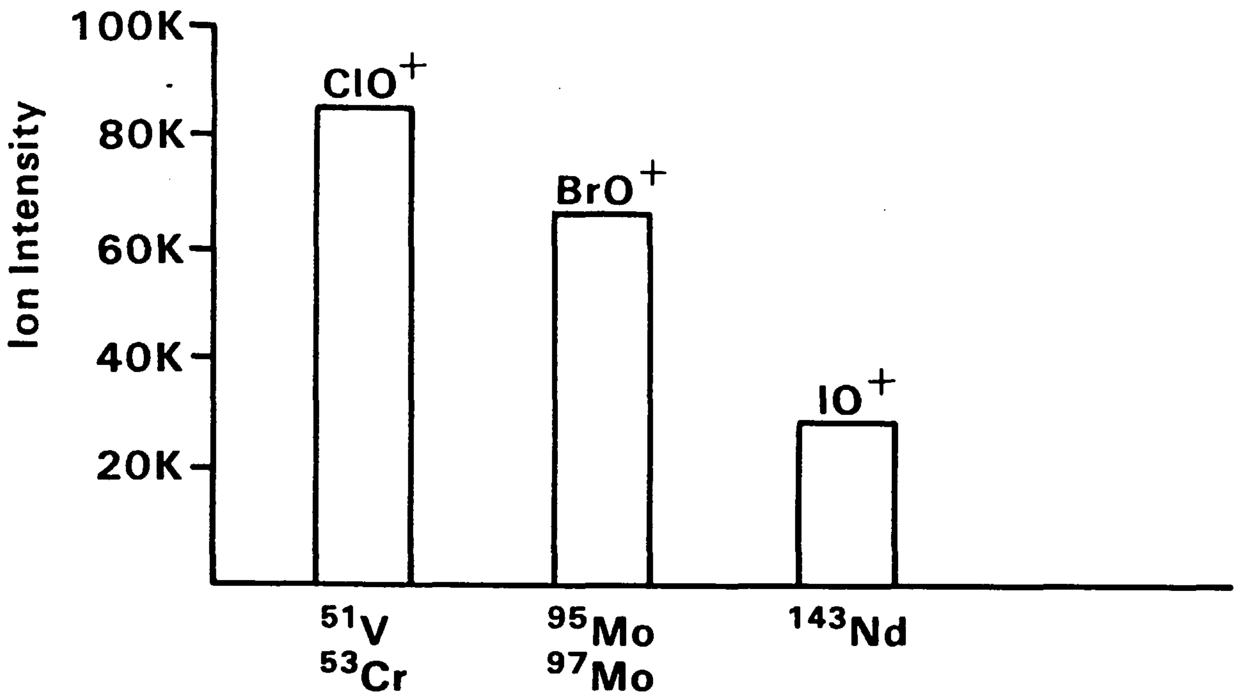

Figure 2. ICP-MS halogen-oxide ion intensities for 0.05 N HX.

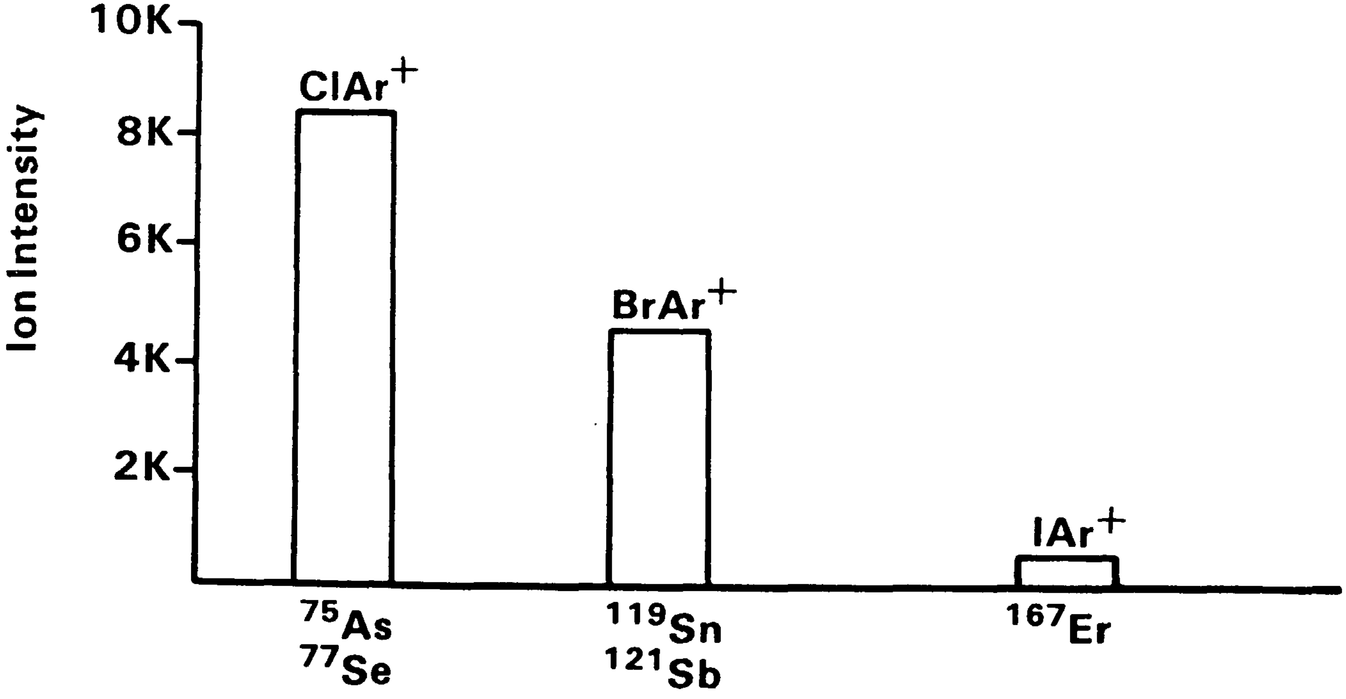

Figure 3. ICP-MS halogen-argon ion intensities for 0.05 N HX.

ICP-MS METHOD 200.8
THE DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES

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ABSTRACT.

EMSL-Cincinnati proposed Method 200.8 has been developed for the determination of trace elements in waters and wastes by inductively coupled plasma - mass spectrometry (ICP-MS). Some of the components of the method which have received special consideration are sample preparation procedures, recommended analytical masses, procedures for sample analysis and calibration, spectral interference corrections and matrix interference correction by the use of internal standardization. Development of the method has been supported by the production and review of a draft version and the design and implementation of a single laboratory validation study to assess the performance of the method for a range of typical sample matrices.

INTRODUCTION

ICP-MS has several characteristics which make it well suited to rapid multi-element determinations at the trace level. Among these are element specificity, extensive element coverage and high sensitivity. In the past few years therefore, ICP-MS has offered an alternative to graphite furnace atomic absorption (GFAA) and inductively coupled plasma - emission spectrometry (ICP-ES) for the analysis of environmental samples. This has resulted in an incentive to develop ICP-MS methodology applicable to the interests of the EPA, and to determine the performance and comparability of the technique using this methodology.

The design of such methodology requires careful consideration. The main goals in the development of this method were to provide enough flexibility such that the method could be used equally successfully with existing commercial instrumentation and to accommodate individual analytical practices in the use of the technique, yet to build in sufficient specified procedures to maintain consistent inter-laboratory performance. Two standard benchmarks for measuring performance are precision and accuracy. Method design will greatly affect the accuracy attained, particularly on a consistent basis. There is a requirement therefore, to address some of the critical factors which will influence accuracy, such as calibration, matrix and spectral interference correction and quality control. In contrast, precision will be influenced more by the quality of the instrumentation concerned and the implementation of good laboratory practices, than by method protocols, although these will be important.

DISCUSSION

Method 200.8 describes procedures for the determination of nineteen elements in waters and wastes. These elements are aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead manganese, molybdenum, nickel, selenium, silver, thallium, uranium, vanadium and zinc. The majority of these are on the EPA's priority pollutant list. Molybdenum and uranium have been included because of the increasing interest in these elements in drinking water and other environmental materials. Instrument detection limits for these elements are listed in Table 1 together with the analytical isotopes which are recommended in the method. The isotopes were chosen to minimize isobaric elemental interferences and known polyatomic ion interferences while providing acceptable detection limits. Of these elements, only selenium has a detection limit greater than 1 µg/l.

For the analysis of solid materials or for the determination of total recoverable elements, sample digestion procedures were chosen to provide compatibility with proposed GFAA and existing ICP procedures, ie using a mixture of nitric and hydrochloric acids for solubilization. Samples prepared by this procedure can be analyzed by any of the three techniques. The concentration of hydrochloric acid in the final preparation is 3% (v/v). This solution is diluted by a further factor of five (0.6% HCl) for ICP-MS analyses in order to minimize chloride

TABLE 1. ICP-MS Instrument Detection Limits.

Element	Recommended Analytical Mass	IDL (µg/l)
Aluminum	27	0.05
Antimony	121	0.08
Arsenic	75	0.9
Barium	137	0.5
Beryllium	9	0.1
Cadmium	114	0.07
Chromium	52	0.07
Cobalt	59	0.03
Copper	63	0.03
Lead	208	0.08
Manganese	55	0.1
Molybdenum	98	0.1
Nickel	60	0.2
Selenium	82	5
Silver	107	0.05
Thallium	205	0.09
Uranium	238	0.02
Vanadium	51	0.02
Zinc	66	0.2

interferences on arsenic, vanadium and chromium. However, data corrections for these interferences are still necessary. The sample preparation procedures were also designed to produce a maximum dissolved solids level of 0.2% (w/v), to attempt to reduce instrument drift and matrix effects from sampling effects at the ICP-mass spectrometer interface.

Prior to running samples, demonstration of instrument stability and mass calibration is required by the method. This is achieved by the running of a tuning solution, with associated acceptance criteria. This tuning solution consists of beryllium, magnesium, cobalt, indium and lead. The isotopes of magnesium and lead are used for adjusting the resolution at low mass and high mass respectively. Following this, the instrument is calibrated for response prior to the running of samples. The method requires that the calibration standard is run as a surrogate sample after every ten analytical samples. An acceptance window of ± 10% of the initial calibration is required. If this window is exceeded by any element, a mandatory recalibration is carried out.

Internal standardization is used in the method to correct for instrument drift or matrix effects. Internal standards accepted for use in the method are lithium, scandium, yttrium, rhodium, indium, terbium, holmium, lutetium and bismuth. For full mass scan determinations, a minimum of three internal standards are required, although five are recommended. The absolute response of these internal standards cannot exceed a window of ± 50% of the original response. If this limit is exceeded, the analysis has to be terminated and the cause of the drift investigated, before restarting any analyses.

Interference correction on acquired data is also a requirement of the method. With a few exceptions, the analytical masses recommended for use with the method are not subject to major spectral interferences. Interferences of significant concern are those of chloride species on arsenic, vanadium and chromium and those of molybdenum oxide on cadmium. However, other interferences have to be monitored where possible by the examination of isotope ratios, and a list of required masses which have to be monitored are included in the method to accommodate this.

Standard quality control protocols are used in the method. In the present version these include an initial demonstration of laboratory performance followed by method quality control involving the use of a laboratory reagent blank, laboratory fortified blank, spiked sample duplicates and the analysis of a quality control sample. Control limits for acceptance criteria are presently under consideration.

A single laboratory validation study is being completed to assess the precision and accuracy of the proposed method. This utilizes a representative set of five waters and three solids consisting of EPA hazardous waste soil, EPA Electroplating Sludge (WP286) and NBS SRM 1645 (river sediment). Most of the materials have an established database which can be used to indicate the performance of the sample preparation procedures. These samples have been digested by the procedures described in the method and sample splits analyzed in parallel by ICP-MS (VG PlasmaQuad) using method 200.8 and by ICP-ES (Jarrell Ash Model 1160 Atomcomp). By using sample splits, sample variability effects were eliminated allowing a direct comparison of the performance of the two techniques. Accuracy has been established in each matrix case by the analysis of spiked duplicates at two concentration levels. Precision has been assessed by analyzing five replicate digests of each matrix.

SUMMARY

EPA method 200.8 provides procedures for the determination of nineteen elements in waters and wastes by ICP-MS. A draft of the method has been prepared, reviewed and tested using a single laboratory validation protocol. Data obtained from the validation study will be considered and the method will be modified as necessary before release to external review.

SELECTED COMPARISONS OF LOW CONCENTRATION MEASUREMENT CAPABILITY ESTIMATES IN TRACE ANALYSIS: METHOD DETECTION LIMIT AND CERTIFIED REPORTING LIMIT

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ABSTRACT. Two large data sets were obtained over a four-day period for graphite furnace atomic absorption spectroscopic measurement of copper (Cu) and reversed-phase high performance liquid chromatographic determination of dinitrobenzene (DNB) at a number of concentrations near the lower limit of measurement. Low concentration measurement capability estimates for each analyte were obtained using the U.S. Environmental Protection Agency's method detection limit (MDL) protocol and the U.S. Army Toxic and Hazardous Materials Agency's certified reporting limit (CRL) protocol. For DNB, analytical variance was found to be homogeneous over the concentration range examined and MDL estimates were independent of concentration over the range of concentration examined. MDL estimates varied by as much as a factor of three from day-to-day emphasizing the uncertainty in these estimates. CRL estimates varied to about the same extent and were numerically quite similar to MDLs when equivalent alpha and beta risks were used. For Cu, analytical variance was found to be proportional to concentration. Thus CRL estimates were very dependent on the concentration range examined. MDLs were less sensitive to this problem. Recommendations regarding the choice of target reporting limits for the CRL protocol were made. The influence of risk assumptions on both MDL and CRL estimates were examined and recommendations for modifications to both procedures made to incorporate an operational beta-risk appropriate to the problem at hand. A case was made for using outlier tests to edit data used to estimate low concentration measurement capabilities.

REPORT OF AN INTERLABORATORY STUDY COMPARING EPA SW 846 METHOD 3050[1] AND AN ALTERNATIVE METHOD FROM THE CALIFORNIA DEPARTMENT OF HEALTH SERVICES

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ABSTRACT

The existing EPA method for the analysis for toxic elements in solid matrices, SW 846 method 3050, cannot accurately or precisely determine (i.e., within SW 846 quality control limits) the concentrations of either antimony or silver and can do so for barium only at lower concentrations. In response to this situation an alternative method was developed by the Southern California Laboratory of the Department of Health Services which could simultaneously solubilize all of the above elements over a broader range of concentrations and can solubilize all other regulated elements with equal or superior success.

As part of the process of validation of this alternative method, an interlaboratory study was conducted with ten public and private laboratories comparing existing methods with the alternative method. A wide range of analytical instrumentation was used including Flame Atomic Absorption Spectroscopy (FAA), Graphite Furnace Atomic Absorption Spectroscopy (GFAA), Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES), and Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). The results of the study clearly show statistically significant differences between method 3050 and the alternative method proposed in this paper.

INTRODUCTION

Federal[2,3] and State laws[4] list antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc (hereafter referred to as the "target elements") as toxic elements. At the present time there are no validated EPA digestion methods for the preparation, by a single digestion, of soils, sludges, sediments and solid waste samples for the analysis of the target elements for determination by FAA, GFAA, or ICP. EPA method 3050 in SW 846 is satisfactory for most of the elements listed above but not for antimony or silver. Consequently, the EPA, in the third edition of SW 846, removed silver and antimony from method 3050's list of validated elements; a decision supported by research here and in other laboratories[5,6]. The SW 846 establishes a 75% to 125% recovery for spikes or reference materials and reproducibility of less than 20% relative percent difference[7]. Silver and antimony cannot be recovered within these limits using method 3050.

Hazardous materials and environmental laboratories are routinely requested to analyze solid phase samples for antimony and silver, usually in conjunction with the other target elements, by legally recognized methods. This leaves the laboratories in the position of using other methods in addition to method 3050, which is time consuming and legally ambiguous.

In response to this problem, a new method has been developed by the Southern California Laboratory (SCL) of the California Department of Health Services (DOHS), hereafter referred to as the SCL method. The proposed method is capable of solubilizing both antimony and silver along with the other target elements, using a single digestion procedure. Data accumulated at SCL indicate this is an effective method for elemental analysis of solid matrices.

Although results from the SCL have demonstrated this new method to be superior method to 3050[6], the possibility of analyst or laboratory bias still exists. To explore these possibilities, an inter-laboratory study was designed to compare the two methods with outside laboratories and analysts.

<u>EXPERIMENTAL SECTION</u>

A) Analytical Methods. (1) EPA SW 846 method 3050 was used as designated. It directs that 1.00-2.00 grams of sample be digested first with 10 mL 1:1 (v/v) nitric acid at 95 C for 15 minutes, then 5 mL conc. nitric acid is added and is refluxed for 30 minutes. This step is repeated until the sample no longer changes in appearance. The digestate is then concentrated to 5 mL. The sample is treated with no more than 10 mL of 30% hydrogen peroxide. Finally, 5 mL of conc. hydrochloric acid and 10 mL of deionized water are added and the sample is refluxed for 15 minutes. The sample is then either filtered (Whatman 41 or equivalent) or centrifuged (2-3,000 rpm for 10 min) and the filtrate (or supernatant) is collected in 100 mL volumetric flask and analyzed by either FAA or ICP.

(2) The SCL method calls for 1.00 - 4.00 grams of sample to be digested in a mixture of 20 mL conc. hydrochloric acid and 5 mL of conc. nitric acid at ambient temperature. The sample and reaction mixture are slowly heated to 95 C to prevent an overly vigorous reaction. The digestion is continued until the disappearance of NO_2 (reddish brown) fumes and no more change in appearance. The digestate is then evaporated to near dryness, washed with about 40 mL of 1%nitric:1%hydrochloric acid (v/v) solution and filtered (Whatman 41 or equivalent). The filter paper is washed with no more than 5 mL hot (95 C) conc. hydrochloric acid, and then 20 mL hot deionized water, all of which is collected into one flask (this will be referred to as the primary filtrate). The filter paper and residue are placed back in the digestion vessel, 5 mL conc. hydrochloric acid are added and refluxed at 95 C until the filter paper disintegrates (approx. 10-15 min.) The disintegrated paper is then washed with deionized water and again filtered (this filtrate will be referred to as

the secondary filtrate.) These filtrates are then analyzed by either ICP or FAA. The results are combined as follows:

$$(X_1 + X_2) * V/w = X_t*V/w = C$$

(equation 1)

X_1 = concentration of element x in primary filtrate
X_2 = concentration of element x in secondary filtrate
X_t = total concentration of element x = $X_1 + X_2$
V = volume of volumetric flask used for both primary and secondary filtrate.
w = weight of sample taken
C = concentration of element x in sample.

B) Statistical Methods. Four statistical tests will be used for analyzing the data. For comparing the variance between methods, SNEDECOR criterion using the F-test[8,9] will be used. For comparing means between methods, the Student t-Test[10] is used. Testing for outliers within a method, a variation of the t-test was used[11]. The term percent relative standard deviation (%RSD) is defined as the standard deviation divided by the mean times one hundred.

C) Laboratories. Eight commercial environmental laboratories were selected to participate. Selection was based on their accreditation with California DOHS, ability to perform hazardous materials analysis and their willingness to participate.

D) Instrumentation. The following ICP-AESs were used, Perkin Elmer 5500, Perkin Elmer Plasma II, Leeman ICP, and Thermo Jarrell Ash 61. A Vg ICP-MS was used at one location. The following FAA and GFAA instruments were used, Perkin Elmer 3030, IL 257, Varian 20, and a Thermo Jerrall Ash V12.

E) Materials. Six solid phase samples and two liquid samples were prepared for the study. The solid phase samples were designated from A to F. The liquid samples were designated "PQL solution" and "Unknown solution". Samples A, B, and C are composites of samples from several industrial sites in southern California with quantifiable levels of some of the target elements in each. Since these materials were homogenized, they represent actual field samples and as such have a greater inherent variance than materials produced in the laboratory. Samples D, E, and F were spiked samples with all of the target elements in each sample. Each analyte was spiked at three different concentrations, designated low, middle, and high. These materials were spiked and homogenized in the laboratory and are very homogeneous. The concentrations in these samples are referred to as the "true" value.

A liquid sample was prepared at a concentration of 1.00 ug/ml for all of the target elements except beryllium, which has a concentration of 0.20 ug/ml in 5% nitric acid/deionized water. This was designated "PQL Solution." This solution was analyzed by all participating laboratories to verify that the instruments used could, in fact, accurately quantify at that level.

A second liquid sample was prepared for the target elements at concentrations ranging from 10 to 90 ug/ml in a solution of approximately 20% acid (nitric and hydrochloric in water.) This solution was designated as an "Unknown solution".

F) Analytical Lines. Each laboratory selected the analytical lines they wished to use for ICP- AES, FAA, and GFAA. Table I lists all of the analytical lines used with the number of laboratories using each by element.

G) Study Design. The study is divided into four parts: quality control, precision, accuracy, and background. Copies of EPA SW 846 method 3050, the SCL method, instruction sheets and reporting sheets were sent out with each set of samples. Each lab was supposed to use only these two methods. One laboratory , however, used its own modification of method 3050 for instrumentation reasons.

1) Quality Control. To meaningfully compare the accuracy and precision of two methods through an interlaboratory study, it is important to control for the variance caused by the inherent differences between the laboratories. The primary sources of this variance are differing levels of analyst skill, types of analytical instruments and choice of spectrographic lines. Three steps were taken to assess the contributions of these factors to the final results.

a) A method blank was run for each method by each laboratory. This consists of running the entire digestion procedure using empty glassware.

b) A Practical Quantitation Limit (PQL) was established at 1.0 ug/mL for all elements except beryllium, which had a limit of 0.2 ug/mL. No value below this limit was to be reported. This was to provide a control for the differences in sensitivities of the various analytical instruments.

c) The "Unknown Solution" was also analyzed by every laboratory. Since this sample was not digested but run directly on the instruments, any variance from this sample is due entirely to the instrumentation. This allowed us to quantify the amount of variance contributed by these differences.

2) Precision (Round I). The objective of this round of study is to compare the variance or precision of each method. Samples A, B, and C were distributed to the laboratories. These samples were to be analyzed in triplicate by each method. The results from each laboratory were checked to see if the triplicates met the SW 846 precision limits for duplicates: 20% for each target element. The results from all the laboratories were averaged and the overall variance between methods was compared using the statistical methods mentioned above.

3) Accuracy (Round II). The goal of this round is to compare the accuracy of each method. Samples D, E, and F were analyzed once by each laboratory and method. Each sample had a "true" value equal to the spiked quantities. A comparison between the methods was done by averaging the results from all laboratories and calculating the means for each method. These were then compared to the "true" value for the samples. The %RSD was also compared between methods.

4) **Background.** A laboratory survey was done using a set of questions about the state of the laboratory. The subjects included sample load, division of labor, and staff qualifications. The goal of this survey was to determine the general state of the participating laboratories.

5) **Criteria for Evaluation.** Five factors have been identified for assessing the relative performance of digestion methods: accuracy, precision, range of elements, linear range of extraction and ease of use.

a) **Accuracy.** The mean value must fall within EPA SW 846 method 6010 8.5.2 limits. These state that a matrix spike must be recovered within 75% to 125% of the known value.

b) **Precision.** Replicate values of a method must fall within the limits set by EPA SW 846 which is that duplicate samples should be within 20%.

c) **Range of Elements.** Methods that can solubilize more of the target elements will be of greater use to analysts.

d) **Linear Range.** The broader the linear range of a method, the better is its performance.

e) **Ease of Use.** The simpler a method is, the fewer the mistakes that will possibly be introduced by the analyst.

RESULTS

Quality control. None of the laboratories showed any significant contamination in their method blanks and most were able to accurately quantify the target elements at the PQL.

Listed on Tables II, III and IV are the %RSD for each element from the "Unknown solution". This number is interpreted as the contribution to the overall variance of each analyte by the differing instrumentation employed.

Precision (Round I). Using the F-test to compare variances requires similar means. As can be seen from table II the high concentrations of barium in sample A and the antimony in sample C are of significantly different means and thus cannot be compared. Despite this, the barium in sample A still had similar %RSDs between methods. Otherwise, all of the target elements gave statistically similar variances.

Accuracy (Round II). The data from this round is listed on tables III, IV, and V. Antimony and silver had lower recoveries in samples E and F by method 3050 than in the SCL method. Barium in sample A was significantly lower in method 3050 than in the SCL method. All of the other target elements had means that were well within the SW 846 limitation of 25% of the "true" value using both methods. There were no significant differences in mean values between methods for any target element except those listed above.

LIMITATIONS. There were three errors in the execution of this study. First, beryllium was not run in round one. Second, beryllium and cadmium were spiked at levels that were too low in sample F of round II. Third, the sample vials containing the Unknown solution were contaminated with zinc, so instrumental variance for zinc is not known. These limitations do not, however, impact the overall conclusions of this study.

DISCUSSION

Accuracy. The accuracy of the mean values in round II for both methods was well within SW 846 limitations. However, three exceptions: low and middle concentrations of antimony by method 3050, high concentrations of barium by both methods, high and middle concentrations of silver by method 3050, and high concentrations of silver by the SCL method. The vast majority of mean values were above 90% of the "true" value and all, with the above exception, were above 80%. Given the large number of outliers, there is no doubt that the recoveries could have been higher.

Apparently, the filter paper can hold up to 1000 ug of antimony, depending on how much is present. Method 3050 and the primary digestion of the SCL method fail to recover this antimony which, at lower absolute concentrations, is a significant percentage. The hot HCl wash can release most of this, so at lower concentrations the HCl wash is enough to get accurate results. This can be seen on table VI. As can be seen in samples E and F, when the concentration of antimony in the soil is lower, all of the trapped antimony is released in the HCl wash. As the concentration increases, the HCl wash can recover less and less (see samples C and D). Antimony reacts with nitric acid to form oxides which are soluble in concentrated HCl[12].

Barium and silver are also trapped in the residue and filter paper but only at higher, not lower concentrations. Silver percipitates as a chloride when using either method, some of which can be liberated by hot HCl[13]. Technique is very important in using this process as evidenced by the high variability in results. Barium exhibits similar behavior but at much higher concentrations as its halides are the least soluble of the group II elements[14].

Precision. As with accuracy, both methods seem to given acceptable reproducibility for most target elements. One exception to this is the high levels of barium in samples A and D. In sample A, each laboratory's triplicates were within 20% of each other; however, the mean values from each laboratory were wildly different for both methods. In sample D the variance between laboratories for barium is also extremely high.

Apparently, at high concentrations, barium is very subject to slight differences in technique.

At higher concentrations silver is very hard to precisely reproduce. This is indicated by the large number of laboratories that did not recover any silver from samples D, E and F. The SCL method has a high %RSD at high concentrations but all of the laboratories recovered some above the PQL. The SCL method is more tolerant of slight differences in technique than is method 3050 for silver.

Likewise, at lower concentrations, antimony does not reproduce well using method 3050. Several times no antimony was recovered (table III). When it was recovered, the amounts recovered were highly variable.

Among the other target elements, the main source of variance seems to be differences in instrumentation rather than differences in methods. Taking lead as an example, the variability due to instrumentation, as measured by the %RSD from the "Unknown" solution, was 16%. In round I, where the sample can not be assumed to be completely homogeneous, the experimental %RSDs were 26% & 23% for sample A, 21% & 28% for sample B, and 23% & 27% for sample C by method 3050 and the SCL method respectively. The variability between methods is only a little higher than that caused by differences between instruments.

In round II, the samples are very homogeneous. Here the experimental variability is generally equal to the variability caused by differences in instrumentation. Again taking lead as the example, the expermimental variability were 15% & 14% for sample D, 15% & 29% for sample E, and 20% & 7.1% for sample F. Notably the results from the sets that had %RSDs of 29% and 20% contained outliers. In a clear majority of the cases, when the %RSD was more than twice the %RSD from the instrumentation, there was an outlier in the set. In most other cases the %RSD was less than twice the %RSD of the instrumentation even if outliers were present. Silver consistently defied this pattern.

From these results it is clear that the SCL method generally yields more precise data on the target elements of this study.

It is possible to challenge this conclusion because of the large number of outliers. In round II for example, out of 828 determinations, 68 outliers were reported including less than PQL results for samples with quantifiable concentrations of target elements. If 11 are eliminated because they represent elements not quantifiable by method 3050, then there are 57 outliers which account for 6.7% of the data. These outliers favor neither method. If it is assumed that the number of outliers should be about 1%, i.e. the number expected outside three standard deviations, then we must assume that the number of outliers is unreasonably high. (A similar number of outliers is obtained by using control charts with three standard deviation limits where the suspected outlier is not factored in.)

It can be argued that this may be caused by possible heterogeneity in the samples, thus invalidating the study. However, there is no pattern to suggest this. For example, one laboratory that reported an outlier for copper, reported chromium close to the true value while an other laboratory reported the opposite. Rather, it can only be concluded that an unreasonable number of analytical errors were committed, the majority of which would seem to be data handling errors as opposed to poor technique. This is indicated by the number of results that are even multiples or fractions of the mean and/or "true" value. This view also supported by the number of simple computational errors committed on the report sheets which were corrected by the authors.

This conclusion is consistent with the data collected as part of the Background study to this report. Every participating laboratory has experienced an explosive growth over last three years. On the average these laboratories experienced a 210% increase in sample load and a 180% increase in professional staff. Notably, fewer and fewer positions are filled by chemists with environmental experience. Only 42% have previous experience which averaged 3 years. While every laboratory turned in at least one outlier, the number of outliers was not distributed evenly among all the laboratories. A few turned in many more than the others. The high incidence of statistical outliers in this study, we feel, is a result of the great flux in the environmental field. Since these errors do not bias the data toward either method, these errors merely increase the variability of both methods and do not invalidate the data.

Range of Elements. EPA SW 846 method 3050 cannot accurately or precisely measure antimony, barium, nor silver at common concentrations, while the SCL method can. Thus the SCL method has a wider range of elements.

Linear Range. For the majority of elements both methods had equal linear ranges. The linear ranges for antimony, barium, and silver are wider for the SCL method than for method 3050,
although neither method is as linear with barium and silver as with the other target elements.

Ease of Use. The method 3050, as written, has at least seven steps, which are repetitive and have rigid time schedules. The SCL method has six steps, few of which require timing or careful observation. The SCL method is hence a simpler and easier method to use. Since the SCL method has no time limitations and uses aqua regia, which digests more vigorously, the SCL method the SCL method is a faster method.

SUMMARY AND RECOMMENDATIONS

Judging from the results of this interlaboratory study, it is clear that the SCL method is superior in all five criteria. It is equally accurate and precise for the most of the same elements that 3050 claims and is more accurate and precise for antimony, barium, and silver over a broader linear range. At the very minimum, we recommend that SW 846 method 3050 should be amended in the method performance section to note that it has only a limited linear range for antimony, barium, and silver. We recommend that the SCL method be adopted as an accepted alternative to method 3050. Finally, further study is needed on the continuing changes in the environmental laboratory industry.

ACKNOWLEDGEMENTS

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Table I
Analytical Lines

Analyte	Wavelength	# of labs	Analyte	Wavelength	# of labs
As	189.04	2	Ni	231.60	5
	193.76	5		323.00	3
Ag	328.07	8	Pb	216.99	1
Ba	233.53	3		220.35	5
	455.40	2		280.8	1
	493.41	1		283.31	1
	543.6	2	Sb	206.83	5
Be	234.8	4		217.58	3
	313.04	4	Se	196.03	7
Cd	214.44	2	Tl	190.86	1
	226.50	2		276.79	4
	228.80	4		351.92	2
Co	228.62	6		377.57	1
	240.7	2	V	292.40	6
Cr	205.55	2		318.4	2
	267.72	4	Zn	213.86	8
	357.87	2			
Cu	224.70	1			
	324.75	7			
Mo	202.03	6			
	313.2	2			

All wavelengths are in nanometers

Table II

Results from Round I
N = 27 (except for As where N = 24)

ANALYTE	SAMPLE I.D.	MEAN VALUES		t-TEST [1]	%RSD VALUES			F-TEST [2]
		3050	DOHS		3050	DOHS	UNKNOWN	
Ag	B	130 [2]	160	2.40	40	24	6.4	0.58
As	C	920	900	0.50	21	21	16	0.97
Ba	A	322	1600	4.17	112	98	10	NA [3]
	B	96	100	0.69	25	28	10	1.49
	C	120	130	0.83	33	36	10	1.37
Cd	A	140	130	0.42	25	25	9.5	0.95
Co	B	400	380	1.24	23	21	8.9	1.52
Cr	A	2200	2200	0.14	23	25	18	0.83
	B	5800	5500	1.11	22	26	18	0.93
	C	320	370	1.89	31	27	18	0.98
Cu	A	15000	15000	0.36	37	28	11	0.78
	B	1700	1600	1.40	33	27	11	1.94
	C	400	420	0.72	26	24	11	0.92
Mo	C	840	860	0.19	49	48	8.3	1.00
Ni	A	290	290	0.30	21	26	9.3	1.26
	B	160	160	0.31	21	24	9.3	1.21
	C	170	200	2.21	26	30	9.3	1.87
Pb	A	2700	2700	0.32	26	23	16	0.89
	B	3000	3000	0.34	21	28	16	1.83
	C	120	130	0.36	23	27	16	1.52
Sb	C	320	830	13.1	61	13	13	NA [3]
Se	C	680	700	0.31	23	34	12	2.31
Tl	C	800	770	1.49	14	8.7	7.1	2.60
V	B	1200	1100	1.12	32	34	14	0.99
	C	1400	1500	1.56	27	28	14	1.31
Zn	A	3500	3500	0.25	25	29		1.15
	B	2400	2000	0.57	27	27		1.08
	C	1600	1500	1.05	35	28		1.78
UNITS		ug/g			PERCENT			

The critical value for t is 2.98 and the critical value for F is 2.58 for alpha = 0.01

[2] **Silver by method 3050 has only 24 data, as 3 data are less than PQL.**

[3] **The F-test is not applicable (NA) to barium or antimony because of the differences in mean values.**

[1] **The values for t and F are dimensionless.**

TABLE III ROUND II Low Values
N = 9 (except for As and Se where N = 8)

ANALYTE	"TRUE" VALUE	SAMPLE I.D.	MEAN VALUE		t-TEST [1]	%RSD VALUES			OUTLIERS		3050[2] <PQL
			3050	SCL		3050	SCL	UNKNOWN	3050	SCL	
Ag	109	D	109	128	0.54	32	28	6.4	0	0	1
As	124	D	127	131	0.20	32	38	16	1	0	0
Ba	197	F	190	206	0.98	18	15	10	0	0	0
Be	< 10	F									
Cd	< 50	F									
Co	154	D	136	138	0.12	26	20	8.9	1	1	0
Cr	128	E	117	143	1.31	21	35	18	0	1	0
Cu	252	F	241	267	0.56	22	45	11	0	1	0
Mo	166	E	153	160	2.06	48	39	8.3	1	1	0
Ni	204	F	195	215	1.50	13	12	9.3	1	0	0
Pb	263	F	260	254	0.30	20	7.1	16	1	0	0
Sb	142	E	94	157	3.09	48	18	13	0	0	3
Se	155	D	139	161	0.94	27	29	12	0	0	0
Tl	77	D	96	124	0.56	83	83	7.1	1	1	2
V	168	E	144	162	0.90	22	28	14	0	0	0
Zn	148	E	153	172	1.00	16	26		0	1	0
UNITS	ug/g					PERCENT					

TABLE IV ROUND II Middle Values
N = 9 (except As and Se where N = 8)

ANALYTE	"TRUE" VALUE	SAMPLE ID	MEAN VALUE		t-TEST [1]	%RSD VALUES			OUTLIERS		3050[2] <PQL
			3050	SCL		3050	SCL	UNKNOWN	3050	SCL	
Ag	257	F	155	223	4.18	19	13	6.4	0	0	3
As	1520	F	1370	1470	0.67	17	19	16	1	2	0
Ba	686	E	633	664	0.51	24	11	10	1	0	0
Be	19.0	E	18.5	18.9	0.34	15	13	11	0	0	0
Cd	432	E	413	446	0.78	21	18	9.5	1	1	0
Co	999	F	912	935	0.23	24	17	8.9	1	0	0
Cr	1920	D	1040	1710	0.91	14	18	18	1	0	0
Cu	2190	E	2030	2010	0.80	14	30	11	1	2	0
Mo	557	D	585	632	0.31	30	46	8.3	2	1	0
Ni	2160	E	2180	2000	0.74	16	30	9.3	1	1	0
Pb	3360	E	3010	2742	0.83	15	29	16	0	1	0
Sb	729	F	340	704	5.57	46	14	13	0	1	0
Se	666	E	554	591	0.63	24	14	12	0	1	0
Tl	486	F	368	390	0.68	22	10	7.1	2	0	0
V	897	D	849	825	0.38	18	11	14	1	0	0
Zn	1030	F	959	1042	0.58	27	30		1	1	3
UNITS	ug/g					PERCENT					

[1] The value for t is dimensionless. Critical value for t = 2.98 for alpha = 0.01

[2] This column notes the number of laboratories that reported <PQL for each analyte by method 3050. The number of data points is thus N - this number.

SOLUBILITY DATA
Table VI

		SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D	SAMPLE E	SAMPLE F
ANTIMONY	3050	<pql	<pql	522	10200	680	188
	SCL prim	<pql	<pql	1520	10000	1420	314
	SCL scdn	<pql	<pql	272	620	<pql	<pql
	SCL total	<pql	<pql	1660	10600	1420	314
BARIUM	3050	646	192	240	1410	1260	380
	SCL prim	560	200	260	1080	1320	410
	SCL scdn	1540	<pql	<pql	1400	<pql	<pql
	SCL total	2100	200	260	2500	1320	410
SILVER	3050	<pql	260	<pql	218 (n=8)	240 (n=5)	310 (n=6)
	SCL prim	<pql	320	<pql	256	442	446
	SCL scdn	<pql	<pql	<pql	<pql	125	<pql
	SCL total	<pql	320	<pql	256	577	<pql
	NO. OF DATA	27	27	27	9	9	9

Numbers in parenthesis represent the number of results above the PQL. All results are in total ug.

TABLE V ROUND II High Values
N = 9 (except As & Se where N = 8)

ANALYTE	"TRUE" VALUE	SAMPLE	MEAN VALUE		t-TEST [1]	%RSD VALUES			OUTLIERS		3050[2] <PQL
			3050	SCL		3050	SCL	UNKNOWN	3050	SCL	
Ag	6940	E	120	334	3.56	25	37	6.4	0	1	4
As	16300	E	13800	15100	0.84	26	14	16	0	0	0
Ba	5000	D	708	2150	2.08	120	82	10	0	0	0
Be	69.7	D	64.3	65.6	0.32	15	7.3	11	1	0	0
Cd	1230	D	1080	1110	0.34	19	15	9.5	1	2	0
Co	5320	E	5310	4840	0.65	25	33	8.9	1	2	0
Cr	10400	F	9050	9840	0.93	17	19	18	0	0	0
Cu	6430	D	5180	6220	1.10	16	9.8	11	1	2	0
Mo	2850	F	2770	2880	0.19	45	35	8.3	1	1	0
Ni	6150	D	5520	5730	0.39	22	15	9.3	0	0	0
Pb	7450	D	7070	7240	0.34	15	14	16	0	0	0
Sb	5630	D	5200	5600	0.87	17	17	13	1	1	0
Se	2450	F	1990	2260	1.05	31	12	12	1	1	0
Tl	3480	E	3070	2970	0.36	20	18	7.1	1	1	0
V	2300	F	1860	2015	0.95	19	14	14	0	0	0
Zn	5670	D	5120	5340	0.35	29	19		1	0	0
UNITS	ug/g					PERCENT					

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[1] The value for t is dimensionless. Critical value for t=2.98, for Alpha=0.01

[2] This column notes the number of laboratories that reported <PQL for each analyte by method 3050. The number of data points is thus N-this no.

A PERFORMANCE EVALUATION OF THE INORGANIC METHODS USED IN THE CONTRACT LABORATORY PROGRAM

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ABSTRACT. Periodically, Inorganic Method Validation Reports are generated for the Contract Laboratory Program (CLP) by the Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV). The reports are an evaluation of each method's performance over the previous year. The information used to generate the reports is taken from the results and Quality Control (QC) data reported from the laboratories on diskettes, from the Quarterly Blind (QB) performance evaluation standard results, and from the operating parameters and conditions reported by the laboratories. Once the information is studied, a report is completed detailing the precision, accuracy, limits of detection, and linear range of the methods for soil and water. Other QC results and data trends, particular to each method, may also be included in the reports. The reports are of value to the CLP because they provide a measure of method performance that is useful for determining if the needs of the program are being met. In the future, the reports also may be helpful in the identification of possible problems and the optimization of the methods.

The presentation will include accuracy and precision results for the inorganic CLP methods from spike, duplicate, laboratory control sample (LCS), and other EPA performance standard results taken from the Method Validation Reports for routine data generated in 1988. Examples of how the method performance can be compared with operating conditions to optimize method performance may also be presented.

STUDIES OF INTELLIGENT AUTOMATION FOR WATER ANALYSIS BY ICP-AES WITH CLP PROTOCOL

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ABSTRACT. Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) has been approved as an EPA method for water analysis. ICP offers excellent detection limits, wide linear working range, and outstanding multi-element capability. The EPA Contract Laboratory Program (CLP) has recently become the most widely used protocol for water analysis because of its stringent quality control procedures, even by laboratories which do not specifically have EPA contracts. Because environmental laboratories typically run high numbers of water samples, with 20 or so elements per sample, the ICP application to the CLP program is ideal.

ICP spectrometers have often been used with automatic sampling devices. These have typically been the carousel type, with which a sequence of samples are analyzed, start to finish, with no deviation possible. This presents a conflict when trying to use this type of automatic sampler with CLP. As required by CLP, a sequence of check standards must be analyzed periodically with the decision to run unknowns depending on the results of the check standards. Out of tolerance results require recalibration, re-analysis of check standards, then analysis of unknowns. The decision-making requirement during a sample run thus precluded the use of an auto-sampler, negating a large part of the advantage of ICP.

In this study, a system was used which employs artificial intelligence to follow the CLP format with full automation. It has long been recognized that the simultaneous ICP offers the most efficient means for high sample throughput, being capable of triplicate analysis and flush-out within two minutes. The more widely used sequential instruments typically take 5 -10 times longer. The instrument evaluated in this study uses simultaneous and sequential spectrometer in combination. The sequential module is employed only as a contingency basis, such as why unusual elements are requested. The vast majority of the determinators are done on the simultaneous module.

A program was developed which enabled the computer to control simultaneous and sequential spectrometers at the same time, as well as, maintaining direct control of the auto-sampler. Communication between spectrometer and auto-sampler via fiber-optic cable is also evaluated. The entire program was designed to support the CLP protocol while operating unattended. This includes analysis of check standards, and based on these results, the decision to recalibrate or to proceed with analysis. After analysis of a prescribed number of samples, the procedure is repeated. When all samples have been analyzed, the computer will shut down the instrument automatically. Analytical results will be stored in the computer.

LABORATORY INFORMATION MANAGEMENT

CUSTOMIZED LIMS DATA TREATMENT THROUGH INTERACTION WITH A USER-DEFINABLE SPREADSHEET

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ABSTRACT

A PC-based LIMS requires a data base management system to handle and track the vast amounts of information generated in today's analytical laboratory. Yet a data base management system is not the most convenient tool for handling analytical calculations, which may require the use of parameters from different records in the data base. For calculations, the spreadsheet has become an indispensable tool, allowing non-programmers to define a desired manipulation of numerical data, by simply specifying algebraic formulas to define the needed calculations. This paper will present an approach to providing straightforward customization of a PC-based LIMS, through integration of the LIMS data base to a user-definable spreadsheet. Example applications will include spreadsheets for raw data entry and post analysis data processing for production of QC charts and management graphs.

INTRODUCTION

A computerized Laboratory Information Management System (LIMS) makes up the heart of organizational management, for many laboratories. The standard functions contained in a full functioning LIMS system include: sample log-in and tracking; generation of worksheets, management reports, results reports, and, if appropriate, invoices; instrument interfacing and automatic data collection; automated quality control; and archiving of sample results, chain-of-custody, and other information.

LIMS systems have traditionally been built around mainframe or large mini computers. These large scale LIMS offer the ability to handle and organize very large informational data bases, but they are frequently difficult to set up, requiring extensive work for customized reporting and data treatment, through expensive and time-consuming custom programming by the manufacturer or by a laboratory's in-house programming staff.

While the raw computer power of a large LIMS system is required for some operations, recent trends have seen the emergence of micro computer based LIMS systems. These systems are usually built around the powerful and fast 80386 hardware, as a file server for a network of PC's, distributed about the laboratory. In addition to a significant initial purchase price advantage, a PC-based LIMS system can be fully operational in a matter of days, and the PC-based system may offer substantially enhanced flexibility for easy customization of report formats and data treatment.

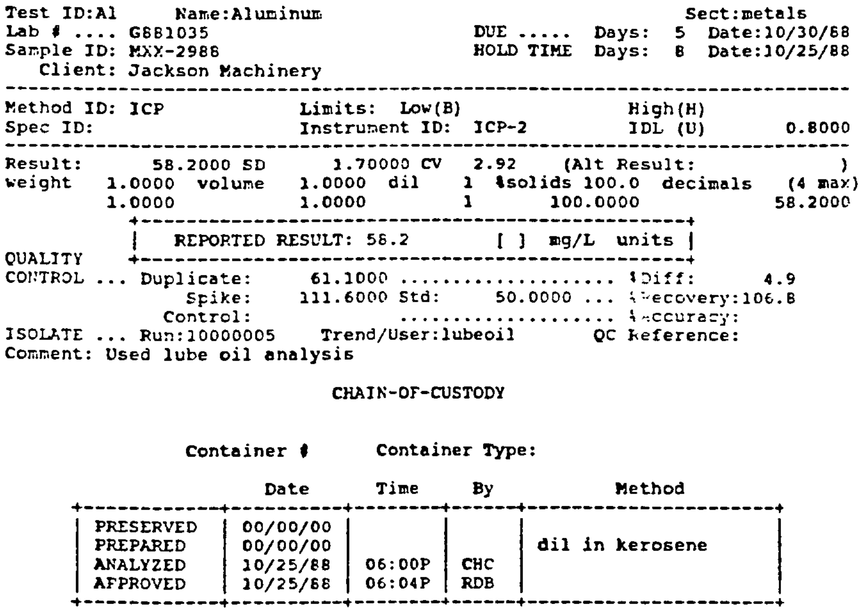
Off-the-shelf software for PC's offer a wide variety of sophisticated applications, which are far more user oriented, than is much of the software for mini and mainframe computers. Some of this software is well suited for use in the laboratory. Data base management and spreadsheet programs are two such applications.

Relational data bases are ideal for storing information and allowing the user to sort and query the data to retrieve any desired information. This makes a relational data base management system the obvious choice for the heart of a PC-based LIMS system. However, many of the functions, which are required in a full-functioning LIMS, are not easily implemented with a data base manager. Complex, multiple-parameter calculations are just one of these areas. On the other hand, a spreadsheet program is ideal for handling the areas where the data base management system is weak. Therefore, the ideal LIMS would consist of a system of interacting data base management and spreadsheet modules, with each module handling those functions for which it was best suited.

"Integrated" software packages, which provide interacting data management and spreadsheet modules, are available for the personal computer. Many of these systems are programmable, to allow creation of dedicated, turn-key applications. TELECATION ASSOCIATES has chosen such an integrated package for development of its "SMARTLAB" (R) Laboratory Information Management System. The package chosen was "SmartWare" (R) from Informix Software, Inc. In addition to the data manager and spreadsheet, SmartWare also provides a word processor, communications program, and other tools, which will also find use in the laboratory. The application of the data manager and spreadsheet to the SMARTLAB LIMS system is discussed below.

THE BENEFITS OF A RELATIONAL DATA BASE

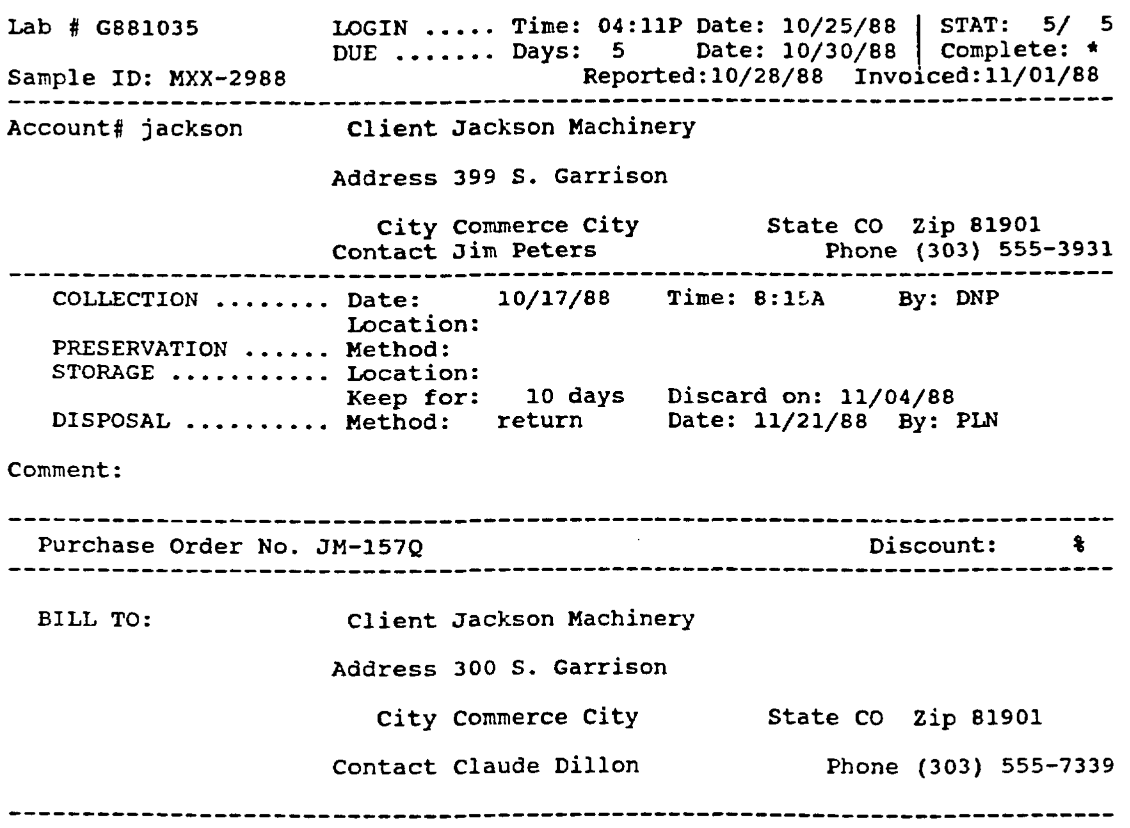
The main benefit of a relational data base management system is its ability to maintain large amounts of information, which can be easily retrieved and tracked by the user. In a LIMS application, the information to be maintained in the data base file includes, among other things, sample and test identification fields, with associated analytical information. To provide maximum flexibility in the tracking of analytical information, each test to be run and tracked occupies its own data base record, which can be retrieved, as needed, from all the other records in the data base. The test specific information maintained in the SMARTLAB "Test" data base record is shown in Figure 1.



```
Test ID:Al     Name:Aluminum                                  Sect:metals
Lab # .... G881035                       DUE .....  Days:  5  Date:10/30/88
Sample ID: MXX-2988                      HOLD TIME  Days:  8  Date:10/25/88
   Client: Jackson Machinery
--------------------------------------------------------------------------
Method ID: ICP              Limits:  Low(B)              High(H)
Spec ID:                    Instrument ID:  ICP-2        IDL (U)      0.8000
--------------------------------------------------------------------------
Result:       58.2000 SD       1.70000 CV   2.92    (Alt Result:           )
weight    1.0000  volume    1.0000  dil    1  %solids 100.0  decimals  (4 max)
          1.0000            1.0000         1        100.0000           58.2000
          +-----------------------------------------------------+
          |   REPORTED RESULT: 58.2          [ ]  mg/L  units   |
QUALITY   +-----------------------------------------------------+
CONTROL ... Duplicate:     61.1000 ..................... %Diff:      4.9
                Spike:    111.6000 Std:     50.0000 ... %Recovery:106.8
              Control:             ..................... %Accuracy:
ISOLATE ... Run:10000005    Trend/User:lubeoil       QC Reference:
Comment: Used lube oil analysis

                              CHAIN-OF-CUSTODY


                Container #        Container Type:

                          Date        Time     By            Method
   +-------------+-----------+---------+------+----------------------+
   | PRESERVED   | 00/00/00  |         |      |                      |
   | PREPARED    | 00/00/00  |         |      | dil in kerosene      |
   | ANALYZED    | 10/25/88  | 06:00P  | CHC  |                      |
   | APPROVED    | 10/25/88  | 06:04P  | RDB  |                      |
   +-------------+-----------+---------+------+----------------------+
```

Figure 1. SMARTLAB "Test" data base record.

In addition to all the test specific information, there are a number of sample specific parameters, shown in Figure 2, which must be maintained in a LIMS data base. Since this sample information is the same for all tests being run on the sample, it is undesirable to record all the sample specific information in every test record. Therefore, a separate "Samples" data base file is used to store sample specific information. Relational data base capabilities allow the "Samples" data base to be linked to the "Tests" data base, to provide complete information on both sample and test specific information.



```
Lab # G881035          LOGIN ..... Time: 04:11P Date: 10/25/88 | STAT:  5/  5
                       DUE ....... Days:  5     Date: 10/30/88 | Complete: *
Sample ID: MXX-2988                   Reported:10/28/88  Invoiced:11/01/88
-------------------------------------------------------------------------------
Account# jackson        Client Jackson Machinery

                       Address 399 S. Garrison

                          City Commerce City          State CO  Zip 81901
                       Contact Jim Peters                 Phone (303) 555-3931
-------------------------------------------------------------------------------
  COLLECTION ........ Date:     10/17/88    Time: 8:15A     By: DNP
                      Location:
  PRESERVATION ...... Method:
  STORAGE ........... Location:
                      Keep for:   10 days   Discard on: 11/04/88
  DISPOSAL .......... Method:   return      Date: 11/21/88  By: PLN

Comment:

-------------------------------------------------------------------------------
 Purchase Order No. JM-157Q                                Discount:     %
-------------------------------------------------------------------------------

 BILL TO:               Client Jackson Machinery

                       Address 300 S. Garrison

                          City Commerce City          State CO  Zip 81901

                       Contact Claude Dillon              Phone (303) 555-7339

-------------------------------------------------------------------------------
```

Figure. 2. SMARTLAB "Samples" data base record.

In order to retrieve desired information from the entire data base of all samples and tests in the laboratory, it is necessary to isolate selected records (query) or rearrange the order of records (sort) in the data base. This kind of manipulation of the data base is easy with a flexible relational data base system.

For those predictable manipulations of the data base, subsets, or "indices" of data base records can be maintained, and these indices may be accessed instantly upon demand, without resorting or requerying. SMARTLAB maintains predefined sort indices for "lab #", "test ID", "client name" and more, to allow immediate user access to sorted data base records. Also, predefined isolated subsets of data base records (e.g., "preparation backlog", "report backlog", "invoice backlog") allow instant recall of those sample test records meeting selected stages of completion. These techniques substantially enhance the speed at which selected information can be accessed.

Another benefit of relational data base systems, is the ability to design custom report formats. Every laboratory has its own idea of what kind of information should be shown on a report, and where that information should be placed. Further, special purpose reports which may be very important to one laboratory, may not even apply in another. Report definition utilities allow generation of report formats to meet individual needs.

Screen oriented report definition utilities are easy to use, in that the report is laid out on the screen exactly as it is to appear on paper. Once created, user-defined report formats may be accessed, as desired, to generate data base reports for any purpose. Predefined SMARTLAB reports include formal analysis reports, invoices, and a variety of management reports. In addition, the report definition utility may be used to edit existing reports, or create completely new formats.

THE BENEFITS OF A SPREADSHEET

While the data base manager serves as the heart of the LIMS by maintaining, tracking, retrieving, and reporting laboratory information, other functions, which are equally important to the overall LIMS application, are more easily accomplished with a spreadsheet. One of these functions is the performance of mathematical calculations. While calculated data base fields can be defined, which automatically show the results of a calculation based on other information in the same data base record, it is very difficult to incorporate parameters from a different data base record into the calculation. Inter-record calculations are, on the other hand, very easy with a spreadsheet. An example of an inter-record calculation, which is easy with a spreadsheet, but difficult to perform from a data base, is the calculation of the percent difference between duplicate sample runs, which involves comparing results from two different data base records.

Most spreadsheet programs also provide graphing utilities, which allow data to be presented in a variety of graphical formats. There are many laboratory applications for this capability. Some of these will be illustrated later.

When manually entering large amounts of information, it is sometimes easier to enter that information into a spreadsheet, rather than a data base. In the two-dimensional row/column spreadsheet layout, the user can randomly access any cell for data entry purposes, while the field-by-field, record-by-record forced sequence for entry into a data base, is sometimes tedious.

DATA BASE - SPREADSHEET INTERACTION

Figure 3 lists the basic functions of a LIMS system and identifies the optimum software tool (data base manager or spreadsheet) which is best suited for implementing each function. Those functions which primarily involve retrieval of information (sample login, laboratory status review, reporting, invoicing, and archiving) are clearly data base applications. Calculation intensive functions (data entry and quality control) are best suited for the spreadsheet. Functions which require both record retrieval and calculation intensive functions, may best be served by a combination of data manager and spreadsheet approaches.

	DATA BASE	SPREAD SHEET	
Sample Login	X		Area 1
Assigning work	X	X	DATA ENTRY APPLICATIONS
Data entry		X	
Data approval		X	
Lab status	X		
Reporting	X		
Invoicing	X		
Archiving & search	X		Area 2
Extended qc, calc. and management	X	X	POST ANALYSIS APPLICATIONS

Figure 3. Data base and spreadsheet functions of a LIMS.

The spreadsheet applications fall into two main areas. Area 1 involves the entry of analytical data into the LIMS system. Since the desired data may be the result of an analytical calculation, the spreadsheet applies. Area 2 involves the post analysis processing of data for quality control and other calculation intensive applications.

Even though a spreadsheet may be used for selected LIMS functions, the data base will always be the permanent "home" of all laboratory information. Therefore, data will have to be moved from the data base to the spreadsheet, whenever any of the spreadsheet functions are to be performed. Additionally, for Area 1 (data entry) applications, data will have to be returned from the spreadsheet to the corresponding data base record, after the spreadsheet function is complete. The required flow of information between data base and spreadsheet, for data entry applications, is illustrated in Figure 4.

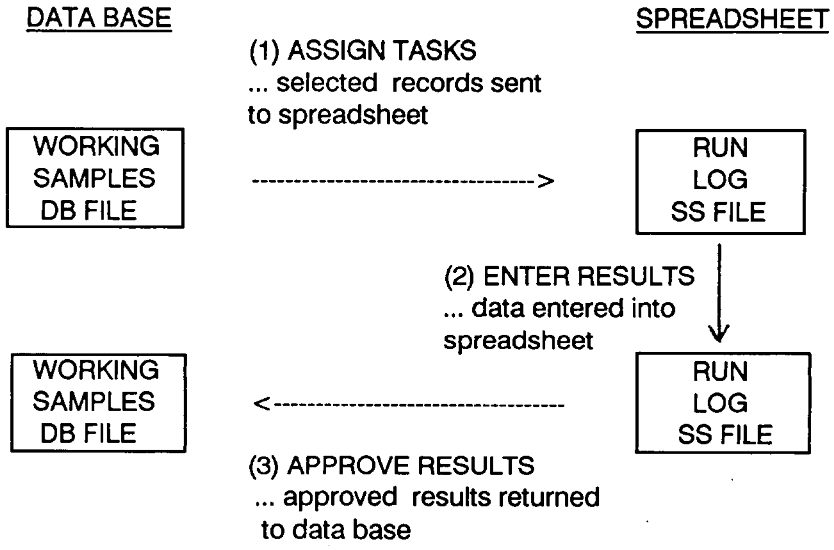


Figure 4. Data entry applications of a spreadsheet.

When samples are logged into the LIMS system, the information is added to a "working samples" data base, consisting of all test records which are awaiting entry of approved test results. During the "ASSIGN TASKS" function, the records in this data base requiring analysis by a common analytical procedure, may be grouped together and the information contained in these records transferred to a predefined spreadsheet, called a "Run Log." The Run Log represents an analytical worksheet. The Run Log can be printed out to provide a hard copy listing of samples requiring a particular analysis, and the corresponding spreadsheet file provides an electronic worksheet, into which the results of the pending analysis will be entered. Any number of Run Log spreadsheet files, containing different groups of analyses to be performed, may be created in the ASSIGN TASKS mode, and saved for subsequent data entry.

When an analytical run of the selected samples has been performed, the "ENTER RESULTS" mode allows the analyst or data entry clerk to access the Run Log corresponding to the completed run, and enter the results into the spreadsheet. Alternately, instrument interface options allow automatic data entry into the Run Log.

Following data entry, security approved personnel may re-access the Run Log in the "APPROVE RESULTS" mode, for the purpose of evaluating the accuracy of the run. During this mode of operation, approved results are transferred from the spreadsheet to the LIMS data base records corresponding to the approved spreadsheet entries.

THE "RUN LOG" WORKSHEET

The spreadsheet is used as a vehicle for analytical data entry for logical, as well as technical reasons. Creating and saving spreadsheet files, which correspond to an analytical worksheet, maintains, intact, a complete analytical run. Data is actually acquired in sample/test groupings corresponding to a single run, and the Run Log provides a data entry worksheet corresponding to that run. The two dimensional row/column access to the worksheet further simplifies data entry. Additionally, the quality of analytical data will likely depend on conditions which existed during the run in which the data was acquired. Therefore, it is proper and in concert with accepted quality control procedures, to review QC data and approve or disapprove results, on a run by run basis.

While the above benefits of spreadsheet data entry are significant, the most powerful benefit is derived from the automatic calculation capabilities of the spreadsheet. The Run Log worksheet, illustrated in Figure 5, is a system defined spreadsheet. The Run Log is a generic spreadsheet, containing columns of information which apply to almost any kind of chemical analysis which might be performed. In addition to columns identifying the samples and tests to be run, additional columns are provided for sample preparation parameters, including sample weight, volume, dilution factor, and percent solids (for dry weight reporting basis). The "calculated result" column is determined from the entered result and sample preparation variables, by the following generally applicable equation:

$$[\text{Calc Result}] = \frac{[\text{Init Result}]*[\text{volume}]*[\text{dil factor}]}{[\text{weight}]*0.01*[\%\text{solids}]}$$

The sample preparation parameter columns always default to a value of 1.0 (100 for % solids), making them mathematically innocuous, when they are not used.

```
ANALYSIS    Run: 10000006       Method: ICP          Date: 10/25/88
RUN LOG      By: CHC          Instr.ID: ICP-2        Time: 06:16P
=============================================================================================
Lab#      Q TestID  Init Result  Weight   Volume  Dil     %Solid     Spk/Ref   Calc Result C Rec/Diff

G881036     Mo        611.0000  1.0000  1.0000  1.0000 100.0000                611.0000
G881036 D Mo          624.0000  1.0000  1.0000  1.0000 100.0000                624.0000        2.1
G881036 S Mo          705.0000  1.0000  1.0000  1.0000 100.0000   100.0000     705.0000       94.0
G881036     Cr       2573.0000  1.0000  1.0000  1.0000 100.0000               2573.0000
G881036     Pb         45.0000  1.0000  1.0000  1.0000 100.0000                 45.0000
control C Mo          767.0000  1.0000  1.0000  1.0000 100.0000   750.0000     767.0000      102.3
control C Cr         2767.0000  1.0000  1.0000  1.0000 100.0000  2800.0000    2767.0000       98.8
control C Pb           38.0000  1.0000  1.0000  1.0000 100.0000    35.0000      38.0000      108.6
G881037     Mo        490.0000  1.0000  1.0000  1.0000 100.0000                490.0000 B
G881037     Cr       3020.0000  1.0000  1.0000  1.0000 100.0000               3020.0000 H
G881037     Pb          0.0530  1.0000  1.0000  1.0000 100.0000                  0.1000 U
G881038     Mo        612.0000  1.0000  1.0000  1.0000 100.0000                612.0000      102.0
G881038     Cr       2485.0000  1.0000  1.0000  1.0000 100.0000               2485.0000       99.4
G881038     Pb         29.0000  1.0000  1.0000  1.0000 100.0000                 29.0000      116.0
```

Figure 5. Standard "Run Log" spreadsheet.

Other predefined columns provide valuable information on the analytical quality of the run. The "C" or concentration flag column automatically displays a flag indicating how the result compares to lower and upper limits which have been predefined for the analysis, and a special detection limit flag indicates when the result is less than the detection limit for the method. In such a case, the calculated result is automatically made equivalent to the detection limit, and the detection limit flag is set. The "Recovery/Difference" column automatically calculates the percent difference between duplicate runs, the percent recovery for spikes, and the percent accuracy for control samples.

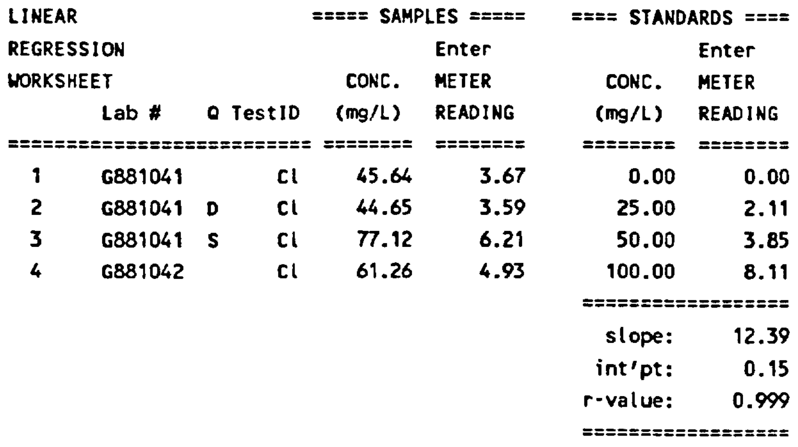
In addition to the above information which is available to all who are authorized to access the Run Log, a "blind QC" feature will automatically display the percent accuracy on special blind control samples only to privileged personnel who have been authorized for approving results. Thus, all QC information is available to the authorized reviewer at the time results are being approved, providing data evaluation criteria at the time it is needed. Based on the information in the Run Log, the reviewer may approve results, transferring them from the Run Log spreadsheet back to the LIMS data base for reporting and archiving, or selected sample analyses may be rejected, requiring them to be reassigned to a subsequent Run Log for re-analysis.

CUSTOM DATA ENTRY WORKSHEETS

While the Run Log spreadsheet is a useful general purpose data entry worksheet, the user programmability of spreadsheets makes feasible an even more powerful application for spreadsheet data entry. The Run Log expects the initial result to be entered in concentration units, to be compatible with the equation for determining the calculated result. However, many times the analysis does not provide results in concentration units. Raw results may, for instance, be presented as "strip chart recorder divisions", "milliliters of titrant", "absorbance", etc. Results in concentration units must then be calculated from this raw data.

In such cases, it would be useful to allow the use of custom spreadsheets, which are definable by the user, for calculating Run Log "initial results" from the raw data generated by different analytical methods. Calculating the initial result from raw data not only expedites the routine calculations which are a part of every laboratory, but also minimizes data entry and human calculation errors prior to entry of results into LIMS. SMARTLAB allows access to user-defined spreadsheets for data entry, and automatically reads the computed result from the custom spreadsheet into the "initial result" cell of the Run Log, whereupon all standard Run Log functions described above are implemented.

An example of a user-defined spreadsheet is shown in Figure 6. This spreadsheet was created to allow entry of raw millivolt readings from an ion selective electrode measurement of chloride. In this spreadsheet, the user need only enter the readings for the standards and the samples in the "Enter Meter Reading" columns, and the concentration is automatically computed for the samples by comparison to a linear least squares calibration, which was automatically determined from the standard readings. A single key stroke will transfer the computed sample concentrations into the "Result" column of the Run Log spreadsheet.



```
LINEAR                      ===== SAMPLES =====   ==== STANDARDS ====
REGRESSION                              Enter                 Enter
WORKSHEET                     CONC.     METER       CONC.     METER
        Lab #    Q TestID    (mg/L)    READING     (mg/L)    READING
======================== ========  ========    ========  ========
  1     G881041       Cl      45.64      3.67        0.00      0.00
  2     G881041  D    Cl      44.65      3.59       25.00      2.11
  3     G881041  S    Cl      77.12      6.21       50.00      3.85
  4     G881042       Cl      61.26      4.93      100.00      8.11
                                                 ==================
                                                   slope:     12.39
                                                  int'pt:      0.15
                                                 r-value:     0.999
                                                 ==================
```

Figure 6. Custom spreadsheet for linear calibration.

POST ANALYSIS DATA PROCESSING AND QUALITY CONTROL USING A SPREADSHEET

SMARTLAB's "EXTENDED QC" mode provides access to the spreadsheet for post analysis data processing, the applications identified as "Area 2" in Figure 3. In the EXTENDED QC mode, the LIMS data base manager is used to sort and query the data base to select the records intended for processing. Then the information from the selected records is transferred to the spreadsheet program, as illustrated in Figure 7. Since for this application, the spreadsheet is used simply as a processor of information from an already completed data base record, the interaction of the spreadsheet with the LIMS data base is less involved, than for applications where spreadsheet results must be returned to the data base. This means that total free use of all spreadsheet functions is possible.

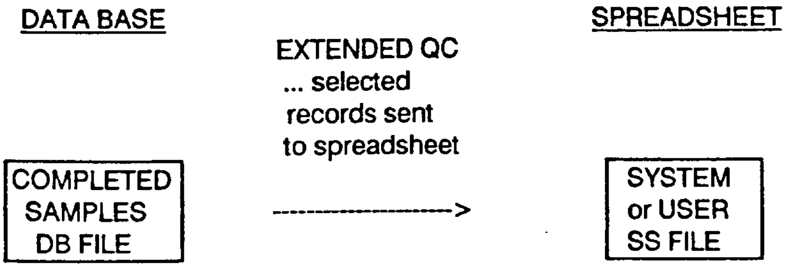


Figure 7. Post analysis applications of a spreadsheet.

For post analysis data processing, the user again has preprogrammed spreadsheet options, as well as user-definable options. System defined options include trend analysis and three types of QC charting. The spreadsheet graphics capabilities are particularly useful for these applications. Examples of trend and QC charts, generated automatically through the EXTENDED QC mode of SMARTLAB, are shown in Figures 8 and 9.

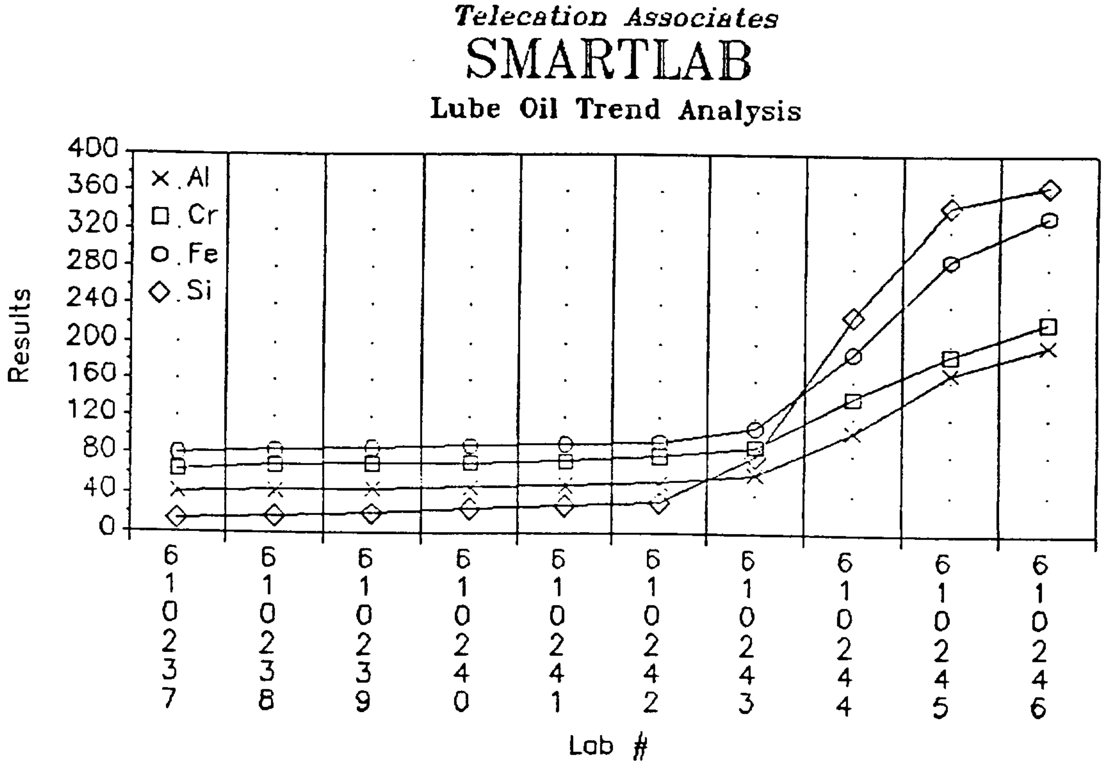


Figure 8. Trend analysis graph from SMARTLAB spreadsheet.

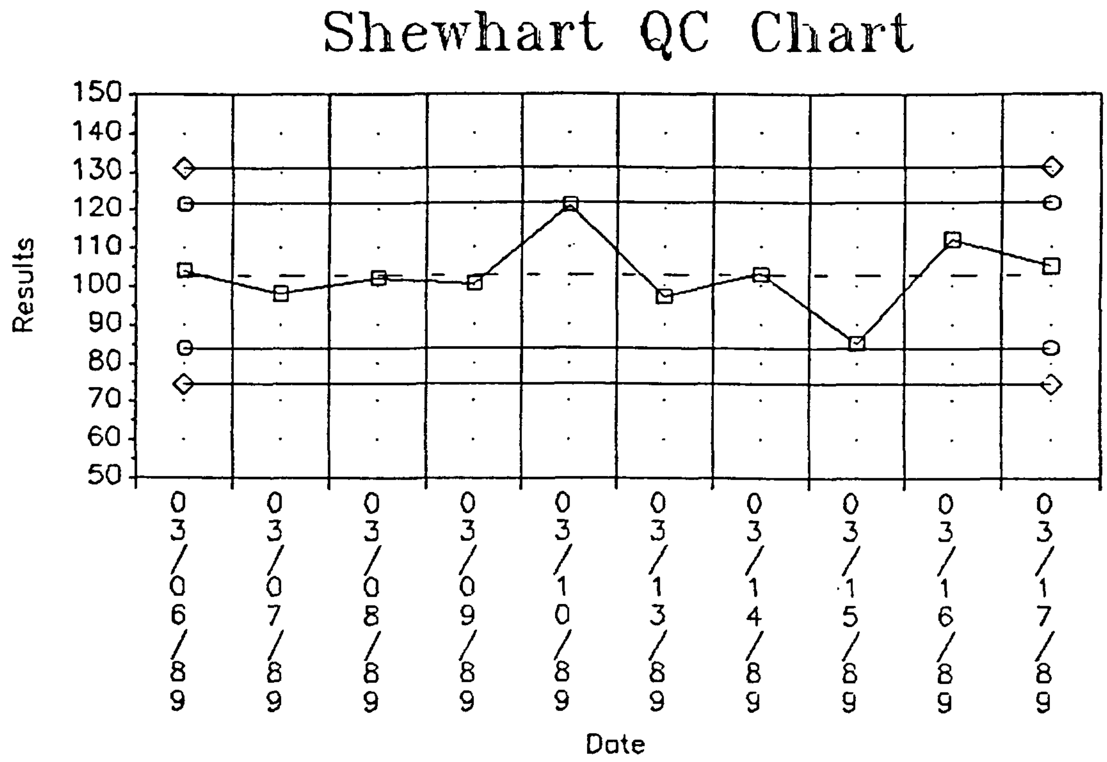


Figure 9. QC chart from SMARTLAB spreadsheet.

CUSTOM SPREADSHEETS FOR POST ANALYSIS APPLICATIONS

As previously identified, calculations involving information contained in multiple data base records are difficult to implement from within the data base, but easy from a spreadsheet. Therefore, any type of user application involving processing of information from multiple tests or LIMS data base records, is a candidate for a user-defined spreadsheet.

One such application is a material balance report for a complete assay of a metal alloy sample. In this application, all components determined in the sample are summed, and the summation result is compared with 100 percent, as a measure of analysis accuracy.

In this application, the EXTENDED QC mode is applied to isolate, from the LIMS data base, only those records which correspond to a test performed on the selected sample. These results are then sent to the spreadsheet to perform the necessary calculations. The user-defined spreadsheet for this application is a simple one. The user need only define a calculated cell with the formula to sum the result column from all the tests. An example of a spreadsheet for this application is shown ir Figure 10.

ALLOY MATERIAL BALANCE

lab#	testid	result
G881030	Al	9.8 %
G881030	Cr	15.4 %
G881030	Cu	18.5 %
G881030	Fe	42.2 %
G881030	Zn	11.6 %
G881030	B	2.8 %
	TOTAL	100.3 %

Figure 10. Custom spreadsheet for material balance calculation.

Simple custom spreadsheets may be defined on the spot, from within the LIMS EXTENDED QC mode, or more complex spreadsheet definitions may be preprogrammed with the SmartWare spreadsheet module, for later routine access. The latter approach makes it possible for data processing clerks, without spreadsheet experience, to generate complex custom spreadsheet reports and charts, without leaving the LIMS system.

In addition to applications dealing with analytical data, other information can be extracted from the LIMS data base and transferred to custom spreadsheets to provide valuable management tools. For instance, the graph in Figure 11 provides an easy comparison of analyst productivity. And Figure 12 indicates that the analytical load on the laboratory's gas chromatographs is nearing capacity, and the purchase of an additional instrument should be considered. Similar spreadsheets could be devised to forecast sample load into the future.

SUMMARY

Integration of a spreadsheet into a LIMS system provides a dramatic enhancement to the usability of information in the LIMS data base. The spreadsheet's powers of calculation and graphics display increase the capabilities of the LIMS system well beyond the abilities of a stand-alone relational data base manager. Additionally, the incorporation of user-definable spreadsheets into the LIMS system, provides an easy mechanism for user customization of LIMS functions by non-programmers. The ability to access both predefined and user-defined spreadsheet applications directly from the LIMS system, without special communication or data transfer programs, makes it possible for these functions to be utilized by the routine user.

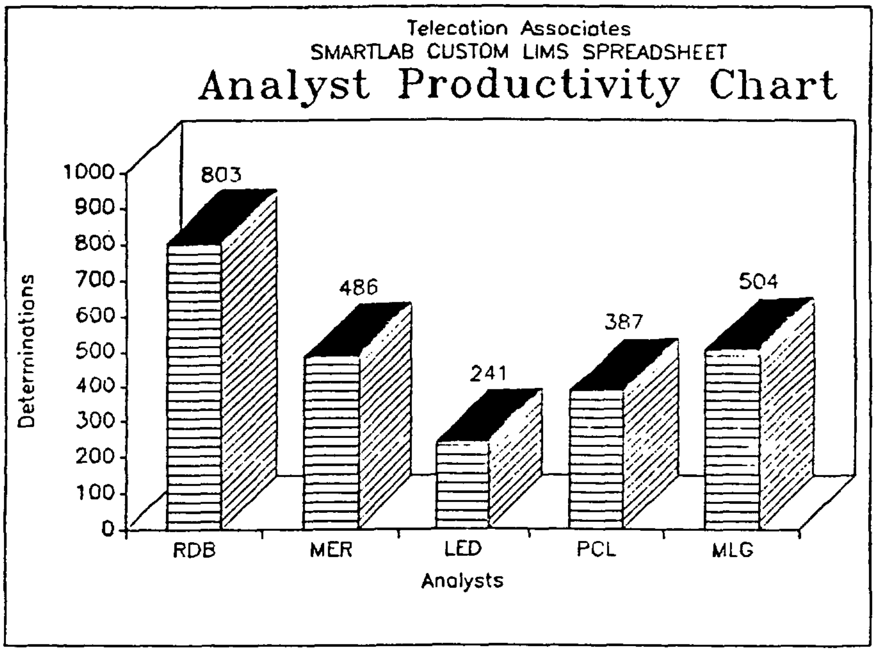


Figure 11. Management report from SMARTLAB spreadsheet.

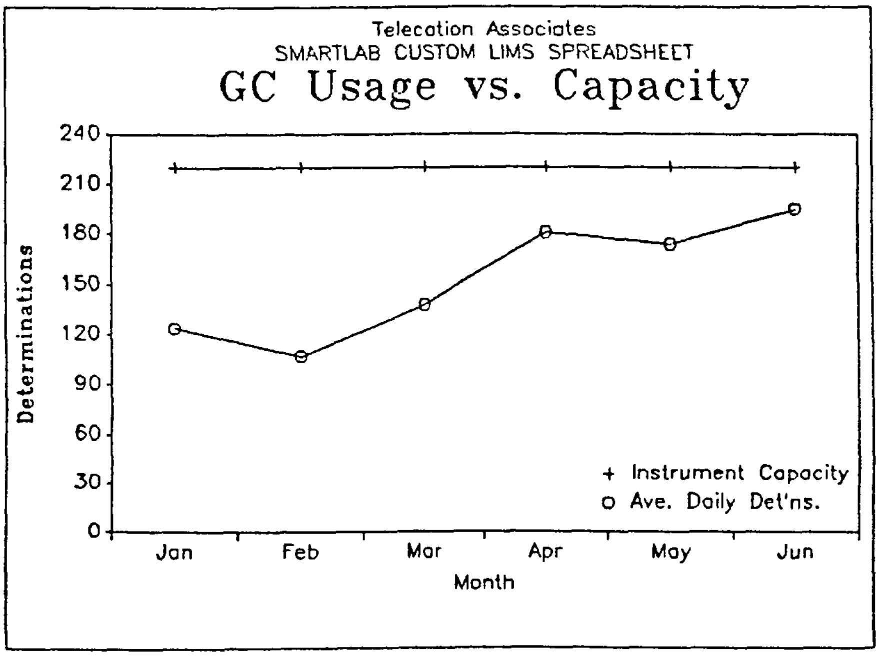


Figure 12. Instrument usage chart.

EARLY WARNING REPORT: AUTOMATED CHECKING OF QC DATA

Robert Peak, Quality Assurance Director, Paul Duerksen, QA Coordinator, Kit Wong, Computer Programmer, Ed Szeto, Computer Programmer, Brown and Caldwell Analytical Laboratories, 373 S. Fair Oaks Avenue, Pasadena, California 91105

ABSTRACT

Sample log-in, work list generation, data entry, and report production are data-handling functions common to most Laboratory Information Management Systems (LIMS's). A newly developed automated review system now extends those functions to include the use of a LIMS for reviewing and evaluating quality control (QC) results. This paper delineates the four major stages involved in creating this automated review system: concept, preliminary design, programming, and testing. Although computer programming is typically system-dependent, the logic employed in QC review should have broad application to many LIMS's. The paper also describes the daily operation of this new LIMS function on-line in three networked commercial laboratories with over 140 employees. This account of the review system's pitfalls, successes, and maintenance requirements can help other LIMS users achieve a smooth, reliable installation.

INTRODUCTION

Environmental laboratories are finding increasing incentives to automate data handling. A Laboratory Information Management System (LIMS) can process large quantities of data with far less labor than a corresponding manual system. Many LIMS's however, have a limited capability for data evaluation. They serve as storehouses and reporters of results, but do very little to examine those results.

Brown and Caldwell Analytical Laboratories (BCAL) uses a custom-written LIMS that contains the typical functions of such systems: means for logging sample data into the computer, printing out work lists for analysts, entering analytical results, and producing final reports. With this system as a base, the Quality Assurance Department set out to add the capability for review and assessment of quality control (QC) results. The development process required close cooperation among QA chemists, in-house programmers, and programming consultants. The final product is our "Early Warning Report" (EWR), a daily report from the data base that evaluates and reports on QC results from throughout the laboratory with regard to archived control limits.

The development of the EWR encompassed four stages: (1) choosing the design concepts; (2) translating those concepts into programming algorithms; (3) actual programming; and (4) testing. Once developed, this type of report can take on part of the data evaluation function required in any analytical laboratory.

BACKGROUND

The BCAL LIMS is commercially available from Inquiry Computer Systems of Laguna Beach, California. As ours was the first installation of this system, our scientists participated in every stage of development. The computer consultant who did the primary programming, Mr. Ben Edmonson, also supplied the hardware and operating system.

The PICK operating system (PICK) works on ADDS/Mentor minicomputers. ADDS is a division of NCR. All three of our laboratories have a minicomputer, each with 32 to 64 ports. The computers are linked through leased-line communications equipment via 16-port modems. PICK is unusually well-suited to LIMS requirements because, unlike most other operating systems, it is itself a data base manager. No "data base" software is run on top of the operating system; it is inherently designed to handle large relational pools of data. Consequently, a LIMS that runs on PICK is hardware conservative. With a minicomputer containing only four megabytes of RAM and 500 megabytes of hard disk, we can keep full records on line and access them for more than a year. In a typical month, our larger laboratories analyze about 2500 samples, with all results archived in the LIMS.

PICK does have some drawbacks. Its programming language, called PICK Basic, is quite similar to other implementations of Basic. Without access to sophisticated engineering languages like Pascal or Fortran, PICK's number-handling capability is limited. Because it is an uncommon operating system, finding an experienced programmer who is also familiar with laboratory operations can be quite challenging.

Functions in the BCAL LIMS are typical of such systems. As samples arrive, they are assigned ID numbers that include a simple sequence; as samples are logged in to the computer, the LIMS offers the next sequential number. Log-in creates a record in the "Order" file, much like the order entry file of a commercial data base. We use specific client codes to track and cross- reference client information and determination codes to identify the analyses required and cross-reference them to a detailed determination file. When log-in is complete, the computer prints out a description of the job to be done. A copy of the printout, called the "traveller," is kept in a suspense file in the laboratory along with the original chain of custody. A copy marked "acknowledgement" goes to the client for review.

Following log-in, the analytical determinations for each sample are dispatched within LIMS to the "Work" file. Every night the computer prints out data from the Work file onto individual worksheets for the analysts. The worksheets show the client's sample description, the laboratory ID number, and the samples sorted by determination and due date.

The LIMS also generates QC work items directly onto the worklists. For all tests, every tenth work item is a laboratory control standard (LCS). Because a true value must be declared for data evaluation, the LCS has two parts: "LC" for the result and "LT" for the true value.

For inorganic analyses, the computer invokes a pair of duplicates and a spike for every tenth determination on a particular sample matrix type. These QC items are designated by suffixes on the sample ID: R1 is the first replicate, R2 the second, S1 the spike result, and T the true value (or expected result) of the spike. For organics analyses, the computer alters the pattern slightly, creating R1 and S1 plus a duplicate spike, S2, and T. Figure 1 illustrates a typical worksheet for a multi-component analysis.

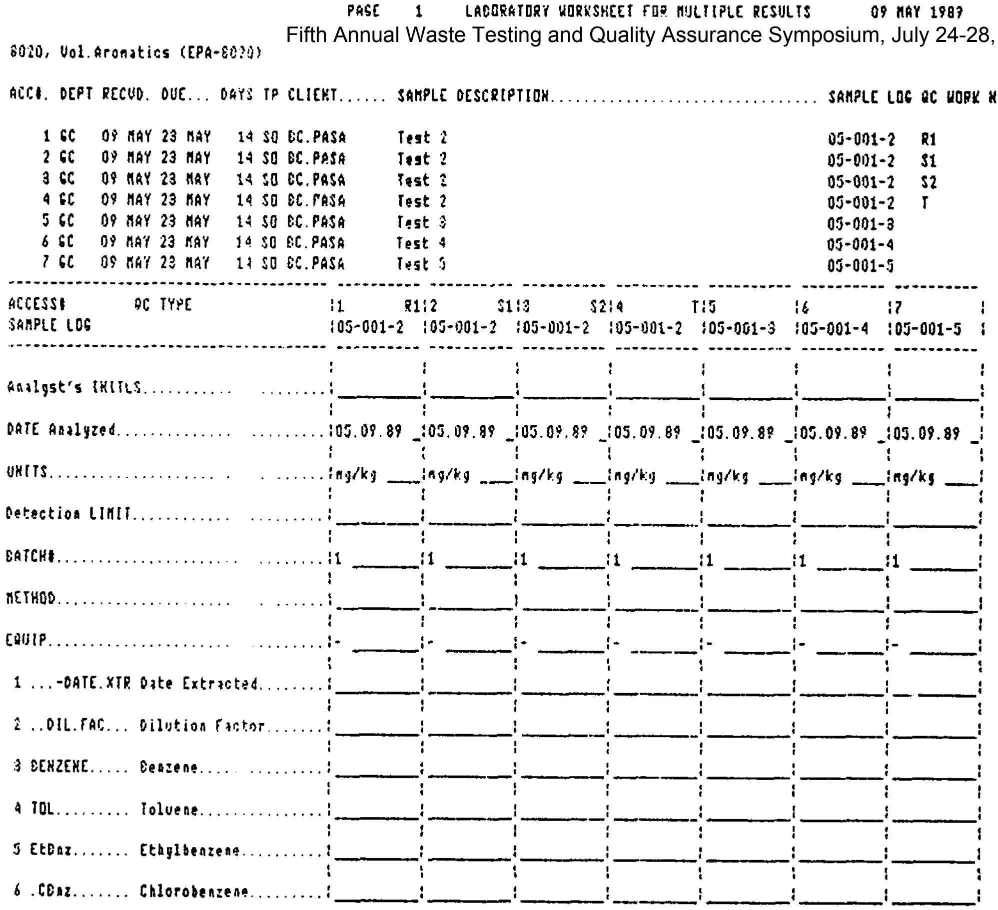
Analysts enter their test results on the worksheets, which then go to a swing-shift data entry operator for keyboarding. Overnight, the computer prints another sheet, called a "Work Approval" (Figure 2). Similar to the original worksheet, the Work Approval displays the results as well as a field for approval initials. A supervisor or group leader compares the printed approval sheet against the original raw data. If results are properly calculated and correctly entered, the reviewer initials the item as approved. Data review takes place early in the morning, with the completed approval sheets turned in by midmorning. Another data entry operator keys in the approval initials. At this stage, a command is executed that moves the item from the Work file into the "Samples" file, the final archive location for results. Corresponding QC items are kept in a parallel file called "Samples,QC".

The program that prints finished reports retrieves the results from the Samples file. Figure 3 illustrates the customary format for reports. As with most such systems, the client and project information are displayed in the header area followed by the individual analytes and results. With this system in place, BCAL decided in late 1985 to look into adding QC evaluation to the LIMS.

DEVELOPMENT

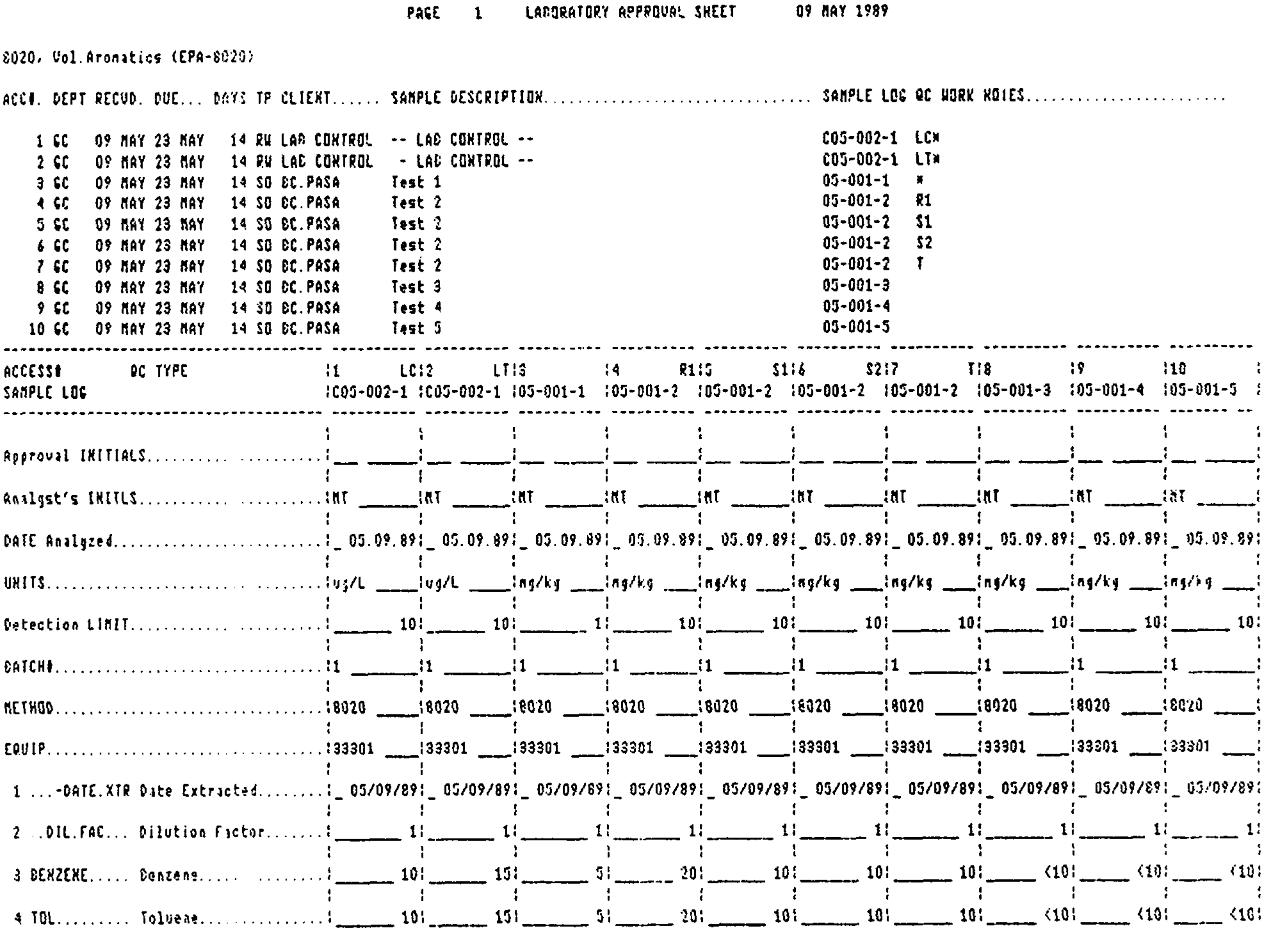
As we began the first stage of developing the EWR, we saw that dialog between the chemists experienced in quality assurance and the computer programmers would be essential. QA chemists alone cannot implement an automated system and programmers cannot know the decisions the QA staff will want made. The project included, at various times, the QA director, the Pasadena laboratory's QA coordinator, two in-house programmers, and two outside programmers (including the LIMS designer). None worked on this development full time.

The first critical design decision was selecting where to intercept the existing process. Our principal considerations were (1) before work approval, (2) after work approval, or (3) at final reporting. We rejected the final report stage as being dangerously late in the analytical process. If a QC problem occurred on the first analysis reported but was not discovered until the last item was complete, the process might be out of control for several days. The next choice was less clear-cut: Evaluation after work approval would allow simple data entry blunders to be corrected before appearing on the EWR; evaluation before work approval would shorten the cycle by one day. The urgency of correcting a process at the earliest possible time prompted us to select option (1)--evaluation before approval.



```
                                   PAGE    1     LABORATORY WORKSHEET FOR MULTIPLE RESULTS       09 MAY 1989
8020, Vol.Aromatics (EPA-8020)

ACC#. DEPT RECVD. DUE... DAYS TP CLIENT...... SAMPLE DESCRIPTION.............................. SAMPLE LOG QC WORK NOTES..................... .

    1 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 2                                           05-001-2   R1
    2 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 2                                           05-001-2   S1
    3 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 2                                           05-001-2   S2
    4 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 2                                           05-001-2   T
    5 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 3                                           05-001-3
    6 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 4                                           05-001-4
    7 GC    09 MAY 23 MAY   14 SO BC.PASA     Test 5                                           05-001-5
------------------------------------ --------- --------- --------- --------- --------- --------- ---------
ACCESS#        QC TYPE              :1       R1:2      S1:3      S2:4       T:5        :6        :7        :
SAMPLE LOG                          :05-001-2 :05-001-2 :05-001-2 :05-001-2 :05-001-3 :05-001-4 :05-001-5 :
------------------------------------ --------- --------- --------- --------- --------- --------- ---------
                                    :         :         :         :         :         :         :         :
Analyst's INITLS...........  .......:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
DATE Analyzed.............  ........:05.09.89 _:05.09.89 _:05.09.89 _:05.09.89 _:05.09.89 _:05.09.89 _:05.09.89 _:
                                    :         :         :         :         :         :         :         :
UNITS.....................  . ......:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:
                                    :         :         :         :         :         :         :         :
Detection LIMIT...........  ........:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
BATCH#....................  ........:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:
                                    :         :         :         :         :         :         :         :
METHOD....................  . ......:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
EQUIP.....................  ........:- _______:- _______:- _______:- _______:- _______:- _______:- _______:
                                    :         :         :         :         :         :         :         :
 1 ...-DATE.XTR Date Extracted.......:_________:_________:_________:_________:_________:_________:__ ______:
                                    :         :         :         :         :         :         :         :
 2 ..DIL.FAC... Dilution Factor......:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
 3 BENZENE..... Benzene....  .........:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
 4 TOL......... Toluene..............:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
 5 EtBnz....... Ethylbenzene..........:_________:_________:_________:_________:_________:_________:_________:
                                    :         :         :         :         :         :         :         :
 6 .CBnz....... Chlorobenzene.........:_________:_________:_________:_________:_________:_________:_________:
```

Figure 1.
Typical BCAL Worksheet



```
                                          PAGE    1     LABORATORY APPROVAL SHEET       09 MAY 1989

8020, Vol.Aromatics (EPA-8020)

ACC#. DEPT RECVD. DUE... DAYS TP CLIENT...... SAMPLE DESCRIPTION.............................. SAMPLE LOG QC WORK NOTES.......................

    1 GC    09 MAY 23 MAY   14 RW LAB CONTROL  -- LAB CONTROL --                             C05-002-1  LC*
    2 GC    09 MAY 23 MAY   14 RW LAB CONTROL   - LAB CONTROL --                             C05-002-1  LT*
    3 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 1                                        05-001-1   *
    4 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 2                                        05-001-2   R1
    5 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 2                                        05-001-2   S1
    6 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 2                                        05-001-2   S2
    7 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 2                                        05-001-2   T
    8 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 3                                        05-001-3
    9 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 4                                        05-001-4
   10 GC    09 MAY 23 MAY   14 SO BC.PASA      Test 5                                        05-001-5
------------------------------------ --------- --------- --------- --------- --------- --------- --------- --------- --------- ---------
ACCESS#        QC TYPE              :1       LC:2      LT:3        :4      R1:5      S1:6      S2:7       T:8        :9        :10       :
SAMPLE LOG                          :C05-002-1 :C05-002-1 :05-001-1 :05-001-2 :05-001-2 :05-001-2 :05-001-2 :05-001-3 :05-001-4 :05-001-5 :
------------------------------------ --------- --------- --------- --------- --------- --------- --------- --------- --------- ------- --
                                    :         :         :         :         :         :         :         :         :         :         :
Approval INITIALS.........  ........:__ ______:__ ______:__ ______:__ ______:__ ______:__ ______:__ ______:__ ______:__ ______:__ ______:
                                    :         :         :         :         :         :         :         :         :         :         :
Analyst's INITLS..........  ........:NT ______:NT ______:NT ______:NT ______:NT ______:NT ______:NT ______:NT ______:NT ______:NT ______:
                                    :         :         :         :         :         :         :         :         :         :         :
DATE Analyzed.......................:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:_ 05.09.89:
                                    :         :         :         :         :         :         :         :         :         :         :
UNITS.....................  ........:ug/L ____:ug/L ____:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:mg/kg ___:
                                    :         :         :         :         :         :         :         :         :         :         :
Detection LIMIT...........  ........:______ 10:______ 10:_______ 1:______ 10:______ 10:______ 10:______ 10:______ 10:______ 10:______ 10:
                                    :         :         :         :         :         :         :         :         :         :         :
BATCH#..............................:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:1 _______:
                                    :         :         :         :         :         :         :         :         :         :         :
METHOD..............................:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:8020 ____:
                                    :         :         :         :         :         :         :         :         :         :         :
EQUIP...............................:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:33301 ___:
                                    :         :         :         :         :         :         :         :         :         :         :
 1 ...-DATE.XTR Date Extracted.......:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:_ 05/09/89:
                                    :         :         :         :         :         :         :         :         :         :         :
 2 ..DIL.FAC... Dilution Factor......:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:_______ 1:
                                    :         :         :         :         :         :         :         :         :         :         :
 3 BENZENE..... Benzene....  .........:______ 10:______ 15:_______ 5:______ 20:______ 10:______ 10:______ 10:_____ <10:_____ <10:_____ <10:
                                    :         :         :         :         :         :         :         :         :         :         :
 4 TOL......... Toluene..............:______ 10:______ 15:_______ 5:______ 20:______ 10:______ 10:______ 10:_____ <10:_____ <10:____ <10:
```

Figure 2.
Work Approval Sheet

BROWN AND CALDWELL LABORATORIES
373 SOUTH FAIR OAKS AVENUE, PASADENA, CA 91105
(818) 795-7553 (213) 681-4655
FAX: (818) 795-8579

ANALYTICAL REPORT

LOG NO: P89-05-001

Received: 09 MAY 89
Reported: 09 MAY 89

Karen Shupe
Brown and Caldwell
150 S. Arroyo Parkway
Pasadena, California 91109

Project: 450-01

REPORT OF ANALYTICAL RESULTS

Page 1

LOG NO	SAMPLE DESCRIPTION, SOIL SAMPLES	DATE SAMPLED
05-001-1	Test 1	09 MAY 89
05-001-2	Test 2	09 MAY 89
05-001-3	Test 3	09 MAY 89
05-001-4	Test 4	09 MAY 89
05-001-5	Test 5	09 MAY 89

PARAMETER	05-001-1	05-001-2	05-001-3	05-001-4	05-001-5
Vol.Aromatics (EPA-8020)					
Date Extracted	05/10/89	05/09/89	05/10/89	05/10/89	05/10/89
Dilution Factor, Times 1	1	1	1	1	1
Chlorobenzene, mg/kg	20	20	<10	30	<10
1,2-Dichlorobenzene, mg/kg	20	20	<10	30	<10
1,3-Dichlorobenzene, mg/kg	20	20	<10	30	<10
1,4-Dichlorobenzene, mg/kg	20	20	<10	30	<10
Benzene, mg/kg	20	20	<10	30	<10
Ethylbenzene, mg/kg	20	20	<10	30	<10
Toluene, mg/kg	20	20	<10	30	<10

Jeffrey A. Erion, Laboratory Manager

Figure 3.

Analytical Report

Next, we had to choose which data to track and what criteria to use for evaluating that data. Already implemented in LIMS were laboratory control standards run on a pure reference matrix and duplicate and spike results run on actual sample matrix types. Thus, we elected to use LCS results as method accuracy criteria, measured as percent recovery. Matrix duplicates would serve for precision verification, measured as relative percent difference (RPD). Both spikes and duplicate spikes are used for matrix accuracy evalution, again measured as percent recovery. For evaluation of precision on those tests subjected to duplicate spikes, we selected the RPD of the spike pair as the precision variable.

Most laboratory QA programs use a combination of historical and mandatory acceptance criteria. Many of the newer analytical methods include guidelines on percent recovery requirements for pure-matrix samples comparable to our LCS. Where these are available, we have adopted the stated standards as our control limits. As these are usually based on something close to three standard deviations of a series of measurements, we have adopted two-thirds of the range (approximately two standard deviations) as our warning limits. For tests without method requirements, we have used a series of at least 20 measurements, gathered during a period when the process is postulated to be "in control," to calculate warning and control limits.

Very few of the methods include requirements for replicate precision. Because the order of analysis is not usually the variable of concern, RPD is expressed without a sign--as absolute value. Consequently, a series of difference calculations makes up a one-tailed curve with zero difference as the lower limit value. To calculate the long-term statistical variation, we used the formula of John K. Taylor of NIST:

$$S^2 = \frac{1}{2k} \sum_{1}^{k} d_i^2$$

Where: k = number of sets of duplicates

d_i = difference of duplicate measurement

S has k degrees of freedom

Once this calculation of S squared--the variance--is completed, the standard deviation is simply S, its square root. We set warning limits at two standard deviations and control limits at three standard deviations. In sum, the variables selected and criteria for comparison were as follows:

Laboratory Control Standard (LC and LT)	Method Accuracy	Percent recovery compared to method requirements, if available. Historical calculation if not in method.

Duplicate Samples (R1 and R2)	Sample Precision	Relative percent difference, compared with historical calculation.
Duplicate Spikes (S1 and S2)	Sample Precision	Relative percent difference, compared with historical calculation.
Spikes or Duplicate Spikes	Sample Accuracy	Percent recovery, compared with historical calculation.

Once we selected these variables and criteria for evaluation, we needed a way to associate them with certain analytical results. That is, if a LCS fails acceptance criteria or a duplicate RPD exceeds a control limit, what sample results are affected? While we were considering this issue, the EPA published specific QC guidance in the third edition of SW-846. We found we could meet our own needs and the requirements of SW-846 by converting our QC testing to a "batch" basis. With this operational change we would define the beginning and end, for every analysis, of a closely related group of samples that are run together at the same time (or sequentially) using the same method, equipment, reagents, and analyst. Within such a batch, the LCS and the matrix QC results will serve as the stamp of approval for release of the entire batch of results. Correspondingly, a QC failure calls into question all of the batch results, potentially requiring reanalysis of the entire batch.

Because the LIMS-initiated QC had originally been structured for a "flow-through" frequency of one-in-ten, some changes were needed to accommodate batch QC. Reprogramming now allows the analyst to add new QC items to the work list as needed to keep QC samples in every batch of client work. We left the automatic generator set at the one-in-ten frequency to provide a reminder, but the analyst can add to, delete, or override the computer-initiated QC items. The fundamental operating rule is that every batch must have QC appropriate to the method being used.

The second stage of EWR development was the production of decision algorithms. The end user--in this case, the quality assurance coordinator--must reduce the judgments to simple yes-or-no decisions if the computer is to handle them readily. Through dialog with the programmer, the user can develop a simple statement about what characteristic is to be compared to what limit. The statement not only includes the logic of the decision, but also incorporates mathematical manipulation of specific variables. Once these are clear, the programmer can translate the algorithms into computer code to create the QC review program. In consideration of the variables and criteria previously selected, the following algorithms were worked out between the QA coordinator and the computer programmer.

Question	Calculation	Algorithm
Does the lab control standard meet acceptance criteria?	Divide LC by LT, multiply by 100 to get percent recovery.	Compare percent recovery with upper and lower warning and control limits. Return an error condition for results out of bounds.
Is duplicate (or duplicate spike) precision acceptable?	Subtract R1-R2 (or S1-S2), divide by mean of the pair, multiply by 100, and take absolute value to get RPD.	Compare the RPD with the upper control limit and the upper warning limit. Return an error condition if it exceeds limits.
Is spike recovery acceptable?	If duplicates run, calculate mean R; if not, use R1. Subtract R from S and from T; divide these results to get spike recovery. Multiply by 100 for percent spike recovery.	Compare percent spike recovery to upper and lower warning and control limits. Return an error condition for results outside limits.
Was spike range appropriate for the sample concentration?	Subtract S-R to get amount spiked. Calculate a value 10 times archived detection limit for this sample matrix; calculate 0.5 times and 5 times R.	Check amount spiked against 10 times detection limit. If less, return an error condition. Compare amount spiked to sample native level. If less than half or more than 5 times, return an error condition.

With these algorithms defined, other questions arise. Among these: Is every error condition equally serious? Should we hold up release of results in every case? In our system, we recognized two levels of error. The first, associated with warning limits, is a "non-terminal error," which warns of QC problems, but does not interrupt data flow. The second, called a "terminal error," prevents data release until corrective action is taken. To accommodate changing requirements in QA programs, the system provides for the future conversion of one level of error to the other through use of a simple error flag.

Another question concerned the location and structure of files that contained so many limits. Besides the calculated or method-mandated acceptance limits, the file must contain matrix-specific detection limits for every parameter. To archive these new features, we selected the file already used to control matrix-specific QC frequency. We prefer that the QA coordinator update these fields manually rather than have the computer update them automatically. Although it increases the labor burden, this practice improves accountability and consistency.

When all parties clearly understand the algorithms, the programmer can begin direct coding. In this, the third stage of development, the system moves from concepts and rules into computer instructions that can actually be executed. Because computer code is so system-dependent, only the logic outline is presented here.

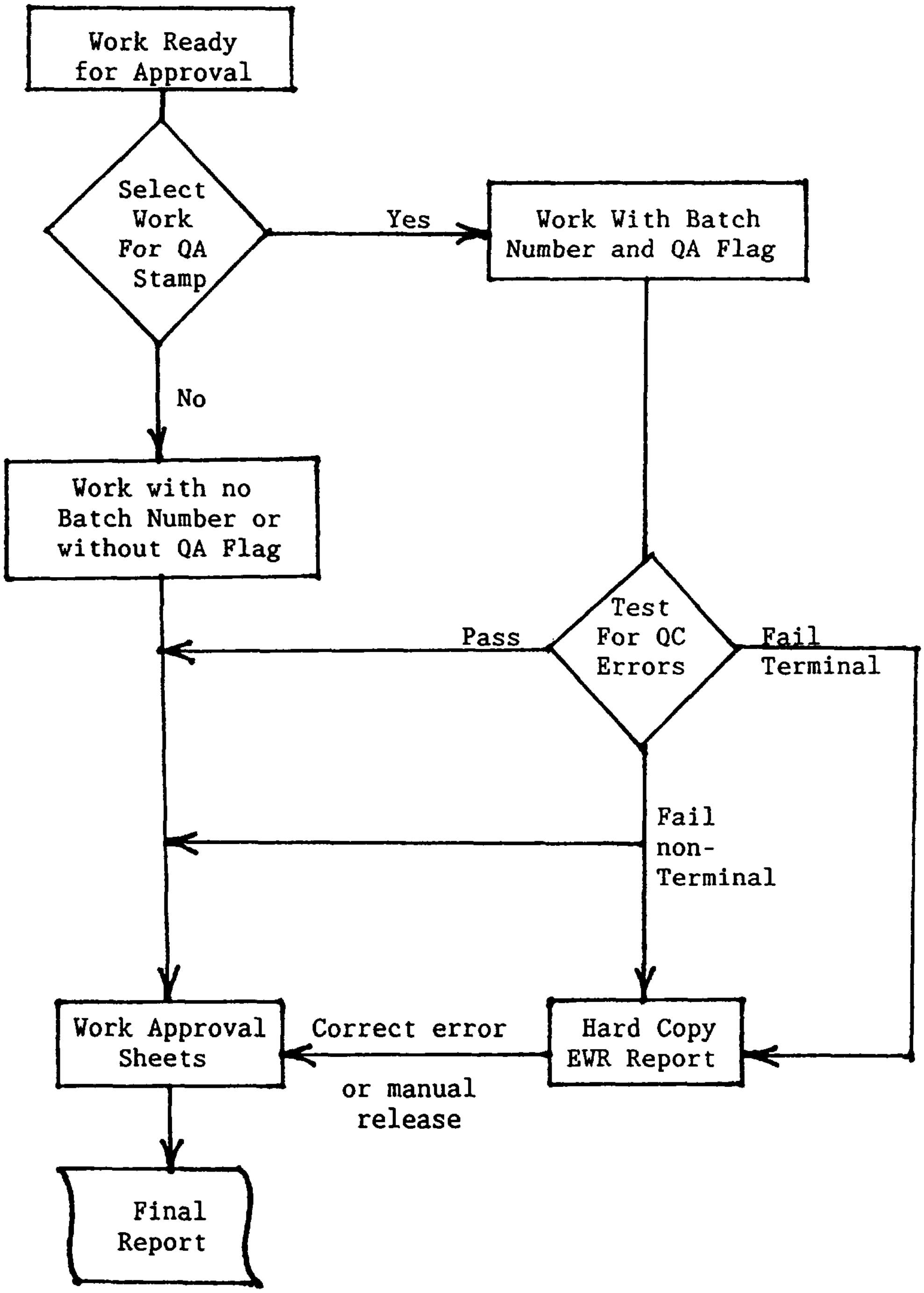
The block at the top of Figure 4 represents the point of intervention in the existing LIMS. A program selects results keyed into the the data base but not yet approved for release. These results are divided into two groups. In the first group are results which do not have batch numbers or are not subjected to QC requirements. Their characteristics might include the date a sample was put on hold, flow figures provided by a wastewater client, or other nonanalytical information. This group is diverted from the review program and sent directly to approval sheets.

The second group, which includes work subject to QC review and with a batch number, goes on for review. This program module carries out the arithmetic calculations and comparison algorithms. As mentioned earlier, three results are possible. (1) If no error condition occurs, the sample results go to the approval sheets without further action. (2) If there is a QC failure, but it is non-terminal, the results are printed on both the EWR and the approval sheets, but with an asterisk to assure careful review. (3) If the QC failure is a terminal error, the results appear on the EWR but not on the approval sheets. Correcting errors is one way to move the results onward. The QA coordinator or a section supervisor can also manually release the results by issuing an override instruction to the program. After all items reach the approval sheets, reporting goes forward as in the original LIMS design.

The fourth major stage of program development is testing. Each of our computers contains a test account where programs can be executed in a simulated version of LIMS. When we tested the EWR in this account, we discovered a few minor errors: some of the alogorithms had not been fully translated into code, and some of the arithmetic comparisons suffered from poor numerical precision in the system. Nonetheless, the difficulties at this stage were minor and relatively easy to correct.

In the second part of testing--provisional implementation--we started the program on one of our three systems and observed its progress. Before startup in our Pasadena laboratory, the QA coordinator met with each analytical group to explain planned changes. The programmers started each error condition as non-terminal, so no client reports would be immediately affected by EWR. Training also involved the data entry operators who would enter the new information being captured in the data base--primarily the batch number.

Figure 4. Block Flow Diagram for Early Warning Report



The system started up smoothly, but one major flaw and two minor ones quickly became apparent. In the initial design, the QA Department had decided that batch numbers could be assigned fresh on each day of analysis. Thus, for antimony tests run on March 28, the first batch of the day would be Antimony Batch Number One; the second batch of the day would be Number Two, and so forth. On March 29 then, the first antimony batch would also be Antimony Batch Number One. During the testing, analysts asked how to handle batches on autosamplers set to run past midnight--the date analyzed for some of the batch was a day later than other members of the same batch. Clearly, this numbering scheme was not adequate.

After vigorous discussions, the computer programmers and the QA and operations staff developed a new scheme. Now the batches are numbered sequentially for each determination. The counters start at number one on January first and advance incrementally with each batch reported. The computer prints on the worksheets the next batch number expected based on the last batch reported. If analysts run more than one batch in a day, they look for the next sequential number and write it on the sheet for the second batch. This system resolved the major problem.

One of the two minor problems concerned holding a batch open for reporting. The designers had assumed the analyst would report all the batch results at the same time on the same worksheet. In actual practice, this is not the case. Rush work, for instance, may be turned in by itself late in the day while the rest of the batch waits another day for complete data reduction. If the QC is reported with the rush results, as it should be, the EWR will indicate an error the next day when the remaining results are reported without batch QC. Some new programming has allowed an analyst to hold open a batch for additional results: The analyst turns in the batch number alone on all associated work, even those items with pending results. Once the batch number is entered, the program holds the QC items suspended for continuing comparison as each new item is archived. When all members of the batch have been reported, the QC results are archived as well.

The second minor problem concerned analysis by closely related determinations. For some clients, we employ special subsets of compound lists. That is, for an ongoing well monitoring program, a client may request routine reporting of benzene, toluene, and ethyl benzene only--rather than a full 8020 list. The analyst will run these short-list tests alongside full 8020 samples in the same batch. Our LIMS uses distinct determination codes to differentiate the short list from the full list, so the two determinations have different batch counters. If the analyst reports QC on one determination, the other appears to the EWR to have been run without QC--an error condition. Because the logic of exactly associating related determinations is more complex than our LIMS can currently handle, we had to settle for a partial solution. Determination codes for major organics reflect their common method numbers. The full 8020 list is determination 8020; the short list adds a period and a suffix, 8020.SHORT. With that consideration, we readjusted the counting routine so all determinations that match exactly up to the period are combined in counting registers.

With these three errors corrected, we implemented the EWR in our other two laboratories, repeating the training cycle and holding roundtable discussions with staff to consider the merits of batch QC and the EWR. In each implementation, startup was smoother than in our initial testing stage. As it now operates in all three laboratories, the EWR tracks and reports on several key quality control variables.

EWR FEATURES

In its final form, the Early Warning Report is a daily summary of QC results that require the further attention of an experienced chemist. Printed out with the worksheets and approval sheets every night, the EWR is divided by department and distributed every morning. Figure 5 displays one page from a typical report.

Potential QC errors are assigned a flag value of "zero" for non-terminal and "one" for terminal. If the error is terminal, all the samples for that batch are printed on the EWR but not on the approval sheets. If the error is non-terminal, the results appear on both EWR and approval sheets. Consequently, non-terminal errors may be overridden by simple approval, whereas terminal errors require the QA coordinator or a supervisor to intervene and manually move the results over to approval sheets--a process called "manual release." To assure that non-terminal errors are not overlooked during the EWR review, an asterisk appears on the approval sheet beside the result for every item with a non-terminal error.

Terminal errors currently in use, which all relate to the LCS:

> <u>Non-numeric results in LC or LT</u>. As the numbers depend upon percent recovery for validity, they should always contain numerical values. Non-numeric data indicates a potentially serious data entry error.
>
> <u>LC or LT missing</u>. No batch may be approved without a laboratory control standard.
>
> <u>LCS >= Upper Control Limit</u>. The percent recovery exceeds the archived upper limit for the parameter in question.
>
> <u>LCS <= Lower Control Limit</u>. The result is below the lower archived level.

Some non-terminal errors that also concern the LCS:

> <u>LCS concentration not on file</u>. The QC data file that contains the limits also contains a customary true concentration for the LCS. A different one indicates either an error or a deliberate choice to deviate. As the choice may be valid, the error is non-terminal.
>
> <u>LCS >= Upper Warning Limit</u>. / <u>LCS <= Lower Warning Limit</u>. These errors correspond to the control limit errors, but refer to the

Figure 5.

Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989, Washington D.C

Early Warning Report

```
BROWN AND CALDWELL EARLY WARNING REPORT       AS OF 09 MAY 1989     PAGE     1


WORK.....................  DATE.... BATCH# CLIENT...... LOG NO.... MULT DET.... UNITS. RESULT... QA OUTLIERS.........................
                           Analyzed                                                              LEVEL DESC
                                                                                *      *         *
8020*PC905002*1*LC         05.09.89 1      LAB CONTROL  05-002-1   Date         ug/L    05/09/89
                                                                   Times                       1
                                                                   BENZENE                    10 *LCS concentration not on file
                                                                   TOL                        10 *LCS concentration not on file
                                                                   EtBnz                      10 *LCS concentration not on file
                                                                   .CBnz                      10 *LCS concentration not on file
                                                                   1,2-DCBnz                  10 *LCS concentration not on file
                                                                   1,3-DCBnz                  10 *LCS concentration not on file
                                                                   1,4-DCBnz                  10 *LCS concentration not on file
8020*PC905002*1*LT         05.09.89 1      LAB CONTROL  05-002-1   Date         ug/L    05/09/89
                                                                   Times                       1
                                                                   BENZENE                    15 *LCS concentration not on file
                                                                   TOL                        15 *LCS concentration not on file
                                                                   EtBnz                      15 *LCS concentration not on file
                                                                   .CBnz                      15 *LCS concentration not on file
                                                                   1,2-DCBnz                  15 *LCS concentration not on file
                                                                   1,3-DCBnz                  15 *LCS concentration not on file
                                                                   1,4-DCBnz                  15 *LCS concentration not on file
8020*P8905001*1            05.09.89 1      BC.PASA      05-001-1   Date         mg/kg   05/09/89
                                                                   Times                       1
                                                                   BENZENE                     5 *LCS concentration not on file
                                                                   TOL                         5 *LCS concentration not on file
                                                                   EtBnz                       5 *LCS concentration not on file
                                                                   .CBnz                       5 *LCS concentration not on file
                                                                   1,2-DCBnz                   5 *LCS concentration not on file
                                                                   1,3-DCBnz                   5 *LCS concentration not on file
                                                                   1,4-DCBnz                   5 *LCS concentration not on file

                                    1

                           05.09.89

                      ***

***
```

narrower windows of the warning limits. They caution the analyst to do a close review of the data, but do not prevent reporting.

Matrix precision, which is reviewed for several non-terminal errors:

R1 Result (or R2 result) <= Detection Limit. If no measurable result was achieved, the RPD calculation will not be valid.

RPD >= Upper Control Limit / RPD >= Upper Warning Limit. This calculation is used for both R1, R2 and S1, S2 pairs. If the difference exceeds the archived limit, this error condition occurs.

Non-numeric data in R1 or R2. If an RPD calculation is attempted but encounters non-numeric results, this error occurs.

Matrix accuracy, which considers spike recoveries:

% Recovery >= Upper Control Limit (or Upper Warning Limit). High spike recoveries are tagged with this message.

% Recovery <= Lower Control Limit (or Lower Warning Limit). The corresponding low-spike error conditions.

Spike value is < 10 times detection limit. If spike is too small to be a reasonable measure of recovery, this condition is noted.

Spike added concentration is < half the sample concentration. This error condition occurs if the spike result is overshadowed by the native concentration of the analyte.

By reviewing all of these features daily, we have greatly reduced the possibility of releasing suspect data. As we gain additional experience with the program, we will likely convert some of the non-terminal errors to terminal status. We are also developing a way to put method blanks on-line as part of each batch record. Some error conditions will be developed to alert us to contaminated blanks once that process is complete.

CONCLUSIONS AND RECOMMENDATIONS

The EWR has been well accepted throughout our laboratories. While a few analysts initially resisted the idea of being checked by a computer, we have integrated the report into routine data-handling activities after only a few months of use. Because the system already ties QC results and associated client samples together, it gave us a platform on which to create a data retrieval program for preparing a Batch QC Report for clients on request.

The EWR provides two distinct benefits not otherwise available without a great expenditure of labor: (1) it reviews every QC result for every test generated every day; (2) it compares those results to absolutely firm limits established by the QA coordinator.

Comparison to rigid limits, especially in the presence of matrix interference, may be too restrictive. The non-terminal error choice allows such conditions to be flagged and reviewed without impeding the flow of approved work.

Any laboratory with a custom-written or adaptable LIMS should be able to create something like EWR. Key steps in the process are as follows:

1. Select a node in the data process where errors can best be captured.
2. Choose a single QA person as primary laboratory contact with the programmer to give a single voice to the laboratory's needs.
3. Create an environment that allows frequent contact and thorough dialog between the QA representative and the programmer.
4. Decide which data will be compared with which criteria before beginning the programming.
5. Involve analysts thoroughly in the testing stages--and plan on time for rewrites.

If your LIMS is at least as adaptable as ours--and most are--your efforts should be well rewarded.

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A QUALITY ASSURANCE AND MANAGEMENT SYSTEM FOR LARGE ENVIRONMENTAL PROJECTS

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ABSTRACT

Environmental investigation often generate massive quantities of analytical data. In investigations that deal with physically large areas, or that are multi-site or multi-media, the problems normally encountered in tracking, validating, and managing the data are compounded.

To more efficiently and effectively evaluate and process data from large projects, particularly those where data/report turnaround is on a critical schedule, a streamlined data management and quality assurance system was devised. The data are tracked from their inception in the field through the entire review process until the final report is prepared. This unique system also allows the project team to know at any point in time the status of any piece of data.

This paper will present the data management process and tracking system. The quality assurance reviews, performed concurrently at the laboratory and within the project team, will also be described.

INTRODUCTION

The management of field and laboratory data has traditionally been a slow process due to segregation of the project data and management activities. Interaction among key players such as laboratory personnel, computer scientists, engineers and scientists rarely occurs. Traditionally, each discipline performs appropriate tasks in sequence, creating a lengthy period of time between sample collection and programmatic data usage. This process is not cost effective for conducting large environmental investigations which require ongoing field activities (RI/FS). An alternative which takes maximum advantage of a multi-disciplinary approach to data management and quality assurance (QA) was developed by a team of scientists and engineers from Roy F. Weston, Inc. (WESTON). The data management team represents disciplines in chemistry, geology, engineering and computer science. The two primary objectives of the team are to streamline various QA functions and to provide input for data assessment. A key factor in this program is that all personnel on any given investigation are intimately involved with project activities and historical data. This enables team members to note discontinuities during data validation, electronic data transfer, and data assessment and plotting. The data management flow scheme is presented in Figure 1.

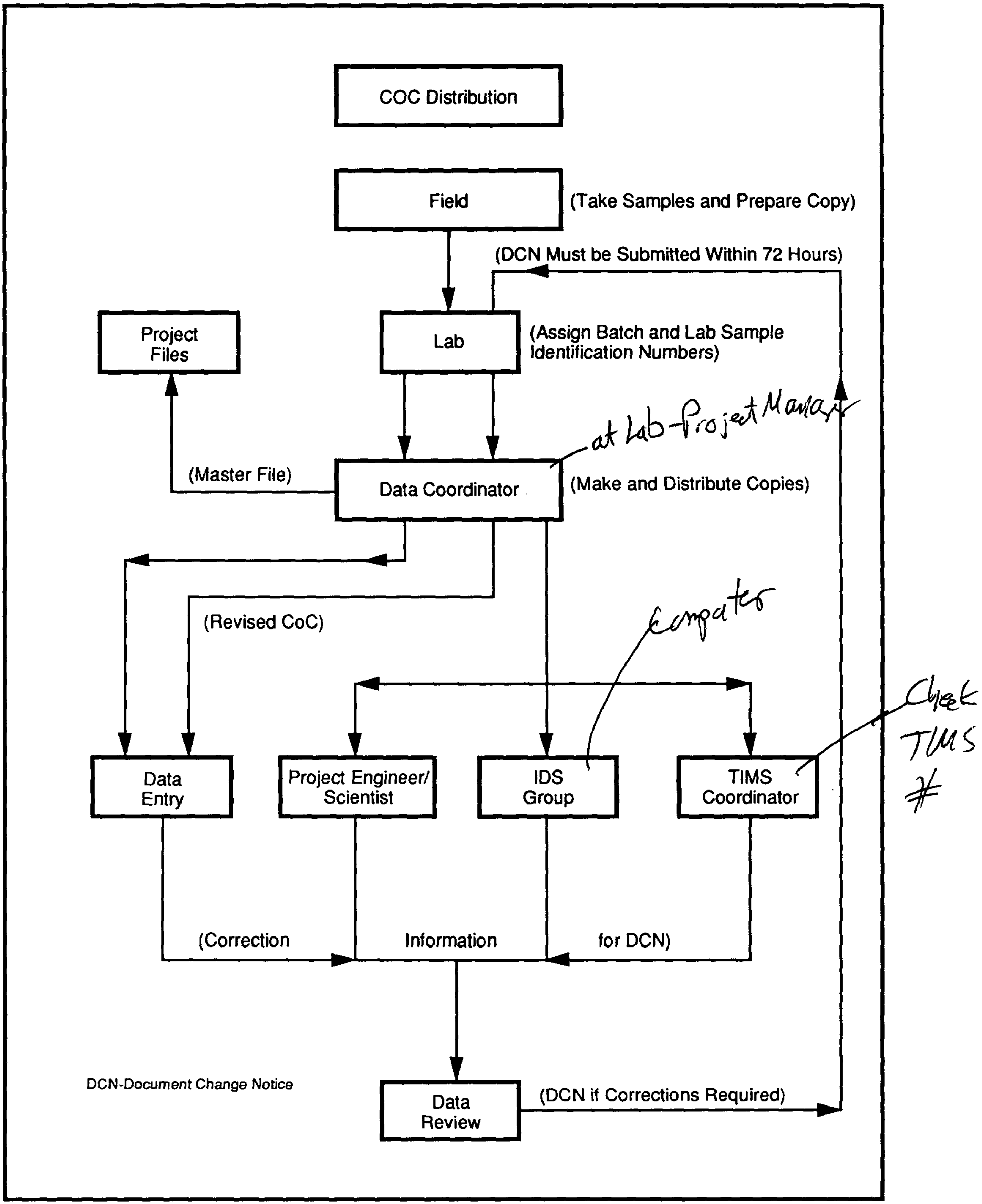

FIGURE 1 DATA MANAGEMENT FLOW SCHEME

SAMPLE GENERATION

Prior to field activities, a sample code is developed to uniquely identify all samples to be taken. This code is referred to as the "client ID" and provides site and sample specific information. It includes the identification of field and laboratory QC samples such as matrix and blank spikes, field, trip, and method blanks, field duplicates, etc. The client ID is also the link to historical data, stored in the Technical Information Management System (TIMS) database, which can be accessed at any time to retrieve and manipulate data.

As samples are collected, they are grouped into laboratory batch-sized lots for shipment (approximately 20 samples). Upon receipt at the lab, they are assigned lab batch and sample numbers (lab sample ID), and logged into the Laboratory Information Management System (LIMS). Analytical instrumentation is tied into the LIMS system. As analytical data are generated, they are collected and stored in LIMS by lab sample ID. LIMS is used to generate the hard copy data reports and also directly interfaces with TIMS so that project analytical data can be directly transferred without the need for manual re-entry or downloading into an intermediate database. LIMS also provides the lab project coordinator with a means of tracking the status of project sample batches as they progress through the laboratory system.

Immediately upon sample receipt and log-in, a copy of the chain-of-custody (COC) with the assigned lab sample IDs is sent to the project team. This allows the site engineer to double-check for field errors before samples are analyzed and data reports are generated. Field information is submitted in a TIMS-ready format, and after a QC check of it and the COC, both are submitted to the data management group for entry into the TIMS database. When the analytical data are received from LIMS, TIMS pairs them with the field data to produce a complete sample data file.

DATA TRACKING

Receipt of the COC also triggers the project data tracking system, which is maintained on a personal computer. Figure 2 is an example of the data tracking system. It is set up so that data can be sorted by site, lab batch number, analyte, or sample location (onsite soils, offsite soils, sediment, special sampling media, groundwater, soil boring, etc.).

The tracking forms are also kept in a notebook, segregated in alphabetical order by site (or whatever is convenient to the project). When a COC is received, the batch number, analytes requested, and sample location/type are entered. This ensures that the batches are in numerical order for each site. When the

					Check-off List				
Batch No.	Anal	Task Code	Data Log No.	Master File No.	Date Data Rec	Date Ret Rec	Date Corr Rec	Date Corr Rec	Date Pkg App
8902-L-462	Pest	GW	005	0265	3/27	3/27	4/04	3/30	3/30
	VOA		010		3/20	3/21	3/28	3/30	3/30
	BNA								
	Metal		015		3/25	–	–	–	3/26
	CN		016		3/25	–	–	–	3/25
8903-L-571	DIOX	ON		0333					
	VOA								
8903-L-590	PCB	OFF	190	0362	4/02	4/02	4/09	4/09	4/10

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FIGURE 2 SAMPLE DATA TRACKING SYSTEM

status of a specific batch is needed, it can be found easily. The master file number is assigned at this time so that the batches are sequential within the project files.

When an analysis for a batch is completed, a hard copy of the laboratory deliverable is submitted to the project team. The hard copy data package typically includes a cover page; a copy of the COC; a chronology detailing lab and client IDs, sampling, extraction, and analysis dates; a spreadsheet data summary; case narrative; full sample and standards chromatograms; and QC. "Short copies" (excluding raw data) are provided for the project manager and the lead engineer. The log number, which is sequential within a project task (such as a round of groundwater sampling), is assigned at this time. The original full package is filed in the master file, and a copy is distributed for Project QA.

The site engineer/scientist begins the QA process by initiating the data review checklist (Figure 3). The client IDs are checked against map locations, and a document change notice (DCN) is filled out to change any erroneous IDs. The COC is checked against the chronology and data summary to be sure that all samples requesting a specific analysis were analyzed. The data are also given a "reasonableness check" for any data that appear anomalous due to sample location (upgradient well, offsite background soil) or a comparison with historical data that indicate a need for a more in-depth review. Any comments are written on the checklist, which is signed, dated, and forwarded to the QA group.

When the data package is received by the QA group, the log number and date received are filled in on the data tracking form. The remainder of the checklist is then completed, which includes a cursory review of chromatograms, standards data, reporting format, and compliance with methodology and project protocol. Any data requests from the project engineer are checked quantitatively.

If the package is correct as submitted, the data review checklist is dated and signed. A copy is given to the project manager, and the original is filed in the master file with the original data package. The date approved is entered on the tracking form. If corrections are necessary, or clarification of an interpretation is needed, the questions/comments are indicated on the checklist, which is telecopied back to the lab. Revised data pages are returned, or comments are answered on the checklist. All dates are entered in the tracking system, allowing approximately one week for corrections. When the package is approved, the checklist with the questions/answers is signed and dated, a copy given to the project manager, and the original with all corrected pages put into the master file. The approval of the hard copy data package also signals the authorization to transfer the analytical data electronically to

Site Name: ____________ Batch # ____________ Analyte: ____________

File #: ____________ Log #: ____________ Today's Date: ____________

Delivery Date; Client ____________ State: ____________

Reviewed by: Geo: ____________ Eng: ____________ Chem: ____________

	Yes	No	NA	Comments
D.C.N. Incorporated in Package				
Chain of Custody Protocols Followed				
Chain of Custody Matches Chronology				
Sample Holding Times Met				
Case Narrative Flagged Samples				
Exceeding Holding Time				
Data Summary Sheet Matches Chronology				
Q.C. Data Included				
Matrix Blanks Clean				
Field/Trip Blanks Clean				
Surrogate Recovery Acceptable				
MS/MSD Recovery Acceptable				
Appropriate Detection Limits/Dilutions				
J - Values Correct				
B - Values Correct				
U - Values Correct				
Case Narrative Describes				
Analytical Difficulties				
Typos				

Other Comments: ____________

Geo: ____________ Eng: ____________ Date: ____________

Project Manager: ____________ Date Submitted to P.M.: ____________

Date Submitted for Revisions: ____________ Response Due Date: ____________

Date Received: ____________

Date of Resubmittal: ____________ Response Due Date: ____________

Date Received: ____________

Date of Package Approval: ____________ Chem: ____________

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FIGURE 3 DATA REVIEW CHECKLIST

TIMS. Prior to release to TIMS, the LIMS electronic data file is compared with the "final" hard copy package to ensure that both are identical and complete. The file is also reviewed by project data management personnel for ID inconsistancies, missing or incomplete data records, and discrepancies between field and laboratory information.

The advantage of this system is that anyone needing to know the status of any data only has to look at the data tracking pages for the site in question. This will tell at a glance what batches have been received at the lab for which analyses, whether a data report have been generated, whether corrections have been requested and when the results are expected, and if the data have been approved. When putting together a site report, it is critical to be able to tell quickly that all data have been reviewed and approved.

CONCLUSION

The data management process described embodies four levels of quality assurance conducted during sample preparation and sample collection, laboratory analysis and validation, engineering and scientific project review, and analytical project review. This multi-disciplinary approach has proven highly successful at WESTON for nearly two years. Numerous large investigations with massive databases have been tracked, managed, and assessed in a fraction of the time normally required. Our success is principally due to the commitment of the various departments for developing the process. Several key elements were the development of TIMS and the LIMS-TIMS tie-in, the code system which allows continuous tracking, and the close working relationship developed between the laboratory and a project team.

The process continues to be refined in the areas of computer data manipulation, computer data validation, advancing LIMS capabilities, and streamlining the project review process. Advanced computer data manipulation holds the greatest promise since other areas have reached practical and economical limits.

ACKNOWLEDGMENTS

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A SMART DATA BASE SYSTEM FOR SELECTING ANALYTICAL METHODS FOR ENVIRONMENTAL ANALYSIS

CONCEPT AND DESIGN

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ABSTRACT

The expansion of legislative requirements for environmental testing and the necessity of appropriate analytical procedures have made the identification of adequate and cost-effective data acquisition, documentation, and validation alternatives a complex process. Smart systems designed to sort options based on information need, analytes, and other criteria represent a consistent, easy-access reference to assist in selection. The approach described in this work uses a relational data base, a user-friendly front end and help function, and essentially real-time data base updates to manage and access information about matrix, analyte, extent of documentation, time and cost requirements, and data quality characteristics for indexed analytical methods.

INTRODUCTION

Cost-effective generation of environmental information requires sampling and analytical techniques that are sufficient as well as efficient to provide the required data. The elements of risk assessment models expand as routes of exposure are added, sampling procedures are characterized and refined, and additional analytical procedures for field and laboratory become available. The options for choosing techniques, analytes, length of study period, management risk, and other elements of environmental studies, are becoming progressively more complex and significant. The primary goal is the selection of optimal sampling and analysis options to maximize the information obtained while minimizing cost and delay. Ultimately, these initial decisions affect the adequacy and cost effectiveness of the information available for making decisions about specific sites. Information is available about how sampling and analytical techniques relate to various matrices, site characteristics, and information needs. However, few individuals possess the integrated experience to identify the optimal set of procedures.

Recent requirements for and development of alternative laboratory and field procedures appropriate for rapid data generation with different data quality characteristics continue to complicate the selection of technical alternatives. In addition, the need for high quality, cost-effective data that includes sample- and matrix-specific qualifications requires choices to be made among various methods.

A common demand for analytical methods information arises from the need to comply with legislative requirements and obtain legally defensible data. Some of the pieces of environmental legislation that require monitoring of specific pollutants are the Federal Water Pollution Control Act (FWPCA), the Safe Drinking Water Act (SDWA), the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund), the Clean Air Act, and the Marine Protection, Research and Sanctuaries Act (MPRSA) [1].

The limited access to expert knowledge about how to obtain required environmental information, the need for rapid identification of appropriate, cost effective options, and the need for a standardized, documented rationale for making selections all indicate a problem that may be appropriate for the application of expert systems. In addition to meeting immediate needs, expert systems frequently function as tutorials to assist users in developing subject areas of expertise. The current requirement for rapid acquisition of appropriate environmental data suggests the evaluation of expert systems as a practical, cost-effective approach.

A needs assessment study performed to support the U.S. Environmental Protection Agency (EPA) Expert System Initiative indicated a high priority for the development of a Smart Method Index [2]. The EPA Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) is responsible for developing this application. In the first phase of development, a prototype has been proposed to test the feasibility of the preliminary design. This work describes the conceptual prototype illustrating option fields, scope, user interface features, and the structural design. Active participation by potential users in the review, evaluation, and design of prototype expansion is essential to provide a usable product.

ANALYTICAL CHEMICAL METHODS FOR ENVIRONMENTAL APPLICATIONS

EPA has fostered the development and validation of analytical chemical methods to measure pollutants of environmental impact included in regulation lists. The EPA Contract Laboratory Program (CLP) organic and inorganic methods have wide application and well-characterized performance and provide legal admissibility of the results. The CLP methods are an adaptation from some of the methods in 40 CFR 136 [3]. The 40 CFR 136 listing now contains 262 analytes and over 500 test methods.

Many other methods applicable to specific analytes and matrices exist or are under development. Some non-CLP methods with wide recognition include the SW-846 methods [4], Drinking Water methods, and National Pollutant Discharge Elimination Systems (NPDES) methods. There are various other organizations involved in developing, validating, and promulgating analytical methods with environmental applicability. Some of these are the National Institute of Occupational Safety and Health (NIOSH), the Association of Official Analytical Chemists (AOAC), the Food and Drug Administration (FDA), and the American Society for Testing Materials (ASTM).

The need to standardize and reduce cost by preventing duplication of effort is well known [5]. For example, a congressional recommendation has been made for "the establishment of a computerized catalogue of the availability, applicability and degree of standardization of methods currently in use in the [U.S. Environmental Protection] Agency" [6]. The microcomputer-based List of Lists (LISTS) system [7], a data base developed by EPA containing over 50 methods, has been proposed for adaptation to meet that mandate. The implementation of the recommended data base is expected to facilitate the selection of appropriate methods and the setting of reasonable data quality objectives for specified applications; promote method consolidation and identify duplications; and increase general knowledge of the available environmental monitoring methods.

Independent attempts have been made to catalogue and to computerize analytical methods for environmental applications. The Index to EPA Test Methods compendium contains over 700 air, water, and waste methods [8]. Microcomputer-based prototypes have been developed for water pollutant analysis methods using Rulemaster® and C language [9], for SW-846 inorganic analysis methods using Pascal language and for SW-846 organic analysis methods using dBase® [10], for SW-846 used-oil methods using Prolog language [11], and for general testing methods using dBase® [12]. The U.S. Department of Defense has prepared a hard-copy compendium of methods in use with applicability for determination of radioactive pollutants [13]. Some of the computerized systems mentioned use expert system techniques in their implementation.

Recently EPA has identified the development, characterization, and application of field analytical methods as an immediate need. For example, ongoing research at EMSL-LV encompasses field X-ray fluorescence [14], soil gas [15], and field gas chromatography [16] techniques. These methods, implemented by EPA, are described in a computerized catalog, of field screening methods covering 31 field methods [17]. In addition, rapid turnaround options for CLP analysis of volatile, PNA, phenol, pesticide, and PCB organic analytes will soon be available. An increasing number of analytical methods are being developed or modified as new technology becomes available and new needs are addressed. An integrated solution to the problem of determining the existence of adequate methods and selecting the most appropriate for an application is critical given the diversity of regulations, method origins, performance needs and characteristics, method categories, sources of information, and user requirements. The implementation of a practical source for method information will require overcoming some of the major shortcomings of some existing systems, such as the limitation in size and performance imposed by most microcomputer environments, the triviality of the functionality allowed by the system, and the difficulty of learning and use for the average user when complex searches and operations become necessary. A time- and cost-saving approach will be one that makes use of the already assembled data bases, but the problem of compatibility and consistency of user interfaces needs to be addressed.

SMART METHOD INDEX CONCEPT

There are several levels of information and assistance that a computerized system can provide. At the lowest level is the plain data base with general method information. A second level is that type of system which provides quantitative information to determine the applicability of a method to a particular use with consideration of performance, quality control, and resource requirements as they relate to the project data quality objectives. A third level of assistance would be provided by a system that, besides making available the necessary information, guides the user in making a decision about the suitability of methods.

A computerized method index that is both efficient and effective will require a comprehensive, high-performance data base system and a powerful, user-friendly interface. Target users for an environmental monitoring methods index have diverse background and range from scientists to concerned citizens and from managers to engineers [6]. Systems with minimal contents and simple functionality could serve as common denominators to such a diverse group, but would fail to meet the needs of EPA investigators and the environmental community. Methods with diverse origin and application should be included. Many separate data bases of related methods have been assembled already and some have been computerized. The integration of some of these previous developments to a more general index could prove to be a cost-effective approach consistent with agency objectives.

The need to store and manage a large amount of information suggests the use of a mini or mainframe computer to implement the system. This centralized approach also presents the most manageable alternative for system maintenance, data base updates, access, user support, and security control. This approach also assures the user that the latest information is always available without depending on the effectiveness and timeliness of software distribution.

EPA already has in place central and regional networks for computer access, which make the centralized approach a realistic option. For wider access, alternative delivery and access channels could be found through other Government, scientific, and private electronic information networks. The integration of several data bases in one system would require an effort to preserve elements of the structure of each data base, since one include-all data base with a common structure could be very inefficient.

This modularization presents a serious problem for data base management and particularly for user operation of the system. An environmental analytical methods data base with the described characteristics will need to be "smart" to provide the user with guidance and help to navigate through the data. Assistance needs to be given to the user to convey the information need, to find the right data in a modularized system with multiple structures, and to produce an output that is both relevant and understandable.

SYSTEM DESIGN

The Smart Method Index prototype development will test the concept and implementation approaches, provide a way to better define the system specifications, and produce tools for expanded development. The system implementation has two major, conceptually separate but operationally interdependent, components: the data base driver and the user interface (front end), as depicted in Figure 1. Depending on the details of the final implementation, a third component for intercommunication may be necessary. Scientists at EMSL-LV are building a prototype system in a mainframe computer to test the performance and suitability of different data base architectures. The system under development initially will provide information at the first level of assistance, as previously described, and will be quickly expanded to a second level of assistance.

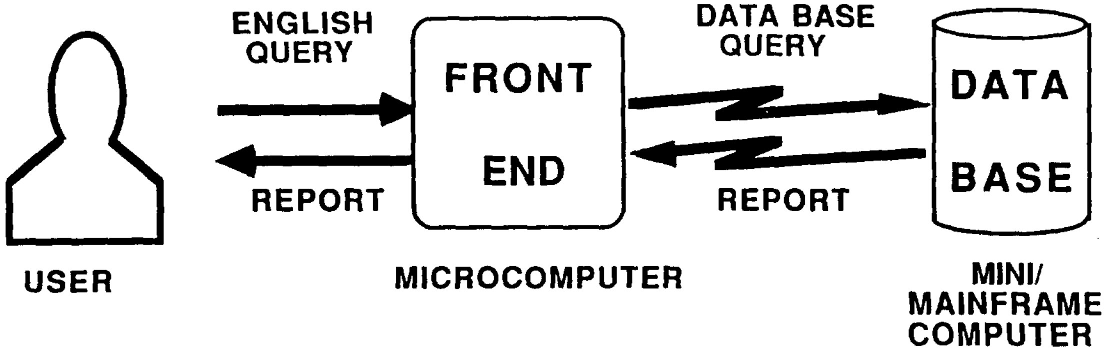
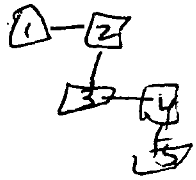


Figure 1. Remote data base access and smart front end concept.

1 2 3 4 5
DQO — Sampling — Analysis — Data Validation — Data Usability



The choice of software in the available mini or mainframe computers is limited. The Statistical Analysis System (SAS®) [18] was selected for use in preparing the prototype because of its flexibility. This software is one of the most widely used and best supported data processing tools. It offers the ability to manipulate multiple data sets and provides built-in functionality for a large number of operations. The SAS® language is a high-level programming environment that can be used to build very refined applications, including high-quality graphics. Prompt-driven or menu-driven user interfaces can be built with SAS®, or alternatively the program can run in the background with an external interface. Besides the modularization of the data base to integrate existing method catalogs, the use of multiple data sets with diverse structures permits the implementation of relational data base models [19]. Relational data bases are a flexible and storage-efficient way to organize interrelated data. Instead of having one large collection of records with a number of fixed fields (e.g., METHOD NAME, ANALYTE NAME, ANALYTE SYNONYM1, ANALYTE SYNONYM2, PRECISION) related information is stored together and several interrelated files are produced. For example, the method name, analyte name and performance information could be stored together in a file, while the analyte name field could be used to access the analyte synonyms stored in a separate file, utilized only when this information is needed. In the same way, method information (such as source, status, and description) could be accessed in a third file through the method name field, if requested. Figure 2 shows an example of a relational data base structure for storing and accessing chemical analytical method information. The relational architecture and operation helps avoid giving the user unwanted information, streamlines searches, facilitates maintenance, and accommodates different data base structures.

The need to access possibly different data structures suggested the exploration of application-independent approaches. Prompts and menus require the user to know how the data base is built and depend on the data base structure for anything but the simplest applications. Another option is the increasingly popular Standard Query Language (SQL) approach, which provides a common query mechanism throughout several data bases; SAS® Version 5 does not support this feature, although it is planned for inclusion in the upcoming version [20]. A "natural language" approach was selected as more user-oriented because it allows the user to ask questions to the system rather freely by typing them in plain English [21]. Appropriate tools for implementation of this user interface are not available in the mainframe computer. Since microcomputers are now in widespread use and can serve as terminals for a central computer, Prolog language [22] running in a microcomputer was selected for the user interface implementation. Prolog is a programming language widely used in artificial intelligence projects and very suitable for natural language application development. The resulting front end should be capable of translating the English-like questions of the user into the corresponding SAS® command or SAS® program code to query the data bases for the sought information [23]. The output of the query will be presented to the user on the computer screen or optionally printed in hard copy. This dialogue-based operation could allow for progressive questioning where the user

METHOD FILE

METHOD NAME
ANALYTICAL TECHNIQUE
METHOD DESCRIPTION
SOURCE NAME
STATUS - APPROVAL
STATUS - DEVELOPMENT
REFERENCE NAMES
ANALYSIS COST
ANALYSIS TIME
DIFFICULTY
QA/QC REQUIREMENTS
SAFETY CONSIDERATIONS
SAMPLE SIZE, CONT, PRES, HT

PERFORMANCE FILE

ANALYTE NAME
METHOD NAME
MATRIX
ACCURACY
PRECISION
DETECTION LIMIT
QUANTITATION LIMIT
REMARKS

ANALYTE FILE

ANALYTE NAME
ANALYTE SYNONYMS
CAS NUMBER
CHEMICAL CLASSES
REGULATION NAMES
REFERENCE NAMES
HAZARD CATEGORIES

SOURCE FILE

SOURCE NAME
ORGANIZATION

REFERENCE FILE

REFERENCE NAME
CITATION
AVAILABILITY

REGULATION FILE

REGULATION NAME
SOURCE NAME
REFERENCE NAMES
REGULATION DESCRIPTION

Figure 2. Analytical methods relational data base example.

starts with general questions and, based on the response obtained, refines the queries to focus on specific areas of interest. In this context-sensitive operation mode, new questions could indirectly refer to the context of previous ones. The microcomputer-based component also takes care of the communication support over data or telephone lines. The increasing affordability of high-speed modems and improvement in the quality of communications help to make this remote approach a practical one. The smart interface capability will provide a vehicle for the future integration of an expert system in the Smart Method Index to reach performance at a third level of assistance.

SUMMARY

A mechanism to assist within the selection of methods for measuring environmental pollutants has been recognized as a high priority need consistent with the requirement for adequate, cost-effective acquisition of environmental information. Several alternative approaches have been initiated which have varying applicability to current needs, future requirements, and the universe of potential users. The objective of the task described here is to provide suggestions and considerations, as well as a proof-of-concept prototype, for the development of a system that is flexible and appropriate to meet a variety of long-term objectives of EPA and the environmental community. Primary considerations include the development of a standardized user interface, the necessity for data base flexibility in a rapidly expanding domain, and the requirement for the development of a standardized, multipurpose data base structure. These considerations are consistent with the original legislative intent to provide optimal information with minimal duplication of effort. The ongoing development of a prototype for the data base and the front end, using SAS® and Prolog, respectively, will allow the testing, refinement, and validation of the proposed approach.

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INTERFACING OF AN HP GC-MS (5970) WITH A 1000A COMPUTER SYSTEM TO A VAX COMPUTER AND DEC LIMS

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ABSTRACT

An integral part of the Environmental Monitoring Laboratories (EML) automation strategy has been the development of instrument management systems. These systems accomodate the electronic transfer of analytical resultant data automatically from the analytical instrumentation data system to the DEC Laboratory Information Management System (LIMS) resident on our DEC VAX-based computer network. This paper addresses the interface developed for transferring resultant data from a Hewlett Packard (HP) 1000A computer with RTE-A operating system, via Forest Computer's VAXLINE file transfer software, to DEC's LIMS/SM residing on a VAX clustered network.

INTRODUCTION

The EML volatile and semi-volatile organics departments utilize eight HP 5970B MSD's with 5890A GC's, linked to four HP 1000A computers with Aquarius software and RTE-A operating system, for the analysis of organic constituents in groundwater samples. The resultant data file generated for a sample is written as an ASCII file to the CI (command interpreter) directory on the 1000A computer by the Aquarius software. The file containing the "raw data" from the analysis is also written to the CI directory. The resultant data ASCII file contains information about the method name, sample name, associated raw data file name, instrument operator, time and date stamp, analyte names, analyte Chemical Abstract Service (CAS) numbers, and analyte concentrations (results). The special HP file name characters (e.g. ^, <, >) are translated into alphanumeric characters (U, G, L) to be consistent with DEC's file nomenclature.

The Forest Computer file transfer module of the VAXLINE software resides on the 1000A computer and is automatically invoked to transfer both the resultant data and raw data CI directories via DECNET to identically named directories within the VMS file structure on the IM LAVC (Instrument Management Local Area VAX Cluster). The raw data files can then be archived from the VAX network and the resultant data files are available for parsing and transfer to LIMS/SM.

The VAX network hardware involved in the interface effort comprise two clustered systems. The CI (computer interconnect) cluster utilizes a VAX 8530 and a VAX 8250 computers to run LIMS/SM (sample management) and LIMS/CS (communication sub-system) software; six RA82 disk drives provide 3.6 Gb (gigabytes) of primary and shadowed memory for LIMS and two more RA82 drives are dedicated to raw data storage. The IM LAVC runs LIMS/CS only on a cluster comprising a VAX 3600 (boot node) and twin µVAX II's (satellite nodes) with two RA 82 disk drives providing 1.2 Gb of memory.

When a sample is logged in to LIMS/SM (on the CI cluster) a test request is generated, and after certain system parameters are met, the test request or requests are sent via LIMS/CS to the appropriate instrument management (LTP) data base resident on the IM LAVC. This test request contains the method name, sample name, analyte names and CAS numbers applicable to the sample, and serves as a temporary database template awaiting the test resultant data. A custom parser routine, developed by EML staff, periodically scans the specified instrument management directory (on the IM LAVC) for resultant data files. When the parser routine finds an appropriate data file it parses the file down to its pertinent information (method name, sample name, analyte names, CAS numbers and results), matches it with the waiting test request template in the IM database, then transfers it via LIMS/CS to LIMS/SM on the CI cluster. The original copy of the completed test request on the IM LAVC is then purged.

If an error is detected during the parsing routine (e.g. incorrect number of analytes, wrong CAS numbers, sample name typos, missing analyte results, etc.) an electronic mail error message is sent to the user's account and a copy of the faulty data file is shipped to an error directory on the IM LAVC for inspection and correction. A successful data transfer initiates an entry to a log file on the IM LAVC.

SUMMARY

A three-vendor instrument interface system has been developed for the purpose of automatically and electronically transferring GC-MS sample results from an HP 1000A computer to DEC LIMS residing on a VAX clustered network.

Forest Computer's VAXLINE software and EML custom parsing software were utilized in developing an instrument management system capable of fast and efficient transmission of the high data output generated by GC-MS analysis of groundwater samples for organic constituents of environmental concern.

MOBILITY METHODS

MIGRATION OF CHLORINATED PHENOL, DIBENZO-P-DIOXINS, AND DIBENZOFURANS IN SOILS CONTAMINATED WITH WOOD TREATMENT OIL.

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ABSTRACT. Soil contamination has resulted at various wood preserving sites from accidental surface spillage and subsurface seepage from unlined surface impoundments. Significant concentrations of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been found in soils at wood preserving plants which use pentachlorophenol (PCP). This study focused on wood-treatment oil and contaminated soil obtained from an abandoned site in Montana.

The objectives of this project were to evaluate laboratory methods to assess the potential release of PCP, PCDDs, and PCDFs and to determine partition coefficients for these compounds in a water-soil-oil system. Extraction test parameters evaluated included the optimum extraction time and the most appropriate method for liquid/solid separation. Partition coefficients for the organic compounds were determined by batch extraction methods for soil-water, oil-water, soil-oil, and water-oil-soil phases.

The optimum duration of soil-water mixing for batch extractions was 18 hours. The most appropriate method for separation of soil and liquid phases for the determination of soil partition coefficients was filtration with a 0.45 um membrane filter. Filtration with 0.45-um membranes produced extracts that were approximately equal to column leachate in PCDDs, PCDFs, and PCP concentrations. Centrifugation was found to be the least desirable solid-liquid phase separation technique.

Measurable soil-water partition coefficients for PCDDs and PCDFs were in the range of 104 to 105, indicating that these compounds are highly partitioned onto the soil matrix. However, PCDDs and PCDFs were highly partitioned into the oil phase in the water-soil-oil phase system. PCP was found to be highly leachable from soil, with partition coefficients ranging from 20 to 50. Partitioning by PCP was approximately equal between soil and oil in the three phase system.

Results of this study suggest that oil-phase migration is the most likely mechanism for off-site subsurface transport of PCDDs, PCDFs, and PCP at wood treatment sites. Therefore, the discovery of a free oil phase in the subsurface environment at a wood-treatment site where PCP was used should be considered to contain significant concentrations of PCDDs and PCDFs in addition to PCP. Removal of the free oil phase from the site may eliminate the greatest potential for off-site migration of these compounds.

LEACH TESTING OF STABILIZED CONTAMINATED SOILS

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ABSTRACT

Soil stabilization or fixation was evaluated as a remedy of choice at three Superfund Sites located in the Pacific Northwest. Fixed soil materials were subjected to a series of leach test procedures designed to determine the effectiveness of the fixation methods in reducing the leachability of the contaminants in the soil.

During the first phase of the testing procedures four vendors were asked to treat samples of soil taken from the Western Processing Site located in Kent, Washington. Samples of the fixed wastes were subjected to the Monofiled Waste Extraction Procedure (MWEP), Toxic Characteristic Leaching Procedure (TCLP), American Nuclear Society (ANS) Test #16.1, and the Materials Characterization Center (MCC) Test #1 along with a suite of biotoxicity tests.

Engineering and chemical testing were also carried out on the materials. The various engineering tests were designed to evaluate the structural properties of the fixed soils as well as the effects of fixation on permeability.

In the second phase two vendors were asked to conduct bench scale fixation of soils at two NPL sites. One vendor treated the soils from the United Chrome NPL Site in Corvallis, Oregon and the other treated soils from the Tacoma Tar Pits NPL Site in Tacoma, Washington. Materials from both of these tests were subjected to a series of bench-scale tests similar to those used in the Western Processing Study. The vendor working on the United Chrome site also carried out a pilot scale fixation of the wastes. The wastes obtained on site during the pilot scale test were subjected to the same tests used during the bench scale study.

DEFINITIONS

The following terms are used in this paper:

Stabilization is a process that alters the form of the chemical pollutant or detoxifies it by chemically altering the form or species of the contaminant. Solidification is a process that accomplishes a reduction in the leachability of the contaminants by improving the physical characteristics of the waste, decreases the surface area of the waste and encapsulates the contaminant. Fixation is a term that is often used to encompass both solidification and stabilization.

INTRODUCTION

Region 10 of the U. S. Environmental Protection Agency (USEPA) has carried out a series of demonstration projects designed to evaluate the efficacy of soil stabilization or solidification as a remedy at Superfund or RCRA sites. This paper reports the results of testing carried out during these demonstrations.

Leach testing carried out under current environmental regulations have not been designed to address wastes that have been fixed. One of the primary purposes of fixation is to reduce the surface area of the waste over which leaching can occur. Grinding of the resulting monolith in order to carry out leaching tests such as the Toxic Characteristic Leaching Procedure (TCLP) or Monofilled Waste Extraction Procedure (MWEP) fails to recognize the primary benefit of solidification.

Region 10 working with the Environmental Monitoring Support Laboratory (EMSL-LV) in Las Vegas, NV and the Center Hill Solid and Hazardous Waste Research Facility (Center Hill) in Cincinnati, OH has used several testing protocols in order to evaluate the effectiveness of the fixation.

STUDIES

This report reviews leaching results from studies carried out on three of the demonstration project sites used by Region 10. The Western Processing NPL Site in Kent, WA was used in 1986 to evaluate the processes used by four vendors. The materials were subjected to the Extraction Procedure - Toxicity (EP), the TCLP, the Solid Waste Leaching Procedure (SWLP) as well as a number of physical tests.

One of the vendors was asked to work with Region 10 in evaluating the efficacy of their product on contaminated soils obtained from the United Chrome NPL Site located in Corvallis, OR. This study was carried out in two phases. The first phase was a bench scale study using screened materials obtained from an abandoned dry well located on the site. The second phase was a pilot scale fixation carried out on the site using materials obtained from the dry well area. The TCLP, the MWEP, the Materials Characterization Center Test No. 1 (MCC-1) and the American Nuclear Society's Test No. 16.1 (ANS 16.1) were used to leach the materials fixed during these studies.

The third site was the Tacoma Tar Pits NPL Site located in Tacoma, WA. A vendor was asked to provide assistance in carrying out the fixation of materials obtained from the site. The materials on this site provided and unusual test for the fixation process used to fix the materials. Not only were there metal contaminants in the soils but also organic chemicals that had leached from an abandoned coal tar disposal area. The soils were mixed with coal tar and with a material known as "auto fluff". Auto fluff is a mixture of foam, rubber, plastic and non-ferrous metal left over from the operation of an automobile shredder. In order for a fixation process to work on this site, it would have to be able to handle the auto fluff and the tarry materials. The TCLP and the ANS 16.1 tests were used to leach the materials fixed in this study.

TESTING PROCEDURES

The testing procedures used in all three of the demonstration studies were designed to provide an assessment of leaching for purposes of evaluating the risk that might occur from the use of fixation as a remedy at Superfund sites. The test protocol used at Western Processing utilized testing methods that are outlined in various environmental regulations. Two primary tests were used at Western Processing; the TCLP and the SWLP. Samples were pulverized for both of these tests; but, a third set of samples were leached as monoliths. Four vendors took part in this demonstration study. Metals were the contaminants of interest at this site.

At United Chrome two additional tests were added. Both of these were patterned after test protocols used by the nuclear industry. The Materials Characterization Center uses a test (MCC-1) that measures the concentration of the saturated leachate. Samples are collected from monoliths that have been leached for different periods of time in site water. This represents the maximum concentration that should be expected in the leachate. The second test used is the American Nuclear Society test (ANS 16.1) for regenerating or flowing leachate. Monolith samples are leached for set periods of time then transferred to fresh leachate. The MWEP was used at United Chrome. This is a new name for the test known as the SWLP; therefore, this is essentially the same test.

The ANS 16.1 test is used to calculate a diffusion coefficient De that is calculated by use of Equation 1.

$$(\Delta F * U / S_a)^2 = 2 * (D_e * \Delta t / \Pi) \quad \text{Eq. 1.}$$

A leaching index is often calculated using Equation 2.

$$L_e = 1/n \left[\sum_i^n (\log 1/D_e)_n \right] \quad \text{Eq. 2.}$$

The United Chrome evaluations were made in both the laboratory at a bench scale and during a pilot scale study carried out in a scaled down version of an actual fixation operation. The vendor used what became known as the mix of record (MOR) to fix the screened samples used in the bench study. This same mixture was used during the pilot scale study with some slight modifications. Cr, Pb and Sr were the contaminants of interest at this site. Manganese was used to provide an evaluation of leaching from the soil components.

At the Tacoma Tar Pits Site a decision was made to reduce the number of tests used in order to be able to test the different materials found at the site. The TCLP and the ANS 16.1 test were the only leaching tests used during this study. The TCLP provided an evaluation of the toxicity of the leachate that might be generated from fixed wastes. The ANS 16.1 represents the type of leachate that could be expected from a sample of undisturbed fixed waste.

RESULTS AND DISCUSSION

The composition of the raw materials used in the fixation studies are listed in Tables 1 through 3. The soil materials were prepared and mixed in the field then transported to the laboratory for testing. The materials from the Western Processing Site were actual site soils; whereas, the United Chrome "soil" was actually a mixture of dried plating sludge and contaminated soil taken from an abandoned dry well used for disposal of liquid wastes from a chrome plating operation.

The TCLP test was used on all three sites. The leachate concentrations for this test are presented in Table 4. The four processes used at the Western Processing Site produced mixed results. The soil at Western Processing failed the TCLP for Ba and Pb. Three of the vendors produced a product that passed the TCLP for both of these metals but the fourth vendor's product failed this test. It is interesting to note that a number of the products exhibited and increase in the amount of material leached from the fixed waste.

At United Chrome the Cr concentrations in the bench scale TCLP leachate dropped adequately after fixing to provide a material that passed the test for toxicity. The pilot scale study material failed the TCLP and actually showed an increase in lead. This later observation is believed to be the result of a materials handling problem encountered during the pilot study. Nodules containing Fe, Pb, and Cr were found in the dry well material. These were not broken apart during processing. The chemicals used to reduce the chromium were unable to penetrate the nodules and therefore both the chromium and lead were available for leaching from the pulverized material used for the TCLP.

All of the materials except benzene passed the TCLP in the Tacoma Tar Pits materials. Fixation of organic materials such as the tar causes a problem with the Portland Cement mixture used in most fixation operations. There are additives that can improve the retention of the organics; but, this was probably not done during this operation. Mixing soil with the tar appears to greatly improve the retention of the benzene. The two metals reported during this study were well within the regulatory limits.

A comparison can be made between the use of the acid leach used in the TCLP with a distilled water leach used in the SWLP by comparing the results from the first leach period for the SWLP with the TCLP. Figure 1 shows this comparison for Cr and Figure 2 for Pb. The distilled water leach removed less Cr than did the acid leach for all vendors products. The case with Pb was mixed. Vendor PC-1's product showed a marked difference between the results of the two leaching media. The results for the other three products were varied.

During the Western Processing study both pulverized and monolithic wastes were tested with the SWLP. Figure 3 shows the results for Pb. The pattern was similar for the other metals although there was some fluctuation especially with the monolith samples. The similarity between these two curves for Pb suggests that something more than just leaching is occurring in these samples.

The extensive sampling carried out at the United Chrome site allowed a number of comparisons to be made that aid in interpreting the data and in evaluating the effectiveness of the vendors product. Unconfined compressive strength (UCS) is often used as a test of the fixation product. Compressive strength results from the set of the Portland Cement in various mixtures used for fixing wastes. UCS generally increases with time as the cement cures. Figure 4 shows the results of curing on UCS with the United Chrome bench study materials.

As the UCS increases there is also a reduction in the permeability of the waste form. This indicates that a waste that meets a particular leaching criterion during a short term test should continue to improve over a period of time measured in years. Although the data was not generated to evaluate the effects of permeability on leaching, a set of data was developed that can be used to infer the effects of decreasing permeability. Figure 6 shows the effects of increasing UCS upon the leaching index (Le). As the leaching index increases the amount of pollutant leached decreases; therefore, materials with a high Le have the smallest leach rate.

The diffusion coefficient (De) which is used to calculate the Le in Equation 2 tends to decrease logarithmically with leaching time. This is the result of the loss of readily leached pollutant from the surface of the waste form and a slower rate of diffusion from the interior of the waste form. This effect is seen in Figure 7 where four different waste samples are examined. Wastes marked C were from a pilot study cell containing a granular mixture that had been compacted. It did not contain the same amount of cement as did the material in the H cell. The bench sample was a small diameter cylinder that appears to behave similar to the compacted granular material. The similarity between the replicates from the C cell is really quite good considering the variability of the materials used in the pilot study.

Table 5 contains the calculated De for both United Chrome and Tacoma Tar Pits materials. Results of two auxiliary studies are also included in this table. Samples that were cured at two different temperatures are compared. There appears to be little effect of the use of the higher curing temperature. The only benefit was in a quicker set of the cement based fixing materials.

United Chrome is located in the Willamette Valley of Oregon. This is an area that goes through an annual wetting and drying cycle; therefore, the fixed wastes were subjected to the wet/dry stress test outlined in SW 846. There appears to be no effect of the wet/dry stressing on the Le.

The De can be used in Equation 1 to estimate the fraction of the mass that would be leached from the monolith over time. The average De for the entire testing period was used to make this estimate for Pb for three of the soil materials. The Tacoma Tar Pits sample showed more leaching than did the two United Chrome materials. It is interesting to note that the pilot scale study appears to show less leaching than did the bench scale study. This is often seen when processes such as fixation are up-scaled to a field situation such as the pilot study.

The authors recommend that the ANS 16.1 or one of the slight modifications to this test that have been proposed (Wiles, 1987; Malone and Jones, 1982; or Ahn, 1988) should be used in order to provide an estimate of the leachability of the wastes. The TCLP or one of the other regulatory tests will probably have to be carried out. The fact that these tests require that the waste be pulverized violates the primary purpose of solidification -- reducing the permeability and the leaching surface of the waste. A positive note on the use of the TCLP type tests is the fact that if the waste passes the test then there is a very good possibility that there will be no problems from the waste in a monolithic form.

The information contained in this paper is covered in detail in a series of reports submitted to USEPA (Mason, 1987, Rupp, 1989 and Mason, 1989.

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TABLE 1
CHEMICAL CONCENTRATIONS IN WESTERN PROCESSING SOIL SAMPLES

STATISTIC	CONCENTRATION (mg/kg)						
	Ba	Cd	Cr	Cu	Pb	Ni	Zn
AVERAGE	74	24	164	100	1113	29	4819
S. D.	8	5	27	15	226	4	730
C. V.	11.15%	19.06%	16.34%	15.01%	20.26%	14.38%	15.15%

TABLE 2
CHEMICAL CONCENTRATIONS IN UNITED CHROME SOIL SAMPLES

MATERIAL	STATISTIC	CONCENTRATION (mg/kg)			
		Cr	Mn	Pb	Sr
DRY WELL	AVERAGE	71796	345	28862	19563
	S. D.	1966	27	3037	2573
	C. V.	2.74%	7.69%	10.52%	13.15%
BACKGROUND	AVERAGE	64.3	350.8	11.3	59.5
	S. D.	23.0	9.8	5.3	15.8
	C. V.	35.83%	2.79%	46.87%	26.53%

TABLE 3
CHEMICAL CONCENTRATIONS IN MATERIALS FROM TACOMA TAR PITS

CONTAMINANT	CONCENTRATION (mg/kg)			
	SOIL	TAR	SOIL:FLUFF	
			1:1	3:1
As	137	-	62	141
Pb	2490	-	3080	2120
Total Phenols	377	201	584	389
Benzene	0.002	-	<.007	<.007
Toluene	0.008	-	<.007	<.007
Xylenes	0.008	-	<.007	<.007
Pyrene	8.3	3200	4.2	7.4
Benzo(a)anthracene	3.4	1200	<1.8	<1.7
Benzo(b)fluoranthene	2.6	350	2.5	2.8
Benzo(k)fluoranthene	2.3	510	<1.8	1.8
Benzo(a)pyrene	3.0	740	1.4	2.6
Indeno(1,2,3-cd)pyrene	1.3	240	1.1	1.4
Dibenz(a,h)anthracene	0.9	200	0.6	0.8
Total PCB's	6.2	198	32	13

TABLE 4
TCLP LEACHATE CONCENTRATIONS (ug/l)

WESTERN PROCESSING

CONTAMINANT	MATERIAL				
	RAW SOIL	FIXED SOIL			
		PC-1	PC-2	PC-3	VIT
Barium	1.1E+03	8.3E+02	<5.0E+01	<5.0E+01	<5.0E+01
Cadmium	1.8E+01	3.4E+02	3.4E+00	3.0E-01	9.5E-01
Chromium	4.7E+01	2.3E+02	5.9E+01	3.5E+01	2.4E+01
Copper	2.0E+02	1.4E+02	1.1E+03	3.2E+01	4.2E+01
Lead	8.6E+03	5.7E+03	8.5E+00	1.6E+01	5.9E+01
Nickel	9.0E+01	2.0E+02	<2.0E+00	<2.0E+00	<2.0E+00
Zinc	2.1E+07	6.3E+02	7.0E+00	3.8E+01	1.3E+03

UNITED CHROME

CONTAMINANT	UNFIXED	FIXED	PILOT
Chromium	3.7E+04	1.3E+03	1.6E+04
Lead	5.6E+01	2.2E+01	4.5E+02
Manganese	3.6E+02	5.7E+00	3.2E+02
Strontium	5.4E+04	4.4E+04	2.8E+04

TACOMA TAR PITS

CONTAMINANT	SOIL	TAR	SOIL:TAR 1:1	SOIL:FLUFF	
				1:1	3:1
Arsenic	2	2	4	8	6
Lead	17	1U	1U	23	11
Phenols	418U	420	1180	23	15
Benzene	-	537	59	-	-
Toluene	-	1000	540	-	-
Xylenes	-	674	505	-	-
Pyrene	12U	4	5	13U	62U
Benzo(a)anthracene	12U	12U	12U	13U	62U
Benzo(b)fluoranthene	12U	12U	12U	13U	62U
Benzo(k)fluoranthene	12U	12U	12U	13U	62U
Benso(a)pyrene	12U	12U	12U	13U	62U
Indeno(1,2,3-cd)pyrene	12U	12U	12U	13U	62U
Dibenzo(a,h)anthracene	12U	12U	12U	13U	62U

U = Undetected at this level.

TABLE 5
AVERAGE LEACHING INDEX CALCULATED FROM ANS 16.1 DATA

UNITED CHROME

CONTAMINANT	MATERIAL AND/OR TEST				
	CURING		WET/DRY CYCLE		
	25 Deg	60 Deg	4th	12 th	20 th
Chromium	16.2	15.1	16.3	16.4	15.7
Lead	17.5	17.5	17.8	17.9	17.9
Manganese	17.0	17.1	17.3	17.3	17.4
Strontium	12.7	12.5	13.0	13.1	13.2

TACOMA TAR PITS

CONTAMINANT	MATERIAL			
	SOIL	TAR	SOIL:TAR 1:1	SOIL:FLUFF 1:1
Arsenic	>13.6	-	-	12.2
Copper	-	-	-	14.6
Lead	>12.2	-	-	>13.2
Phenols	12.4	8.9	8.9	11.7
Pyrene	>12.5	>13.2	>12.7	>12.2
Napthalene	>9.2	10.9	10.3	-
Benzo(a)pyrene	>13.1	>15.2	>14.7	-
PCB's	>12.1	-	-	>13.4

FIG. 1: COMPARISON OF TCLP AND SWLP

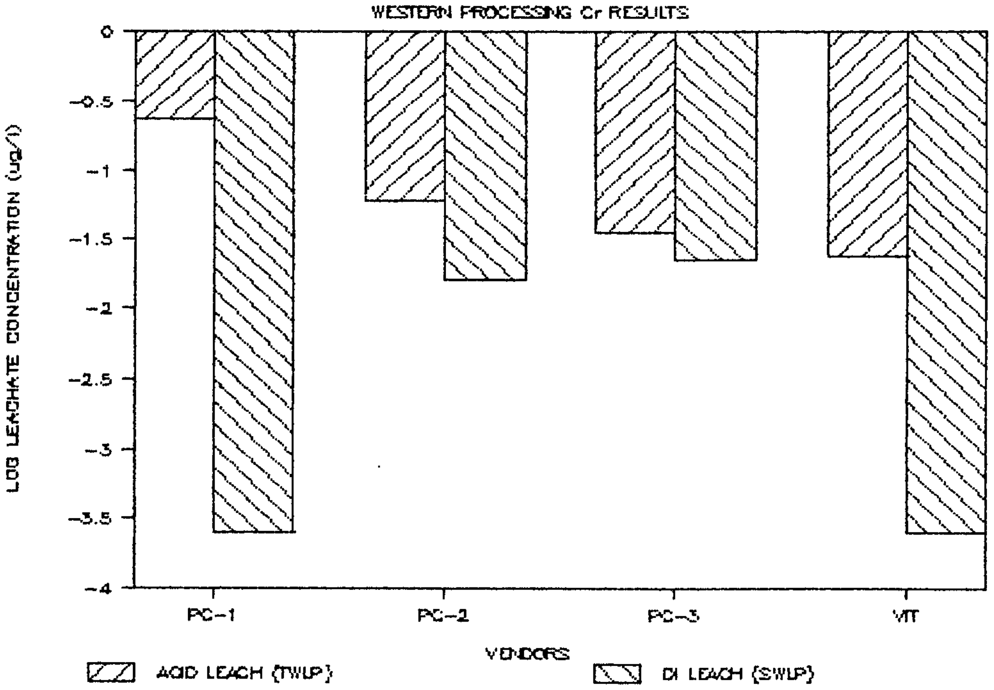


FIG. 2: COMPARISON OF TCLP AND SWLP

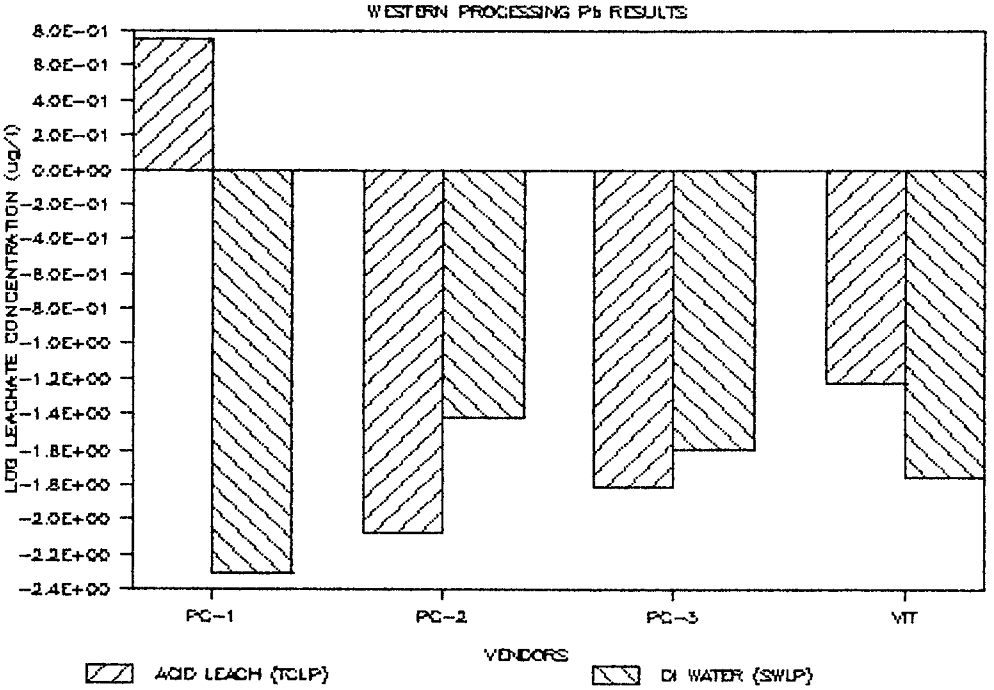


FIG. 3: COMPARISON OF SAMPLE TYPES

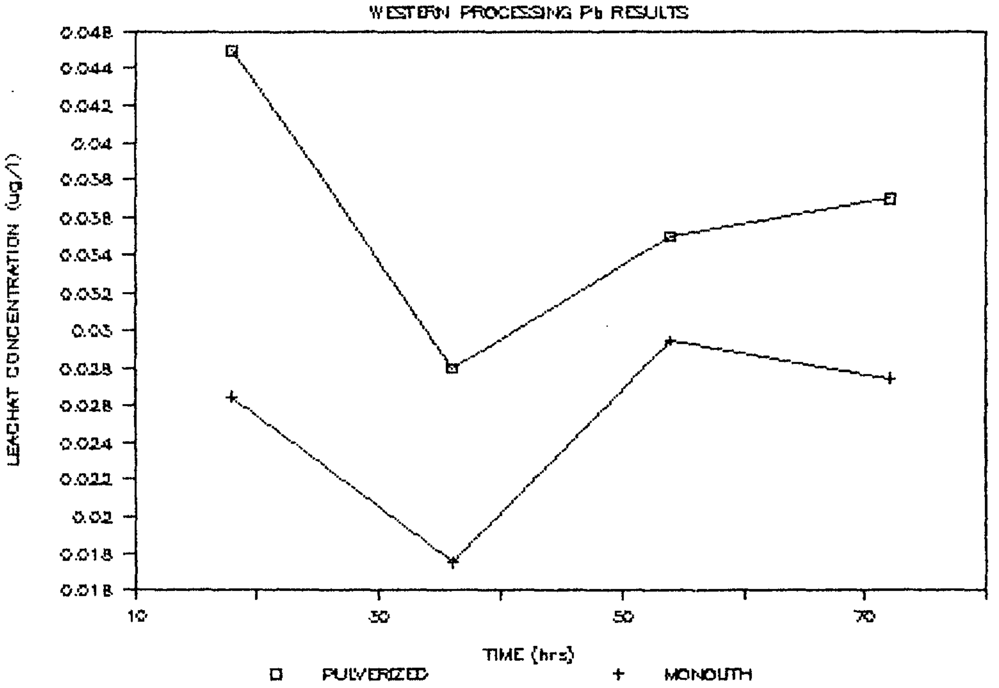

WESTERN PROCESSING Pb RESULTS

FIG. 4: EFFECT OF CURING TIME ON UCS

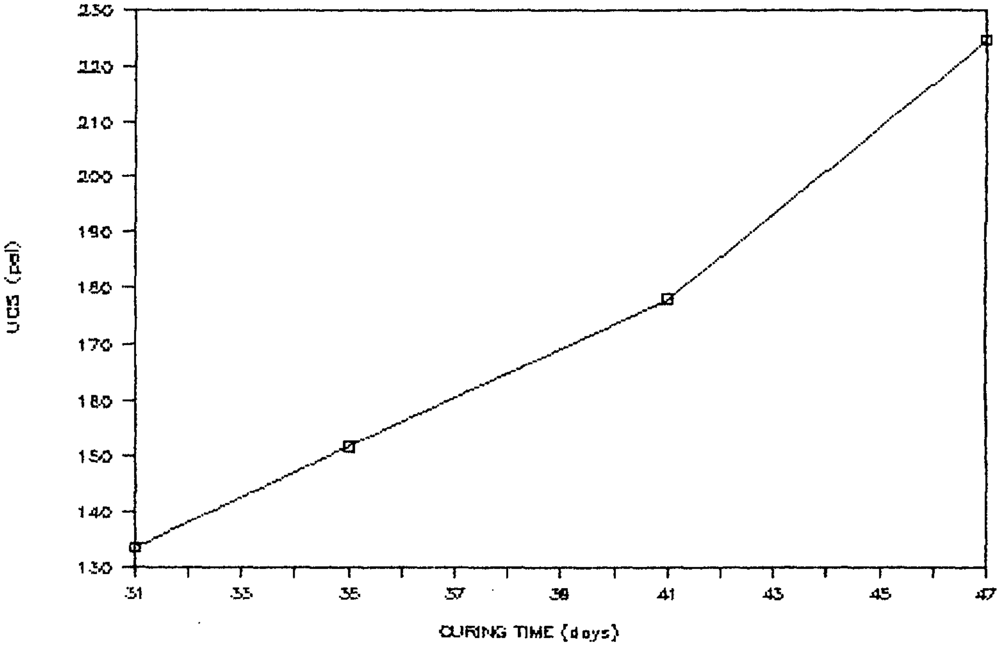


FIG. 5: EFFECT OF UCS ON PERMEABILITY

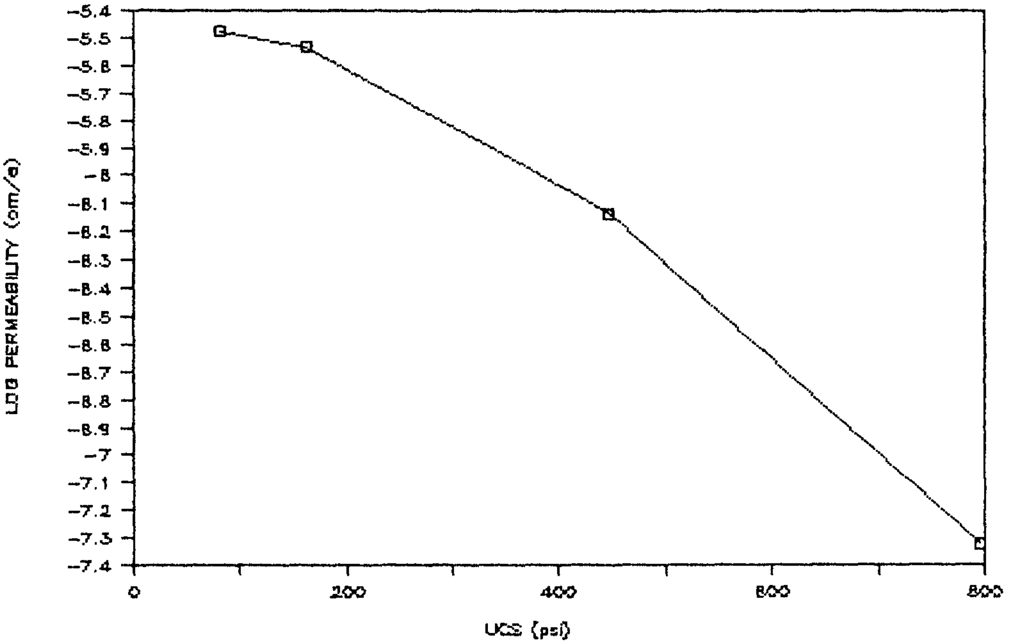


FIG. 6: EFFECTS OF UCS ON Le

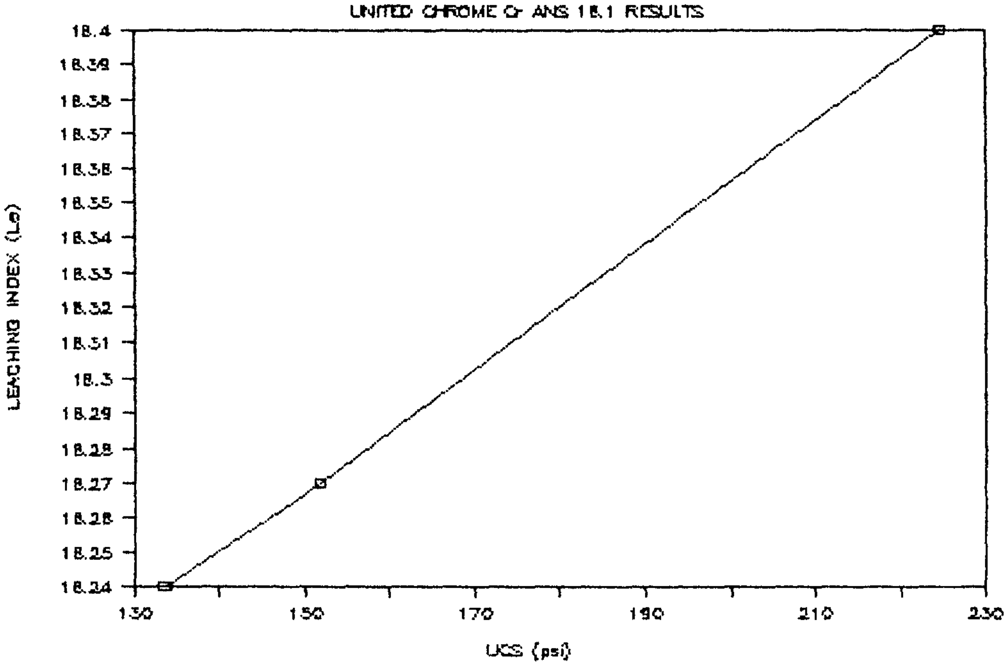


FIG. 7: EFFECT OF LEACHING TIME ON De

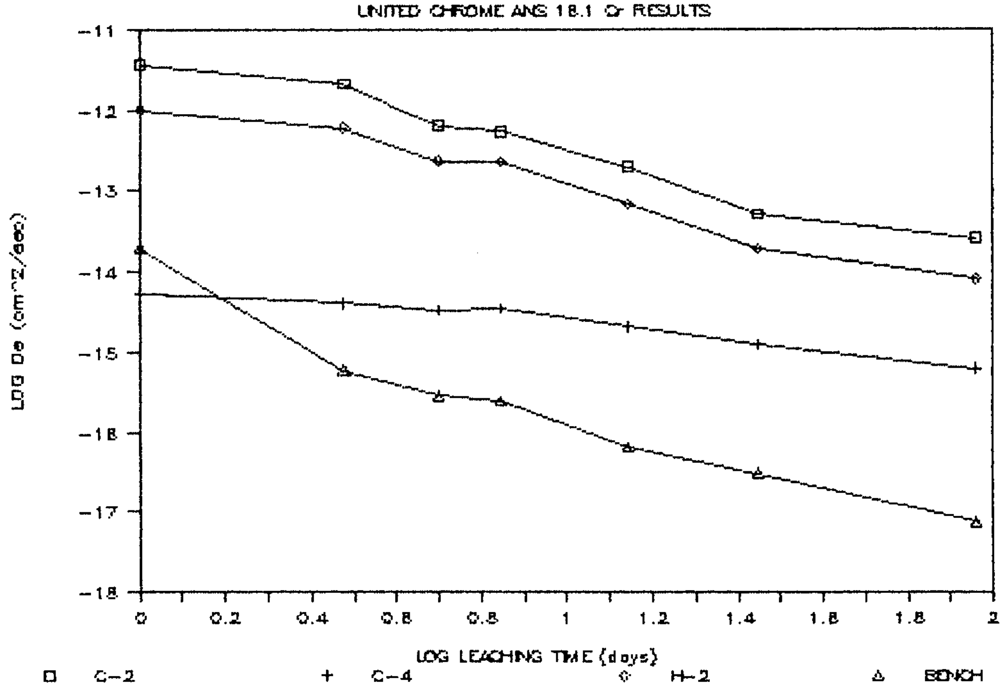
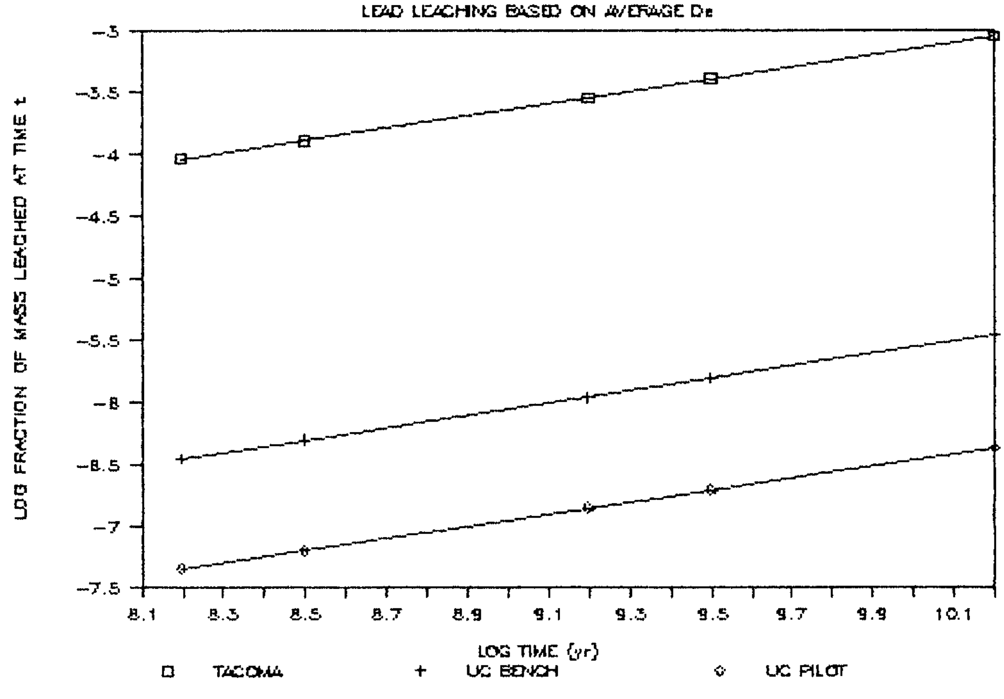


FIG. 8: FRACTION LEACHED FROM MONOLITH



GEOCHEMICAL BASIS FOR PREDICTING LEACHING OF INORGANIC CONSTITUENTS FROM COAL-COMBUSTION RESIDUES

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ABSTRACT

Pore waters, leachates, and waste-water extracts associated with electric utilities' wastes and waste disposal ponds exhibit extremely variable aqueous elemental concentrations. When ionic strength and aqueous complexation are accounted for, however, the activities of free species exhibit behavior with pH similar to those in equilibrium with known solid phases. By comparing observed ion activity products (IAP) with calculated IAPs from thermodynamic data for selected solid phases, solubility-controlling solids may be indirectly identified or suggested for various elements. To date, $AlOHSO_4$, $Al(OH)_3$, $BaSO_4$, $CaSO_4$, $Cr(OH)_3/(Cr,Fe)(OH)_3$, CuO, SiO_2, $SrSO_4$, ZnO, and several solid solution/coprecipitates have been suggested to be the solubility-controlling solid phases for different elements over a wide range of waste compositions, waste types, an disposal conditions. These results indicate that the composition of leachates from coal combustion wastes, with respect to several elements, can be estimated from fundamental reactions involving solubility-controlling solids of these elements. The results obtained thus far using this approach are summarized in this paper.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) provides the statutory authority for the U.S. Environmental Protection Agency (USEPA) to regulate solid waste disposal. One of the major concerns associated with the disposal of solid wastes on land is the release into groundwater of chemicals with a potential for causing environmental degradation and possible harm to humans. For the purpose of defining appropriate management requirements, several federal regulations have been promulgated to list, ban, or classify wastes as hazardous or non-hazardous. One of the four criteria USEPA uses in classifying solid wastes is the "toxicity characteristic." The USEPA has developed laboratory tests to evaluate the leachability and toxicity of the leachates resulting from land disposal. Since 1980, the USEPA has used the Extraction Procedure

(EP) for this purpose (USEPA 1982). The USEPA is currently in the process of finalizing a new (USEPA 1986) Toxicity Characteristic Leaching Procedure (TCLP) to replace the EP. Both the EP and TCLP use a prescribed leaching fluid in laboratory extraction of waste constituents. Both procedures are intended to extract soluble quantities of chemicals from the waste to simulate a waste mismanagement practice of codisposal of many kinds of wastes into a municipal landfill.

The electric utility industry annually generates over 80 million tons of solid wastes as byproducts of coal combustion. About 80% of these wastes are disposed of in landfills and surface impoundments at the power plants where they are generated. These landfills and impoundments are distributed across the entire United States and seldom contain the mixture of wastes that occurs in municipal landfills. Therefore, utilities need a more appropriate alternative to using the EP or TCLP methods, because these methods do not accurately simulate the compositions of infiltrating fluids and the resulting leachates. Furthermore, accurate information on leachate composition, quantities, and release duration is essential for reliably predicting the potential for groundwater pollution. EPRI research completed to date (Ainsworth and Rai 1987; Rai et al. 1988, 1989; Fruchter et al. 1988) indicates that geochemical reactions between coal combustion solids and infiltrating water could reliably be used to calculate the inorganic chemical composition of leachates. In this paper, we describe the geochemical basis for such calculations.

COAL COMBUSTION WASTES

The coal burned in electric power plants contains inorganic constituents (minerals and other impurities) that are left behind as fly ash or bottom ash that must be disposed of or beneficially used. In addition, the scrubbing of flue gas to remove sulfur results in flue gas desulfurization (FGD) sludges that also require disposal. The total chemical compositions of these wastes vary a great deal (Table 1), depending on the coal. However, the types of compounds initially present in the wastes are expected to have similarities caused by the high temperatures reached during coal-burning. For example, kaolinites can be expected to convert to mullite, most aluminosilicate minerals to glass, carbonates to oxides, and gypsum to anhydride. Among such compounds, those that have relatively low solubilities and rapid precipitation/dissolution kinetics, and that are present in large enough amounts will control the concentrations of their constituent elements in leachates.

Table 1. Concentrations of Selected Elements in Utility Wastes (from Rai et al. 1987)

Element	Fly Ash	Bottom Ash	FGD Sludge
	Major Elements (wt%)		
Aluminum	0.1 - 20.85	3.05 - 18.5	0.64 - 9.69
Calcium	0.11 - 22.30	0.22 - 24.10	0 - 34.50
Iron	1.0 - 27.56	0.4 - 20.10	0.13 - 13.80
Silicon	1.02 - 31.78	5.10 - 31.20	0.27 - 17.70
Sulfur	0.04 - 6.44	<0.04 - 7.40	0.08 - 22.80
	Minor Elements (μg/g)		
Arsenic	2.3 - 6,300	0.02 - 168	0.8 - 53.1
Barium	1 - 13,800	109 - 9,360	<25 - 2,280
Boron	10 - 5,000	1.5 - 513	42 - 530
Chromium	3.6 - 900	<0.2 - 5,820	1.6 - 180
Copper	14 - 2,200	3.7 - 932	6 - 340
Lead	3 - 2,120	0.4 - 1,082	0.25 - 290
Molybdenum	1.2 - 236	0.84 - 443	<4.0 - 52.6
Selenium	0.2 - 134	0.08 - 14	<2 - 162
Strontium	30 - 7,600	170 - 6,440	70.8 - 2,990
Vanadium	12 - 1,180	12 - 537	<50 - 261
Zinc	14 - 3,500	3.8 - 1,796	7.7 - 612

When such compounds are present, leachate concentrations are predictable, provided the identity of the solubility-controlling solid is known and thermodynamic data for the solubility product and the associated aqueous complexes for the elements involved are available. In testing this predictive approach in the laboratory and in field studies, we have found that many elements (e.g., Al, Ba, Ca, Cr, Cu, Fe, S, Si, Sr, Zn) in coal combustion wastes are most likely controlled by precipitation/dissolution reactions (Ainsworth and Rai 1987; Rai et al. 1989; Fruchter et al. 1988; Rai and Szelmeczka 1989; Rai et al. unpublished data). Other researchers (Roy and Griffin 1984; Talbot et al. 1978; Henry and Knapp 1980) have also noted that concentrations of some of these elements (e.g., Al, Ca, S) are solubility controlled. Studies are now under way to confirm the identities and quantities of the solubility-controlling solids for these and a number of additional elements.

Completed and ongoing laboratory and field studies under EPRI sponsorship are relating the aqueous elemental concentrations in pore waters, leachates, and waste-water extracts to solubility-controlling solid phases with well-established thermodynamic equilibrium reactions. These studies are briefly described in the following section.

LABORATORY STUDIES TO IDENTIFY GEOCHEMICAL BASIS

A total of more than 90 samples of fly ash, bottom ash, FGD sludge, and oil ash that covered a range of chemical characteristics were collected and analyzed by Ainsworth and Rai (1987). Hot-water extracts were among the analyses performed. The quantities of several elements in the hot-water extracts were extremely variable from waste type to waste type and also from sample to sample within a given type of waste. Geochemical modeling of the measured concentrations revealed, however, that the large variabilities in extract compositions could be accounted for by the effects of pH, aqueous complexation, ionic strength, and the type of the solubility-controlling solid phases. For example, the aqueous concentration of Al in extracts from different wastes and waste types varied over four orders of magnitude (Figure 1), showing a recognizable amphoteric behavior. However, the Al^{3+} activities, which correct the concentrations for the differences in aqueous complexes and ionic strength, vary as a smooth function of pH (Figure 2). The similarity of these Al^{3+} activities to those in equilibrium with known Al solid phases suggests that Al concentrations are controlled by $AlOHSO_4$ at pH values <6 and by $Al(OH)_3(am)/Al(OH)_3(c)$ at pH values >5.5. Comparisons of ion activity products (IAPs) indicated that aqueous concentrations of several other elements are also controlled by solubility phenomena: Ca and S by $CaSO_4 \cdot 2H_2O/CaSO_4$, Si by $SiO_2(am)$ and hydrated $CaSiO_3$, Mo by $CaMoO_4$, and Ba and Sr by, perhaps, their SO_4 compounds. No solubility controls were postulated for trace metals.

Ainsworth and Rai (1987) and Rai et al. (1987, 1988) showed that this mechanistic approach to predicting aqueous elemental concentrations is applicable to fossil fuel wastes. However, Ainsworth and Rai's (1987) interpretations of solubility-controlling solids are based on elemental activities as a function of either pH or a given ligand in extracts from various samples. Although high temperatures during burning of coal are expected to

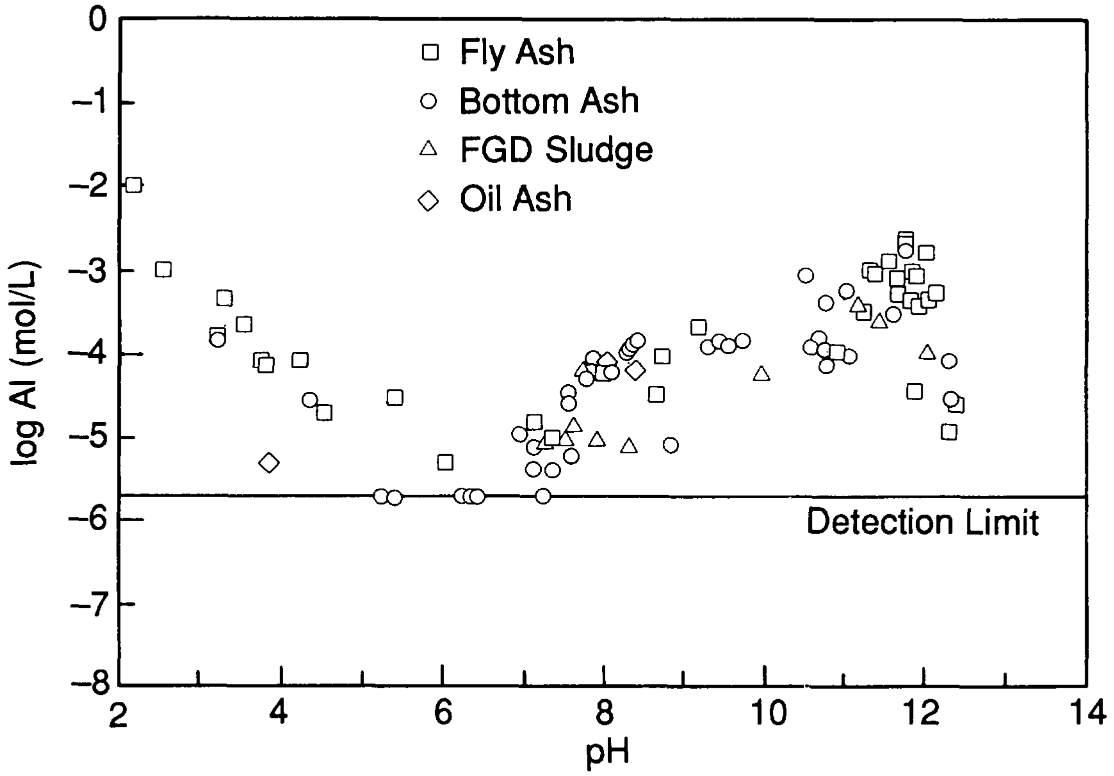

Figure 1. Variation in total aqueous Al concentration in different wastes as a function of pH and waste type. (From Ainsworth and Rai 1987).

produce similar solids in all wastes, the conclusions of Ainsworth and Rai (1987) cannot be relied upon without information on changes in activities of a given element as a function of pH or ligand concentrations from extracts of subsamples of a given waste. In addition, further information is needed 1) to confirm the nature and the amounts of the solubility-controlling solids and 2) to identify solubility-controlling solids of trace elements.

Therefore, studies are continuing with four fly ashes whose chemical characteristics vary over a wide range (Table 2). These studies involve size, density, and magnetic fractionation to enhance the characterization of solid phases by such techniques as X-ray diffraction. Subsamples of fly ashes are equilibrated both at different pH values and with and without additions of either

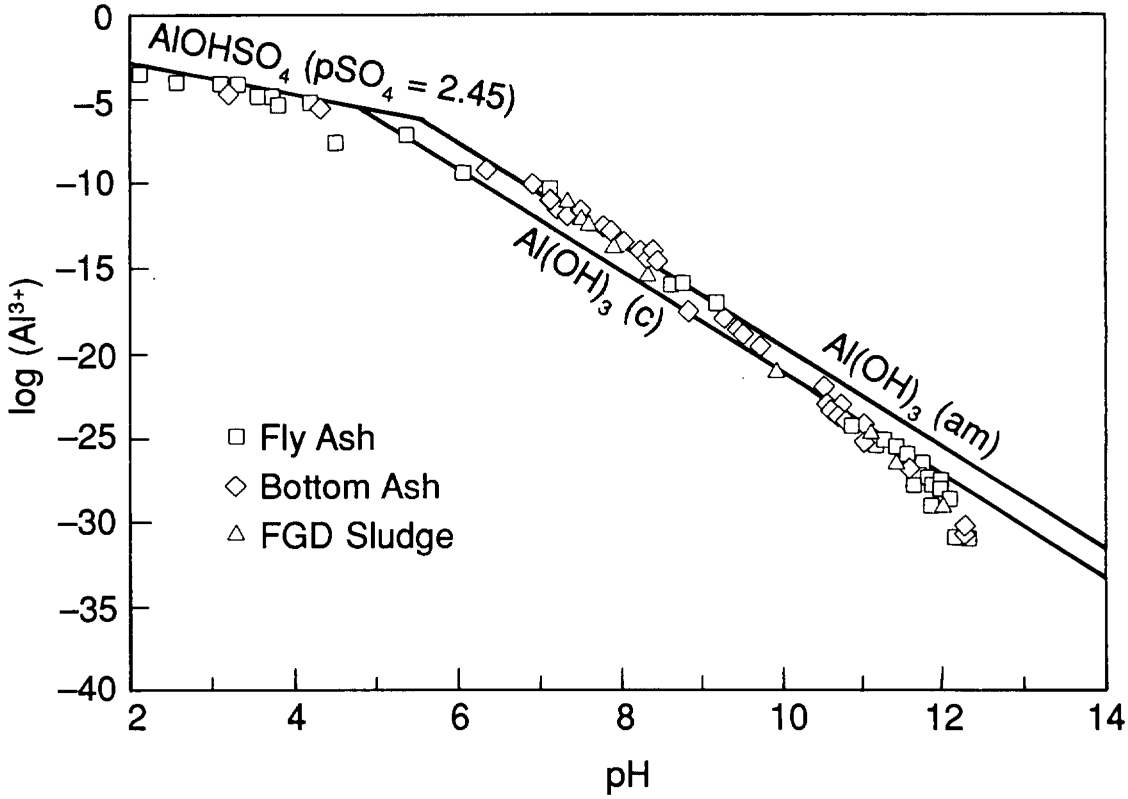

Figure 2. Variation in Al^{3+} activity, determined from the hot-water solution concentration data using MINTEQ, as a function of pH of coal-derived waste samples. Solid lines represent Al^{3+} activities in equilibrium with different Al solid phases, calculated from thermochemical data at an observed average pSO_4 of 2.45 for pH <6 waste samples. (From Ainsworth and Rai 1987).

known aqueous concentrations or solid phases of a given element. The purpose of these studies is to identify solubility-controlling solids indirectly by comparing the observed IAPs with the IAPs calculated from either the published thermodynamic data or the estimates that we developed for those solid and aqueous species for which the data were either unavailable or inaccurate. The results of these studies have shown that 1) the predictions of Ainsworth and Rai (1987) are reasonable, 2) direct techniques for identifying solid phases, such as X-ray diffraction, are not very successful even when elaborate preparations are made to concentrate the elements by means of size and density fractionations, 3) indirect techniques are successful in identifying the solid phases not only for the major elements but also for trace elements,

Table 2. Total Concentrations of Selected Elements in the Four Fly Ashes

	Sample 102	104	112	131
	Major Elements (wt%)			
Aluminum	10.3	12.6	9.3	14.0
Calcium	1.07	0.91	3.34	0.95
Iron	17.7	8.2	13.7	6.5
Silicon	20.2	19.9	23.6	20.8
	Minor Elements (wt%)			
Chromium	0.024	0.018	0.022	0.016
Copper	0.011	0.021	0.007	0.022
Strontium	0.026	0.111	0.029	0.081
Vanadium	0.040	0.035	0.019	0.032
Zinc	0.048	0.029	0.044	0.017
pH (1:1 paste)	4.1	6.8	13.8	9.1

4) solid solutions/coprecipitates play an important role for several constituents [e.g., Ba, Cr(III), CrO_4, SO_4, Sr], and 5) in most cases, necessary thermodynamic data are not yet available. A few specific findings from these studies are discussed below. The compounds CuO and ZnO were found to be the solubility-controlling solids for Cu and Zn. Amounts of CuO and ZnO available for leaching were also determined. In the four fly ashes, Cr was found to be present entirely as Cr(III), and aqueous Cr(III) concentrations were found to be controlled at low pH values by $(Fe,Cr)(OH)_3$ and at higher pH values by $(Fe,Cr)(OH)_3/Cr(OH)_3(am)$ (Figure 3). The $(Ba,Sr)(SO_4,CrO_4)$ compounds play an important role in controlling aqueous concentrations of Ba, Sr, and CrO_4. Studies are currently under way to ascertain the solubility-controlling solid phases of other trace elements.

Field Studies to Evaluate Applicability of Mechanistic Basis

Although the laboratory results and data analysis indicated that for several chemicals we can rely on the mechanistic approach for

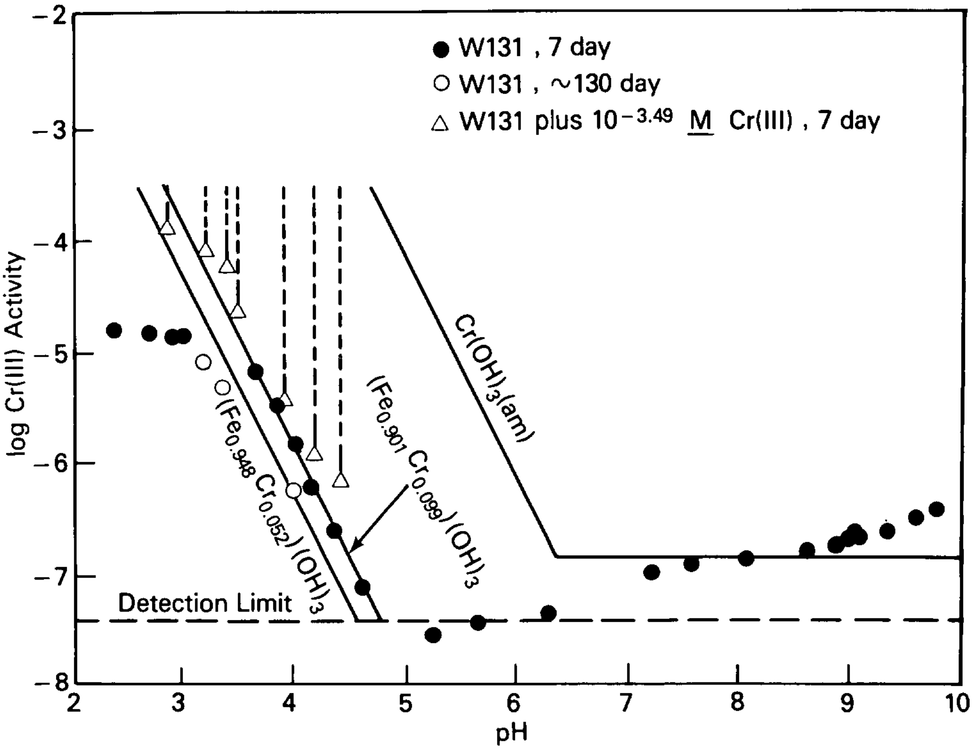

Figure 3. Observed aqueous Cr(III) activities in pH-adjusted fly ash are compared with the Cr(III) activities (solid lines) calculated from the thermodynamic data (From Rai and Szelmeczka 1989).

defining leachate compositions from coal combustion wastes, questions immediately arose as to how these findings would apply to field conditions and how solubility controls might change with leaching times. To address these and other questions, two field leaching studies were completed--one in a fly ash test landfill and another in an FGD sludge pond. In both cases, the leachates generated by the respective wastes and the rainfall or sluicing waters were collected and chemically analyzed for several inorganic constituents. Results from both studies are briefly discussed below.

A fly ash landfill, measuring 100 ft x 100 ft at the base and 60 ft x 60 ft at the top, with a height of 10 ft, was constructed in 1985 by the Pennsylvania Power and Light Company. Natural rainfall has infiltrated through the landfill since late 1985 (Rehm et al. 1987). Leachates were collected from the bottom and from several depths of the test landfill in late 1987 and the chemical compositions of the leachates were analyzed. The measured aqueous concentrations were examined using an equilibrium geochemical speciation computer code. The results of the analyses show that the equilibrium solubility controls identified in the laboratory (e.g., $(Ba,Sr)SO_4$ for Ba and Sr, $CaSO_4 \cdot 2H_2O/CaSO_4$ for Ca, and CuO for Cu) are also applicable to the field-scale leachates. The results also indicated that some of the constituents show a leaching trend that has not yet been identified as being solubility controlled (Fruchter et al. 1988).

A full-scale FGD sludge pond, now inactive, was sampled and analyzed for chemical composition of leachates (Rai et al. 1989). The FGD sludge disposal unit operated as a pond from 1976 to 1979. Since 1979, the standing water has been drained, and the pond now acts as a landfill for most of the year. Sludge cores were taken at three points in the FGD sludge disposal unit. An elaborate laboratory set-up was used to separate leachate (or pore water in this case) from the solids. The Eh and pH of the aqueous phase leachates were measured in situ and in the laboratory. Because of very reducing conditions and the presence of sulfides, aqueous concentrations of Cd, Cu, Ni, Pb, and Zn were found to be at the detection limits as a result of the solubility controls imposed by the sulfide solids of these elements (Rai et al. 1989). Additional elements that were found to be controlled by solubility phenomena included Ba, Ca, Cr, Fe, S, Si, and Sr. Among the trace elements, only B and As were present in measurable quantities. As in the laboratory and the fly ash landfill studies, the results of this study bear out the applicability of the mechanistic approach.

MODEL TO PREDICT LEACHATE COMPOSITIONS

Already, the empirical data and the mechanistic formulations developed thus far for the coal combustion wastes have been used to develop an interim Fossil Fuel Combustion Waste Leaching (FOWL™)(1) code (Hostetler et al. 1988). The FOWL™ code is structured to predict the composition and quantity of leachates produced as a function of time by solid-waste disposal facilities containing coal combustion wastes. The current version of FOWL™ runs on an IBM®(2) PC and is available in executable form through the Electric Power Software Center; the user's manual is available from the EPRI Research Reports Center. The code contains a geochemical calculation algorithm and a water-balance calculation routine. The mechanistically based portion of the code deals with Al, Ba, Ca, Cr, Mo, S, Si, and Sr, which have been found to be controlled by solubility-limiting solids. The empirically based portion of the code deals with As, B, Cd, Cu, Fe, Mg, Na, Ni, Se, and Zn. Improvements in the fundamental basis are being made as continuing laboratory experiments and field measurements clarify the solubility controls for the major and trace elements listed above, the multitude of solid phases involved, and the role of kinetics. Improvements in the computer code will follow accordingly.

SUMMARY

Field sampling and laboratory extractions have yielded many valuable insights into the geochemical basis of leaching of coal combustion solid wastes. It is clear that fundamental chemical reactions between water (leaching fluid) and the solids in the disposal units govern the chemical compositions of the leachates. Precipitation/dissolution reactions at equilibrium with a given solid phase form the basis for leaching. For several inorganic constituents, the controlling reactions are now known and the thermochemical data appear to be adequate. However, for several other constituents, either the controls are not yet known or adequate thermochemical data are not available. Unfortunately, because the amounts of controlling solids involved in the quite complex matrix of coal combustion wastes may be very small, it is not possible to directly measure the types and amounts of the solid phases involved. Therefore, many laboratory experiments and field measurements must be made to identify and define the solubility controls, the changes in solid phase assemblages, and the short-term and long-term leaching characteristics. Research of this nature is in progress, and we expect to complete this work within the next three years.

NOTES

(1) FOWL™ is a trademark of Electric Power Research Institute, Palo Alto, California.

(2) IBM® is a registered trademark of International Business Machines Corporation, Boca Raton, Florida.

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EVALUATION OF METHOD 1311 FOR DETERMINING THE RELEASE POTENTIAL OF OILY WASTES

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ABSTRACT. Method 1311, or the Toxicity Characteristic Leaching Procedure, was designed to model release of contaminants in leachate from a reasonable worst-case waste mismanagement scenario: codisposal of 5 percent industrial waste with 95 percent municipal refuse in an unlined sanitary landfill. Previous work indicated that Method 1311, as currently proposed, is not suitable for certain oily wastes (e.g., slop oil emulsion, creosote sludge, waste motor oil) because filter clogging during the initial filtration step can overestimate a waste's percent solids, thereby underestimating the release potential of the primary waste leachate.

Several filtration step modifications were investigated to solve this problem. For five difficult-to-filter wastes, percent solids results for each modification were compared with the percent of waste immobile in soil columns designed to replicate waste release from a reasonable worst-case sanitary landfill. These experiments indicated that a porous media sintered stainless steel filter most accurately estimates waste mobility. The steel filter also showed good reproducibility, with percent relative standard deviation (%RSD) of percent solids results ranging from 9 to 28 percent for three oily wastes.

Further evaluation of the steel filters demonstrated that the filters are adequately precise and accurate for use in a modified Method 1311. The %RSD of the modified procedure ranged from 2 to 16 percent for five volatile organic waste constituents and from 6 to 32 percent for three inorganic constituents. Precision and accuracy of the modified procedure also was determined for semivolatile organic constituents. Accuracy was determined by comparing the final analyte concentrations determined by the modified method with concentrations in the leachate from the soil column experiments. For these determinations, spikes of deuterated polycyclic aromatic hydrocarbons were added to each waste aliquot prior to the experiments. This provided convenient marker compounds at known concentrations to follow through the experiments and to compare in the final extracts and column leachates. (Complete precision and accuracy data for semivolatile organics are not available at the time of submission of this abstract).

The results of this study indicate that the modified Method 1311 is a significant improvement over the existing method for many difficult-to-filter wastes. The steel filter can filter wastes that clog the glass fiber filter used in Method 1311, thereby improving the accuracy of this step in estimating the release of toxic waste constituents associated with the liquid portion of an oily waste. A full collaborative study of the modified method is necessary prior to proposal as a standard RCRA test method. Our experience indicates that careful waste selection, characterization, and aliquoting is critical to the success of such a study.

THE LIQUID RELEASE TEST

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Abstract

Under Section 3004 of the Hazardous and Solid Waste Amendments of 1984, Congress directed the U.S. EPA to promulgate regulations to minimize the presence of free liquids in containerized hazardous wastes to be disposed in landfills. The regulations should specifically prohibit landfill disposal of wastes absorbed in materials that release liquids when compressed, as might occur in a landfill. As part of the response to this directive, EPA engaged the Research Triangle Institute (RTI) to develop a suitable test to determine if liquid is released when an absorbed waste is subjected to a 50 psi load. The objective established by EPA required a test capable of detecting liquid release from an absorbed waste when the liquid loading exceeds the saturated concentration by no more than 10 percent.

The result of this method development effort is a Liquid Release Test (LRT) protocol that is easily performed in the laboratory or field. The LRT requires a device capable of applying 50 psi continuously to the top of a confined cylindrical sample. The device consists of a sample holder, the pressure application device, filter papers to detect released liquid, supporting screens (to separate the sample from the release detection filters), and a spacing grid to prevent wicking. The LRT is an attribute test (i.e., the result is either "release detected" or "no release detected"), rather than a continuous variable measurement test.

The LRT development entailed extensive testing to evaluate different equipment designs; release detection techniques; and the effect of test duration, temperature, and sample size on performance. The LRT was evaluated in a collaborative study in November 1988 to determine interlaboratory variability of the test using the device developed by the Associated Design and Manufacturing Company. The collaborative study also provided an opportunity for other manufacturers to demonstrate equivalency of their devices to detect liquid release.

RESIDUAL FUEL OIL AS POTENTIAL SOURCE OF GROUNDWATER CONTAMINATION

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ABSTRACT

As part of the Environmental Protection Agency's (EPA's) continuing effort to develop the basis for listing certain refinery wastes as hazardous, residual fuel oil tank bottoms were characterized for semivolatile organic compounds including selected polycyclic aromatic hydrocarbons (PAHs).

No. 6 fuel oil samples were collected from four regions in the United States. Soxhlet extraction with methylene chloride, followed by fractionation on alumina, were used to isolate the PAHs in fuel oil samples. The sample extracts were analyzed by high resolution gas chromatography and gas chromatography/mass spectrometry. Total selected PAH concentrations in the fuel oil samples ranged from 71 to 6,560 ug/g. Higher concentrations of other aromatic compounds including alkylated PAHs and sulfur-containing aromatic hydrocarbons were also detected in the samples.

Additionally, laboratory-scale soils columns (2 cm ID and approximately 10 cm long) were used to model the transport of oily waste in the subsurface and potential migration into the groundwater. In one set of the experiments, the oil was introduced on the top of the soil using a disposable minipipet and was then allowed to disperse freely. In the second set of experiments, the soil columns were subjected to a small pressure using pure nitrogen gas. All the studies were conducted at room temperature and the soil columns were saturated with water prior to the addition of the fuel oil.

Several oil mobility studies were performed with fine and coarse soil. The fine soils initially showed no visible mobility for the fuel oil sample during the 17-day experimental period. However, additional experiments using oil/soil ratios of 1:1 and 1:2 (30 g of soil) showed movement of the fuel oil through the entire length of the fine soil column (10 cm). The oil moved through the coarse sandy soil column and also eluted from the coarse column when the same oil/soil ratios as above were used. The fuel oil passed through the columns with little adsorption

(in a matter of minutes or hours) when the columns were pressurized with nitrogen gas.

In a related study, several Toxicity Characteristic Leaching Procedure, "TCLP" experiments (1) were conducted to assess the feasibility of using TCLP for this type of oily waste and to compare the TCLP results with the corresponding soil column studies. In light of the results obtained in this set of experiments, the applicability of TCLP to this type of oily waste must be cautioned. Furthermore, due to dissimilar processes and experimental conditions involved in the TCLP and column studies, it was concluded that comparison of the two procedures may not be appropriate.

INTRODUCTION

A large volume of crude oil is refined throughout the U.S. to produce a variety of petroleum-based fuels. For example, over 60 billion gallons of crude oil were refined by the petroleum refinery industry in 1984 alone, resulting in the annual production of approximately 4 billion gallons of residual fuel oil (2). Some of the other major products include motor gasoline, distillate fuel oil (diesel), and jet fuel.

These petroleum fuels are commonly contained in underground storage tanks before usage. Leakage of oil from the storage tanks and potential for groundwater contamination have recently become a matter of national concern (3,4). According to one study (5), 35% of such underground storage tank systems were estimated to be leaking at the average rate of 0.32 gal/h.

The Hazardous and Solid Amendment to the Resource Conservation and Recovery Act (RCRA) require that the EPA characterize, and regulate if necessary, the wastes generated by petroleum refineries.

In order to assist the EPA in developing a data base for listing certain refinery wastes as hazardous, residual fuel oil tank bottoms were characterized for semivolatile organic compounds including selected PAHs. Furthermore, the extent of movement of the fuel oil through soil and potential for groundwater contamination were investigated by conducting laboratory-scale column experiments.

A secondary objective of this research was to evaluate the feasibility of using TCLP to test the leachability of No. 6 fuel oil. Although TCLP is designed and presently is used to model the mobility of contaminants in aqueous and solid wastes (6), the applicability of the procedure to this type of oily matrix has not been fully investigated.

EXPERIMENTAL

Instrumentation

A varian Model 3700 gas chromatograph was equipped with flame ionization detector (FID), manual splitless injector and DB-5, 30-m, 0.25-mm ID fused silica capillary column (J & W Scientific, Inc., Folsom, California). Conditions for GC analyses of all the sample extracts were identical and were as follows: initial temperature, 40°C; initial hold-time, 4 min; final temperature, 280°C; final hold-time, 10 min; program rate, 10°C/min; injector temperature, 280°C; detector temperature, 300°C; carrier gas helium at 30 mL/min; time for splitless injection, 1 min; chart speed, 2.56 cm/min; and attenuation range, from 16 X 10^{-12} to 2.56 X 10^{-12} amps. A Finnigan Model 5100 gas chromatograph/mass spectrometer GC/MS) was equipped with manual splitless injection port, and 30-m DB-5 fused silica capillary column. Chromatographic conditions were identical for scanning GC/MS and GC/FID analyses. Mass spectrometry conditions for scanning analyses were the following: low mass, 35 amu; high mass, 500 amu; scan speed, 1 scan/s; and electron multiplier voltage, 1500 V. Sample extract volumes in GC and GC/MS analyses were 1 uL delivered using a 10-uL syringe (Hamilton Company).

Extraction and Treatment of Samples

All the fuel oil samples were extracted, treated and analyzed using the sample procedures except as noted. A 1.0-g aliquot of each of the four fuel oil samples from different sources was diluted to 10.0 mL using a 1:1 mixture of hexane/methylene chloride. A 1.0-mL portion of the diluted solution was spiked with 200 uL of base/neutral surrogate PAH standard, 500 ug/mL, and adsorbed onto 3.0 g of neutral alumina (EM Science, West Germany) activated at 150°C overnight. The samples were allowed to air-dry for 1 hour and then were transferred quantitatively to the top of 2 cm ID column which already contained 7 g of neutral alumina, and 1 g of sodium sulfate packed on the top. The samples were subsequently eluted with the following chromatographic grade solvents: fraction 1, total of 20 mL of hexane; fraction 2, 50 mL of benzene. The extracts were then concentrated to approximately 4-10 mL by K-D technique and further adjusted to an exact 10 mL (for Kansas City fuel) and 4 mL for other samples with a gentle stream of dry nitrogen gas. Similar procedures have successfully been applied for the separation of PAHs in other high boiling petroleum distillate (7), synthetic fuel (8), and wastes from natural gas production (9, 10). The condensed extracts were then screened by GC/FID. The resulting chromatograms showed a major removal of the aliphatic hydrocarbon interferences in the hexane fraction and a complex mixture of aromatics in the benzene fraction.

A 1 mL aliquot of each of the benzene extracts including one method blank was analyzed by GC/MS for selected(target) PAHs as well as approximately 25 major non-target semivolatile compounds excluding aliphatic hydrocarbons. The analysis was conducted according to EPA Method 8270 (11), which involves initial tuning of GC/MS using decafluorotriphenyl phosphine (DFTP) and use of internal standards, calibration standards, surrogate standards, system performance check compounds and calibration check compounds. Calibration standards were analyzed at six concentrations including 1.0, 2.0, 5.0, 10.0, 50.0 and 100.0 ug/mL under identical conditions with those for the sample extracts to establish a working curve. These calibration standards contained target PAHs, surrogate standards, and calibration check compounds as per Method 8270.

RESULTS AND DISCUSSION

Characterization Of Fuel Oil Samples

The residual fuel oil sample was too complex a mixture for simple solvent extraction and direct analysis, although a high resolution capillary column was used. However, a rapid one-step alumina column cleanup procedure was effective in removing most of the background and hydrocarbon interferences.

The quality assurance data for surrogate recoveries in the benzene extracts including the method blank were very good. The average percent recoveries for 2-fluorobenzene, D_{10}-pyrene, and D_{14}-p-terphenyl were 92.9%, 108%, and 113%, respectively. D_5-nitrobenzene surrogate was not detected in any of the extracts since this compound is frequently retained by the alumina cleanup column.

A complex mixture of PAHs and other aromatic compounds were observed for all the samples. However, the fuel oil sample from Kansas City had the highest abundance of the aromatics among the samples. A 1:10 dilution of this sample extract had to be used as compared to 1:4 dilution for other oil samples. The identification of these target PAHs was based on a relative retention time with respect to corresponding internal standards, mass spectra of the standards under the same analysis conditions, and also favorable match to mass spectra in the EPA/NIH data base. The results for quantitation of target PAHs in these samples are given in Table 1. Total target PAH concentrations in the fuel oil samples ranged from 71 ug/g to 6,560 ug/g.

The fuel oil samples including one method blank were also characterized for some 20 major semivolatile compounds (SMVs). The majority of these compounds were alkylated PAHs with the highest concentrations found in the Kansas City fuel oil sample. These concentrations were less by almost one order of magnitude in other oil samples (Chevron). The differences in concentrations between Kansas City fuel oil and Chevron samples might be due to different origins or different processes involved in the production of the No. 6 fuel oil. It is important to note that all fuel oil samples except the one from Kansas City had undergone cracking processes to provide a wide variety of product mixes and levels. This was confirmed by the presence of the highest abundance of large molecular weight aromatic hydrocarbons in the fuel oil collected from Kansas City. On the other hand, the Chevron samples showed the presence of low molecular weight aromatic hydrocarbons. It is believed that the large aromatic hydrocarbons were decomposed to lighter hydrocarbons during various cracking processes.

An interesting observation which seems to support the different origin and/or processes for the fuel oil samples, was the presence of sulfur-containing aromatic compounds such as benz- and dibenzothiophene in all Chevron fuel oil samples. No such class of compounds was detected in fuel oil samples from Kansas City.

Column Experiments

Several glass mini columns containing fine and coarse sandy soils were tested to monitor the bulk movement of the fuel oil. In the first set of experiments, approximately 30 g of soil was packed uniformly in glass mini columns (2 cm ID) and about 5 g of the fuel oil sample was introduced on the top of the soil column using a disposable minipipet. The fuel oil was then allowed to disperse freely. Two different sizes of soil, fine (5 um) and coarse (4Q-ROC, 1.5 mm or smaller) crushed silica, obtained from Berkely, West Virginia were used in this study. All the conducted at room temperature (23°C - 25°C), and the soil columns were saturated with water prior to the addition of the fuel oil. The fine soils showed no visible mobility for the fuel oil sample during the 17-day experimental period. The coarse sand showed rather low resistance to the oil transport.

The porosity of the column packing material was estimated from the volume of water used to saturate the soil column. Fine-textured soils tend to have greater porosity than the coarse-textured soils (12,13). Similarly, values for the porosity in our column studies decreased in the order fine (5um, Berkeley) >intermediate coarse (1mm, 2Q-ROC) > coarse (1.5 mm, 4 Q-ROC).

Additional column experiments containing oil/soil ratios of 1:1 and 1:2 (30 g of soil in each experiment) were also conducted. The objective of this study was to compare the movement of fuel oil through the column with the previous studies in which a smaller oil/soil ratio was used (5 g of oil to 30 g of soil). The column dimensions and experimental conditions were kept identical to the previous set of experiments.

These results are plotted as depth profiles in Figures 1 and 2 (vertical movement of the oil from the top of the column vs. time). The weight of the packed soil was kept constant (30 g) in all the experiments, while the amounts of the oil were varied as 5, 15 and 30 g. In general, similar trends were observed for both coarse and fine soil, and the transport of oil through the column decreased in the following order: 30 g > 15 g > 5 g.

The oil eluted from the coarse soil columns when higher oil/soil ratios were used (1:1 and 1:2). The amount of oil eluted versus time during this study are shown in Figure 3. Little or no mobility was observed with 5 g of oil using fine Berkeley soil. These results are consistent with the fact that a minimum amount of oil (usually greater than the pore volume of the soil) is needed to observe any significant movement. As expected, coarse soil showed more mobility for oil than the fine soil.

Application Of TCLP To Fuel Oil And Comparison Of The Results With Soil Column Studies

Three TCLP experiments using 30 g of Kansas City fuel oil alone and a 1:1 mixture of fuel oil and soil (fine and coarse Berkeley, 30 g each) were conducted. The first experiment, containing the fuel oil sample only, was performed to assess the feasibility of using TCLP for this type of oily waste. It was suspected that the oily waste might not filter even during application of pressure.

According to TCLP protocol, "When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-min period), filtration is stopped. When this procedure was strictly followed, the amount of filtrate for the fuel oil sample was 1.56 g., while no filtrates were obtained using the fuel oil/soil mixtures. The pressures at which the filtrate was measured, following TCLP guidelines as outlined above, were 20, 10 and 50 psi for the fuel oil, and mixture of oil/coarse and fine soil, respectively.

An experiment was then conducted to attempt to increase the pressure to a maximum of 50 psi during the TCLP experiment for each sample matrix. The maximum pressures that were able to be attained for fuel oil and oil/coarse soil mixture were 30 and 35 psi, respectively. In these two experiments, the N_2 gas immediately started to move through the filter, as was noticed by a decrease in the applied pressure. However, under these increased pressures, the amount of the filtrates obtained for oil and for the oil/coarse soil mixture were 11.5 and 10.5 g, respectively.

The corresponding soil column studies using 1:1 mixture of fuel oil and soil (30 g each) were also completed. The oil was allowed to disperse freely, and the transport of the oil through the column, as well as the amount of the oil eluted from the column, were monitored with time. The total amount of oil that eluted from the coarse soil column was 24 g over a 23-day period. Although the oil moved through the fine soil and eventually reached the bottom of the column (8.6 cm), no oil eluted from this column during the experimental period. These results along with the TCLP data are summarized in Table 2.

In light of the dissimilar processes and experimental conditions involved in the TCLP and the column studies, the discrepancies in the results are not surprising. One might argue that there is a 50% correlation between the two results, since no amount of filtrate or eluted oil was obtained during TCLP or the corresponding column study using the fine soil. However, this comparison cannot differentiate between "no movement" and "maximum movement" through the soil, when no elution of the oil from the column occurs. In fact, the fuel oil moved through the entire length of the fine soil column in our column studies. There are other important differences between the two methods which would make their comparison more difficult. Specifically, some of these differences are as follows:

1. "TCLP" and "soil mobility study" are two different concepts, with two distinct mechanisms. The former is a separation method based on "high pressure filtration" while the latter is a transport process due to "diffusion, accelerated by gravity." While these two phenomena might be related, there does not seem to be a simple or linear correlation between them.

2. The comparison of the two methods does not take into account the fundamental factor of time in transport phenomenon. The amount of oil eluted from the coarse soil column ranged from 1.2 g after approximately 1 day to a maximum of 24 g over a 23-day experimental period. It is not clear which one of these amounts should be compared to the corresponding TCLP experiment. Furthermore, according to TCLP protocol, the filtration is stopped if it does not result in any additional filtrate <u>within a 2-min period.</u> However, the equivalent stopping period for the soil column study has not been defined.

3. Another parameter, which would substantially affect the results, is the surface area of soil in contact with the fuel oil. While the amounts of fuel/soil in both TCLP and column studies were identical, the diameters of the filtration device (in TCLP) and the soil columns were 14.2 and 2 cm, respectively. Therefore, the extent of contact of oil with the surface of soil in TCLP is more than the corresponding column study during the same time period. However, there are other factors which would make the comparison of the two methods even more complex. There is a different experimental period for TCLP (several minutes) as compared to that for the soil mobility study (several days). This would account for the larger amount of oil eluted during the soil column studies than the amount of filtrate obtained in TCLP, as was confirmed by our results. More importantly, the available soil adsorption sites in the two methods are not identical. The oil was mixed with the soil to yield a homogenous mixture prior to TCLP, while the oil was introduced on the top of the soil for the column studies.

4. The moisture content of the soil is another important factor, which affects the flow of oil through the soil and thus contributes to the discrepancies in the two

results. The infiltration rate of a waste through the soil is highest when the soil is dry. However, this rate decreases with increased moisture and approaches a steady-state value as the soil remains saturated and porous (12,14). In our column studies, the soil was completely saturated with water while it was used as received in the TCLP experiment.

SUMMARY

It may not be feasible to compare TCLP and soil mobility results due to the intrinsic differences in the mechanisms of the two methods, as well as so many different experimental conditions. Additionally, in the TCLP protocol, the applicability of TCLP to oily wastes has been cautioned. This caution has to be taken seriously in light of the very small amount of the oily filtrate produced in TCLP and the fact that the nitrogen gas almost immediately started to move through the filter at low pressure (~ 20 psi). Moreover, all the attempts to increase the pressure to a maximum of 50 psi failed when using the fuel oil sample. In each attempt, the increase in applied pressure was offset by reduction of the pressure due to passage of the nitrogen gas through the filter in the TCLP filtration device.

AKNOWLEDGEMENT

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TABLE 1

TARGET PAH CONCENTRATIONS IN NO. 6 FUEL OIL SAMPLES INCLUDING THE METHOD BLANK

Analytes	Sample #6560 (From KC) (ug/g)	Sample #5630 (ug/g)	Sample #6060 (ug/g)	Sample #6963 (ug/g)	Method Blank
Naphthalene	147	TR (12.5)	TR (2.09)	TR (7.33)	ND
Phenanthrene	450	TR (38.4)	40.0	TR (20.6)	ND
Anthracene	TR (49.7)	ND	ND	ND	ND
Benz(a) anthracene	1,520	ND	TR (29.3)	ND	ND
Chrysene	3,090	TR (29.2)	80.1	TR (35.6)	ND
Benz(b)+(k) fluoranthene	436	ND	ND	ND	ND
Benzo(a)pyrene					
Indeno(1,2,3-cd) pyrene	101	ND	ND	ND	ND

ND compound not detected at quantitation limit

TR compound detected, but at a level less than quantitation limit

Quantitation limit for KC fuel oil was 100 ug/g; for others including the method blank was 40 ug/g.

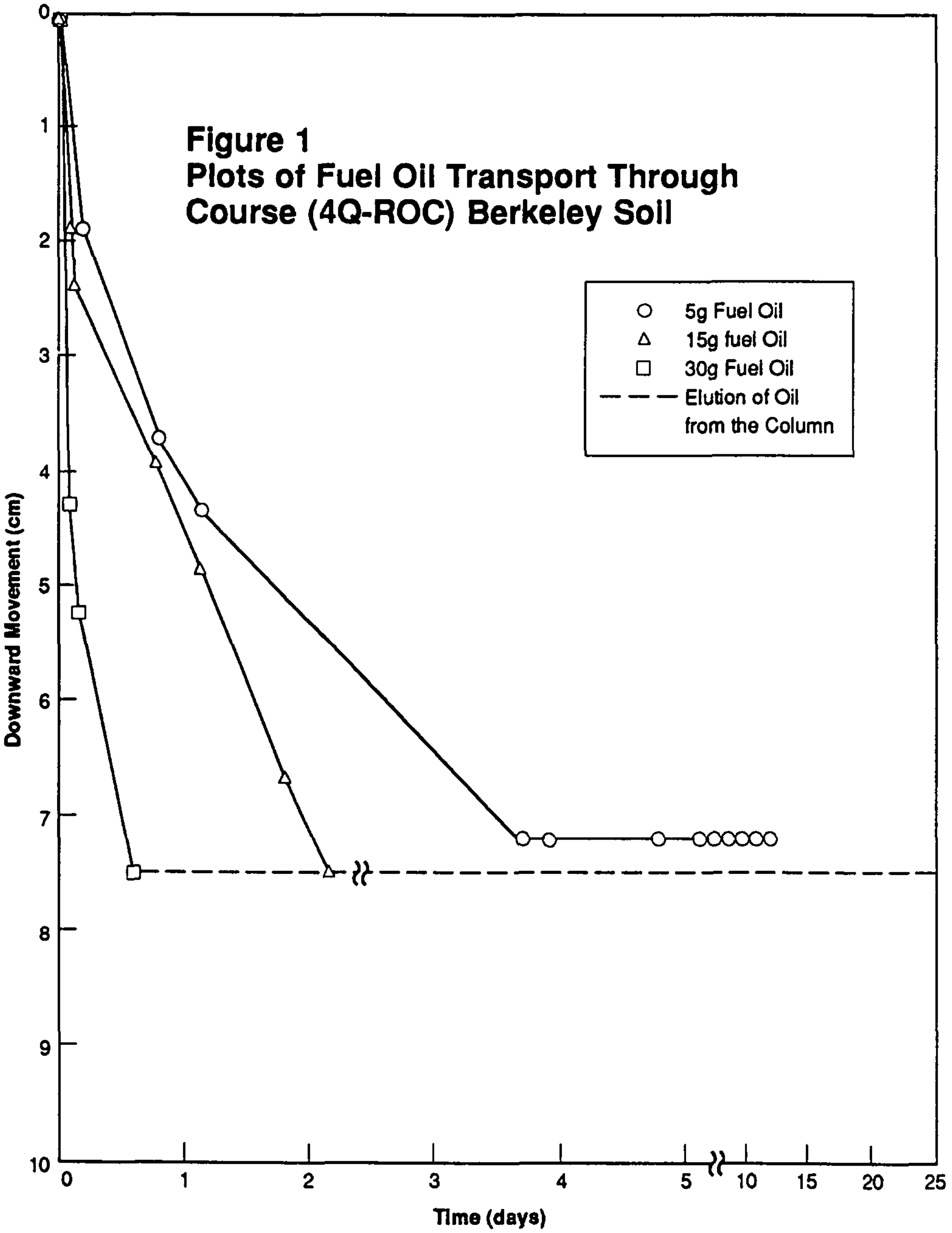

Figure 1
Plots of Fuel Oil Transport Through Course (4Q-ROC) Berkeley Soil

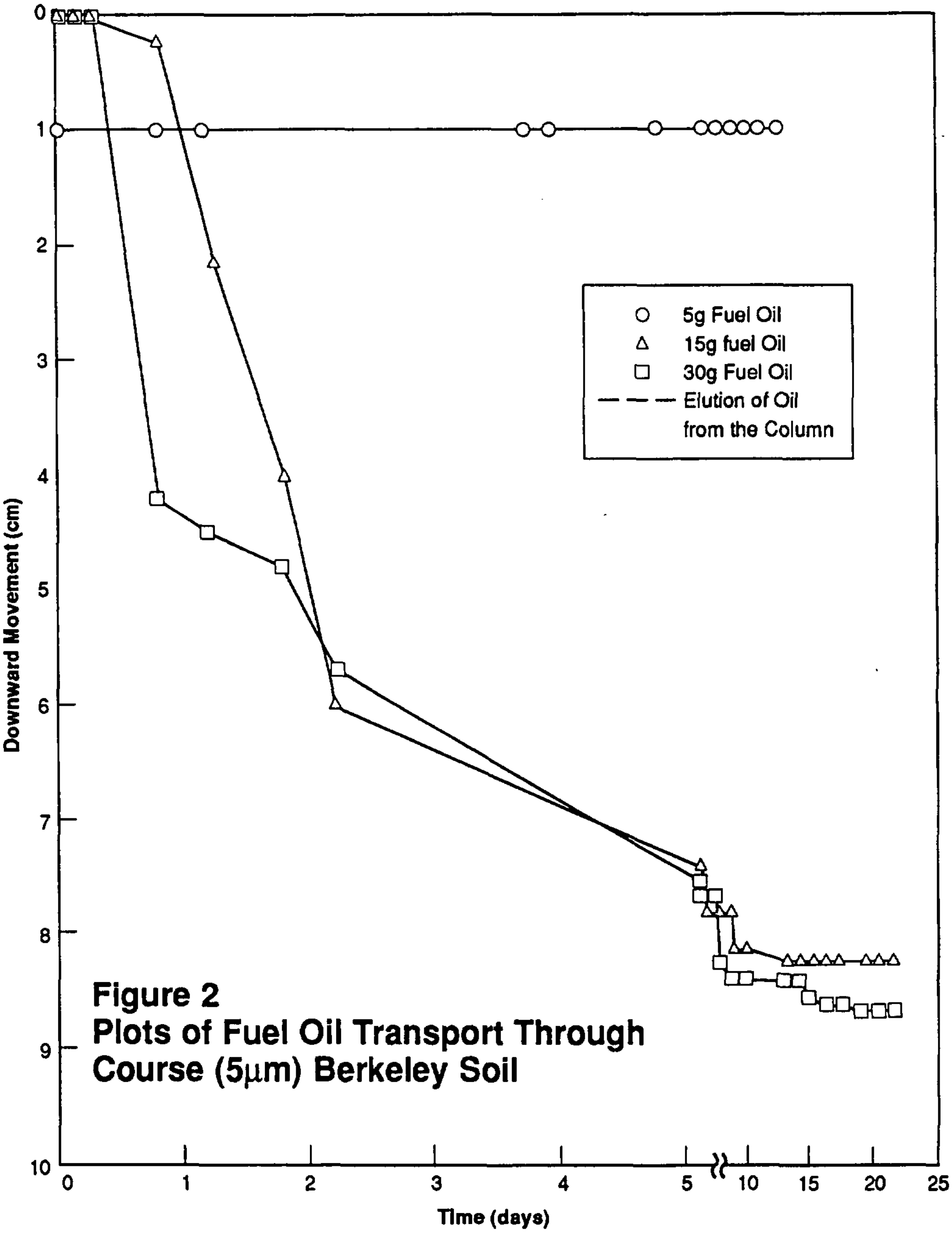

Figure 2
Plots of Fuel Oil Transport Through Course (5µm) Berkeley Soil

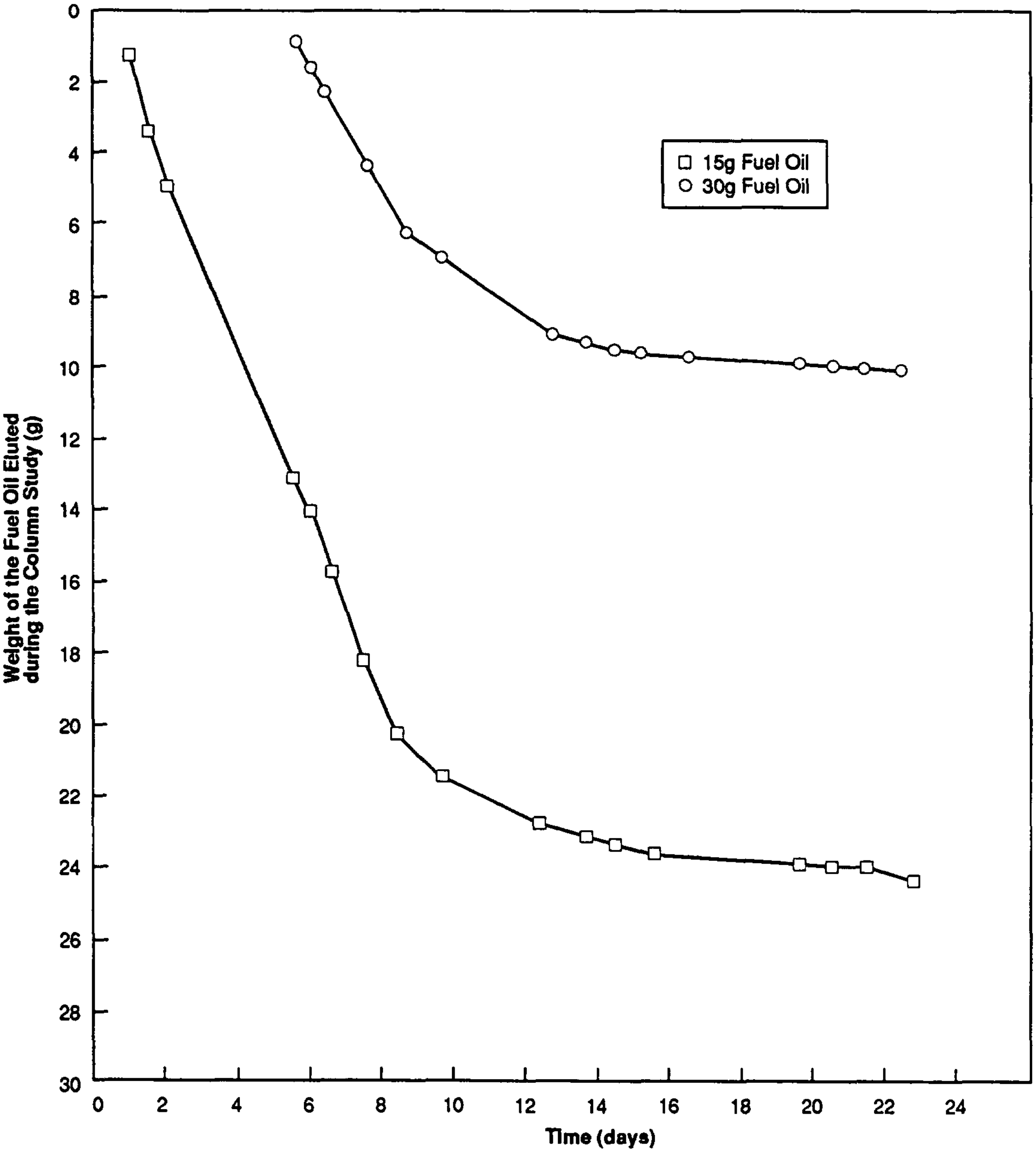

Figure 3
Breakthrough Curves for Two Amounts of the Fuel Oil Using Coarse (4Q-ROC) Berkeley Soil

TABLE 2.
COMPARISON OF THE AMOUNTS OF OIL ELUTED DURING COLUMN STUDIES WITH THE FILTRATE DURING TCLP

Type of Matrix	Amount of oil eluted from the Column (g)	Wt. of Filtrate in TCLP[a]	Wt. of Filtrate under Max. pressure attained[b]
Oil/coarse Berkeley Soil (1:1 mixture, 30 g each)	24.0	Zero	10.5
Oil/fine Berkeley Soil (1:1 mixture, 30 g each)	Zero	Zero	Zero

[a] Measured at pressures of 10 and 50 psi for mixtures of oil/coarse and fine soil, respectively.

[b] The maximum pressures attained for the two above matrices were 35 and 50 psi, respectively.

LEACHABILITY OF CHEMICALS FROM HAZARDOUS WASTE LAND TREATMENT SITE SOILS

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ABSTRACT

Chemicals in soil can be subjected to environmental factors which may influence their mobility. Climatic stress can play a significant role in altering soil structure and metal and organic chemical retaining properties. Local site conditions also may result in soils with low pH which can influence chemical mobility. To assess mobility of chemicals, the Toxicity Characteristic Leaching Procedure (TCLP) has been proposed and is being used. The objectives of this research are to: (a) determine the leachability of specific metals and organics from soils at hazardous waste land treatment sites using the TCLP, (b) evaluate the mobility of hazardous constituents as a function of soil depth for these sites, and (c) determine the effects of weathering cycles on the leachability of these constituents.

This paper presents the results of work in which soils from several hazardous waste land treatment sites were initially characterized for selected metals and organics and then their mobility determined using the TCLP. The soils then were subjected to repetitive freeze/thaw and wet/dry cycles, and retested using the TCLP to determine whether significant changes in leaching were caused by the weathering action.

Metals analyses for both the weathered and non-weathered samples indicated that, of the six metals tested, only zinc exceeded background levels consistently. No clear differences were detected when metal concentrations in TCLP extracts from weathered and non-weathered samples were compared. Organic compounds were not detected in either of the two sets of extracts.

INTRODUCTION

The 1984 amendments to RCRA (Resource Conservation and Recovery Act) prohibit the disposal of hazardous wastes on land beyond specified dates unless the United States Environmental Protection Agency (EPA) determines on a case-by-case basis that such a method is protective of human health and the environment. Land treatment is a land disposal method affected by the amendments. Land treatment is an engineering process in which a waste is incorporated into the surface soil layer. The native microbial population aided by chemical and physical soil processes degrade and immobilize the applied wastes. Land treatment of hazardous materials is permitted if it can be demonstrated that there will be no migration of the hazardous constituents for as long as the wastes remain hazardous.

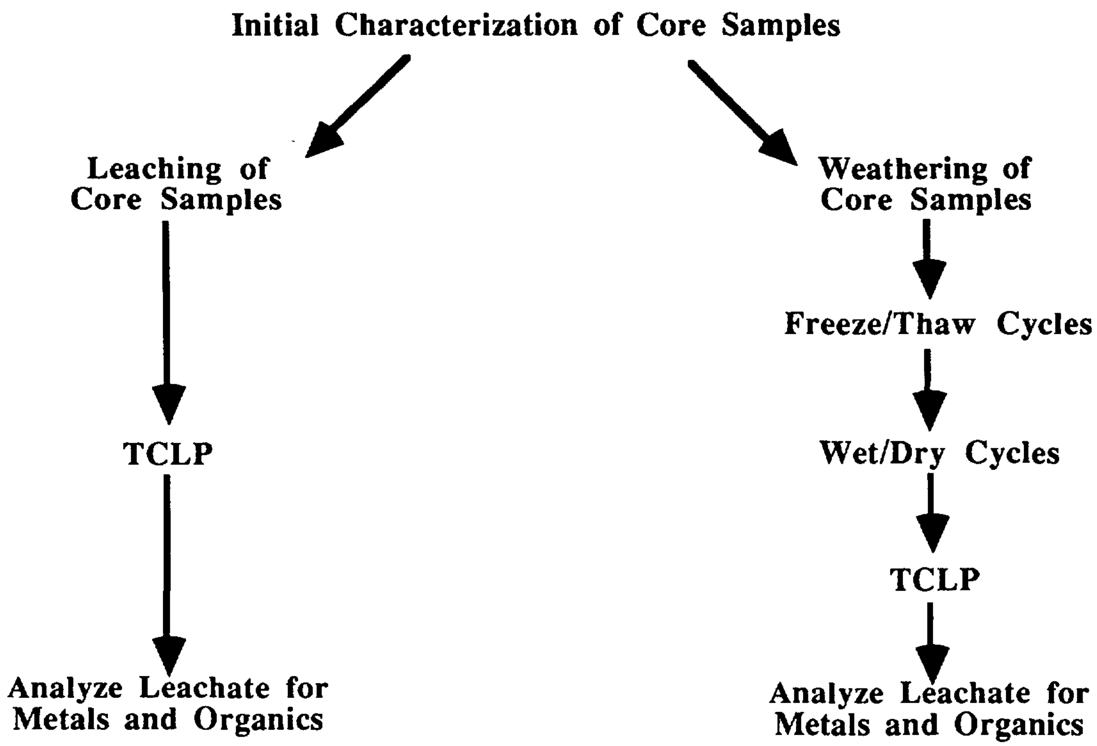
The fate of the waste remaining at the site after a land treatment site is closed will depend upon local site conditions and post-closure management. It is possible that the wastes will continue to degrade on-site or remain immobilized and pose no threat to the environment. A second possibility is that the wastes will migrate into the unsaturated and saturated zones below the treatment zone, thereby posing a threat to the groundwater. Factors affecting the mobility of chemicals remaining during post-closure at land treatment facilities include local soil characteristics, weather, and the type of wastes present. For sites having high levels of relatively impermeable clay and scant rainfall, the chance of chemical leaching out will be lower than at sites with sandy soil and having abundant precipitation.

This paper presents the results of a study in which the potential mobility of metals and organics in soils from land treatment sites was investigated. This work was supported through EPA Cooperative Agreement CR-814490. The objectives of this research were to: (a) determine the leachability of specified metals and organics from soils at hazardous waste land treatment sites using the TCLP, (b) evaluate the mobility of hazardous constituents as a function of soil depth and site characteristics, and (c) determine the effects of weathering cycles on the leachability of these constituents.

MATERIALS AND METHODS

For this study, soils were collected and characterized for chemical content. They then were used in leaching and weathering tests. A flow chart detailing the tests is shown in Figure 1 and details of the laboratory procedures follow.

FIGURE 1
OUTLINE OF TEST PROCEDURES



Site Selection and Sample Collection

Soils used in this study were sampled from three existing land treatment sites having certain characteristics. These sites had been in operation for at least ten years and had received oil refinery or wood-preserving waste. The sites also were accessible for sampling and records of past waste application practices were available. The sites sampled were:

- oil refinery site in Washington state
- oil refinery site in Oklahoma
- wood-preserving site in Montana

At the individual sites, soil core samples were collected with increasing depth to evaluate the concentration of constituents as a function of depth. Core samples were taken from sides of test pits, dug by a backhoe at each site, at 0-6, 6-12, 12-24, 24-36, 36-54, and 54-72 inch depths below the surface. At each of the six depths, duplicate samples were collected and placed in separate three liter glass jars capped with teflon-lined screw-top lids. The jars then were placed in fiberboard containers and shipped to the Environmental and Water Resources Engineering Laboratory at The University of Texas (EWRE-UT), Austin, Texas, for the leaching and weathering studies.

Initial Soil Characterization

The core samples were analyzed for total concentrations of organics and metals to aid in interpreting the results from the leaching tests. Soils found to have high concentrations of certain chemicals could be expected to show recoverable levels of the same chemicals in the TCLP extracts. These soils analyses also provided background information for determining the extent of in-situ migration of chemicals by observing the depth to which the chemicals were found. The specific analyses performed and the analysis method used are shown in Table 1.

TABLE 1

TESTS AND METHODS FOR INITIAL SOIL SAMPLE CHARACTERIZATION

Test	SW 846 Method (U.S. EPA, 1986)(1)
Soil pH	9045
Freon Extractables	9071
Polynuclear Aromatic Hydrocarbons	8310
Total Metals	3050
Microtox	Beckman Microtox Method

The noted analyses were selected because these categories included the principal hazardous constituents expected to be in the soil-residue matrix. The pH of the soil was of interest for determining the correct leaching fluid for subsequent leaching tests and to determine whether past waste applications had produced either alkaline or acidic conditions which could influence the migration of chemicals in the soils. Freon extractable analyses provided a simple means of estimating the nonvolatile hydrocarbon content in the test soils.

The specific metals tested for were: cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn). The polynuclear aromatic hydrocarbons (PAH's) were the sixteen compounds listed in Table 2. Microtox is a microbial analysis useful for determining the relative toxicity of the soils analyzed. The toxicity of the soils was measured to screen for toxic compounds not specifically tested for which might have been present in the samples.

TABLE 2

POLYNUCLEAR AROMATIC HYDROCARBONS TESTED

Naphthalene	Benzo(a)anthracene
Acenaphthene	Chrysene
Acenaphthylene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Benzo(a)pyrene
Anthracene	Dibenzo(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	Indeno(1,2,3-c,d)pyrene

Soil Leaching Experiments

Soil from each of the six levels sampled was extracted using the TCLP(2). The basic procedure is described below.

Twenty-five grams of soil passing through a No. 9 sieve was placed in a Zero Head Extractor (ZHE). Five hundred mL of Extraction Fluid (TCLP fluid #1) were added to the vessel and the apparatus was sealed. For each run, four extractors were set up, placed in a rotary tumbler and rotated at approximately 30 rpm for eighteen hours.

After the eighteen-hour extraction was completed, the vessels were removed from the tumbler and the contents of each were pressure filtered through an acid-rinsed glass fiber filter. The individual filtrates were collected in glass bottles and refrigerated pending analysis.

The TCLP leachates were analyzed for the noted six metals following method 3010 (SW 846, U.S. EPA, 1986), using a Perkin-Elmer 303 flame atomic absorption spectrometer. The analysis of the same metals in the soils and leachates permitted a comparison of the concentrations of the metals in the two matrices.

The leachates also were surveyed for the presence of chromatographable organic compounds. One hundred mL of the leachate was extracted in methylene chloride (SW 846 Method 3510). The extracts were analyzed on a Hewlett Packard 5890 gas chromatograph. It was not known what organics might be present in the extracts, so selected TCLP samples were spiked with known amounts of specific organics to provide a means of evaluating the relative abundance of organics present in the extracts. The added compounds were 2,4,6-trichlorophenol, diphenylamine, 2,4-dinitrotoluene, and ortho-cresol. From the GC analysis, the extracts which showed the presence of organics above background were tested using gas chromatography mass spectroscopy (GC/MS). Any peaks which appeared were tentatively identified by library searches of stored reference spectra.

Weathering Procedures

The methods used for the simulated weathering cycles were adapted from ASTM methods for tests of soil-cement mixtures(3). The ANSI/ASTM D569 and ANSI/ASTM D559 methods were used for the freeze/thaw and wet/dry weathering experiments respectively. The procedures assume the use of samples in the form of monoliths and for this study 50 grams of loose soil was used. Consequently, modification of the methods was made in which the samples were "packaged" in a double layer of nylon. This served to contain the soil and still permit good exposure to the wet/dry and freeze/thaw cycles.

Samples from each of the six depths collected at each of the sites were subjected to the weathering cycles. Briefly, the procedure for the freeze/thaw cycles began by saturating the samples with distilled/deionized water (DDW) over a seven-day period. The soils then were chilled to -10° F for 24 hours. At the end of this period, the samples were warmed to 73° F at 100 percent relative humidity for 23 hours. This two-day period of freezing and thawing constituted one cycle of the test. The cycle was repeated for a total of 11 cycles.

Samples subjected to the freeze/thaw procedure were weathered further using the wet/dry procedure in which the soils first were saturated with DDW. They then were placed in a 160° F zero humidity room for 42 hours. The cycle was repeated for a total of 11 cycles.

Leaching of Weathered Samples

The samples which underwent the weathering cycles were leached using the TCLP. The procedure described in the Soil Leaching Experiments section was followed.

RESULTS AND DISCUSSION

A large number of samples was analyzed for several different chemicals. All of the results could not be presented here, so, as an alternative, selected data representative of the overall trends observed are shown. The complete results will be available in 1990 as an EPA project report.

Soil Core Characterization

The soil characterization provided information regarding the physical characteristics of the soils as well as the concentration of organic compounds and metals. The pH of the core samples from each of the four sites was between 6.0 and 8.1. The Microtox assays determined also that the soils were nontoxic to the test microorganism. These results indicated that there were no unusual conditions which might inhibit the natural degradation of organics in the soil, or facilitate movement of contaminants through the soils, such as a low pH. The amount of organic waste applied to the four sites varied from site to site and the freon extractable data provided an estimate of nonvolatile organics remaining in the soils on the dates sampled. These data indicated that the highest levels of organics remained near the surface zone of incorporation. Example freon extractable data for the Washington and Oklahoma sites are shown in Table 3.

TABLE 3

FREON EXTRACTABLE CONCENTRATIONS IN SOIL (mg/kg)

Depth (inches) -- Washington	Freon Extractables	Depth (inches) -- Oklahoma	Freon Extractables
0-6	61,700	0-6	5,500
6-12	56,600	6-12	<1,000
12-24	8,350	12-24	<1,000
24-36	<1,000	24-36	<1,000
36-54	1,700	36-54	<1,000
54-72	<1,000	54-72	<1,000

The freon extractable data in Table 3 show the concentrations of such organics decreased quickly with increasing depth. The concentrations of PAH compounds also decreased as the depth increased. An example of the PAH data is shown in Table 4. Similar trends in the Montana and Oklahoma data were observed (data not shown).

TABLE 4

PAH CONCENTRATIONS IN WASHINGTON SITE SOIL (mg/kg)

Compound	Depth (inches)				
	0-6	12-24	24-36	36-54	Detection Limit
Naphthalene	<5	<5	<5	<5	5
Acenaphthylene	<10	<10	<10	<10	10
Acenaphthene	<5	<5	<5	<5	5
Fluorene	8	6	<1	<1	1
Phenanthrene	5	3	2	<0.5	0.5
Anthracene	<0.5	2	<0.5	<0.5	0.5
Benzo(a)anthracene	<0.5	<0.5	3.4	<0.5	0.5
Chrysene	98	60	2	0.6	0.5
Benzo(b)fluoranthene	144	32	<1	<1	1
Benzo(k)fluoranthene	<0.5	<0.5	<0.5	<0.5	0.5
Benzo(a)pyrene	220	62	<0.5	<0.5	0.5
Dibenzo(a,h)anthracene	310	47	<1	<1	1
Benzo(g,h,i)perylene	66	8	<1	<1	1
Indeno(1,2,3-c,d)pyrene	15	6	<0.5	<0.5	0.5

For metals, the total concentrations of cadmium, chromium, copper, nickel, lead, and zinc also were determined as a function of depth. The analyses indicated that the metals were confined primarily to the top 0-12 inches of soil. Data from the Washington site are shown in Table 5.

TABLE 5

METAL CONCENTRATIONS IN WASHINGTON SITE SOIL (mg/kg)

Depth (inches)	Cadmium	Chromium	Copper	Nickel	Zinc	Lead
0-6	<10	320	100	94	230	130
6-12	<10	340	130	96	250	230
12-24	<10	110	30	45	87	27
24-36	<10	160	28	70	62	6
36-54	<10	140	27	63	65	6
54-72	<10	80	29	61	61	6

Soil Leaching and Soil Weathering

The TCLP procedure was developed as a means of estimating the potential for wastes codisposed with municipal refuse to leach inorganic and organic chemicals. In this study, it was used as a standardized approach to simulate the leaching of chemicals from the land treatment soils. As described in the MATERIALS AND METHODS section, core samples and weathered core samples were leached using the test.

Organic compounds at concentrations above detection limits were not recovered from any of the samples tested using either gas chromatography or gas chromatography mass spectrometry. Many of the organics present in these soils were high molecular weight compounds with low solubilities in water. It is not surprising that they were not recovered from the aqueous leaching solution.

Analysis of the six metals showed that each of the metals except cadmium were found in varying amounts in the TCLP extracts from each of the sites. The TCLP test method was published with threshold limits for classified hazardous wastes. None of the extracts contained metal concentrations in excess of the threshold limits.

Weathering had no appreciable effect on the concentration of metals in the TCLP extracts from the top soil layers. Where metals were present below the 12-inch layer, concentrations appeared slightly lower in the TCLP extracts from the weathered samples. This may have resulted from the weathering having more of an effect on the core samples than on the surface samples which had already been exposed to natural weathering. Examples of the TCLP metal analysis results for non-weathered and weathered samples from the Washington site are presented in Tables 6 and 7, respectively. Also shown in Table 6 are the TCLP regulatory limits for cadmium, chromium, and lead. Limits for copper, nickel, and zinc concentrations in TCLP leachates have not been published.

TABLE 6
METAL CONCENTRATIONS IN WASHINGTON SITE TCLP EXTRACTS
Non-Weathered Samples (mg/L)

Depth	Cadmium	Chromium	Copper	Nickel	Zinc	Lead
0-6	<0.1	0.25	<0.1	<0.1	0.2	<0.1
6-12	<0.1	<0.1	<0.1	0.7	0.2	<0.1
12-24	<0.1	<0.1	<0.1	<0.1	0.8	<0.1
24-36	<0.1	0.3	<0.1	<0.1	0.3	<0.1
36-54	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
54-72	<0.1	<0.1	<0.1	0.2	0.2	<0.1
Threshold Limit	1.0	5.0	*	*	*	5.0

**Regulatory levels for these elements have not been published.*

TABLE 7
METAL CONCENTRATIONS IN WASHINGTON SITE TCLP EXTRACTS
Weathered Samples (mg/L)

Depth (Inches)	Cadmium	Chromium	Copper	Nickel	Zinc	Lead
0-6	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
6-12	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
12-24	<0.1	<0.1	<0.1	<0.1	0.4	<0.1
24-36	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
36-54	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
54-72	<0.1	<0.1	<0.1	<0.1	0.1	<0.1

SUMMARY AND CONCLUSIONS

This paper presented results from a study in which the mobility of contaminants in soils was investigated. The wastes which had been applied to the plots sampled consisted of oil refinery and wood-preserving wastes, and had been present for at least ten years. Soil samples were collected at the sites from depths down to six feet below the surface. The PAH compounds, freon extractables, and metals were confined primarily to the upper 12 inches of the soil at the sites.

Soils from the sites were extracted using the TCLP. In addition, soils weathered using repetitive freeze/thaw and wet/dry cycles also were extracted with the TCLP. Results showed that organics were not extracted from either the weathered or non-weathered samples. The concentrations of metals tested in the leachates from the weathered and non-weathered soils were below the regulatory levels designated by EPA for the TCLP.

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EVALUATION OF LEACHABILITY OF RADIUM CONTAMINATED SOIL

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ABSTRACT. Composite samples of radium contaminated soil were batch extracted at pH 5 and pH 3 in a modification of ASTM Method D3987-81 to evaluate the relative leachability of radium-226 from soil which had been blended with a non-contaminated soil, in order to achieve approximate background concentrations of radium in the soil mix. Comparisons were made between contaminated soil, diluent soil and the resulting amended mix. Analysis for radium was conducted by deemanation of radon-222. Data from the extractions were used to evaluate a bench-scale demonstration of soil blending, which was judged to be a technically feasible disposition alternative for soil contaminated with relatively low levels of radium.

Soils with radium concentrations of approximately 60 pCi/gm were amended with soil with a mean radium concentration of 0.7 pCi/gm to yield mixtures with a mean activity of 2.6 pCi/gm. Extraction yielded mean radium releases of 10.4 pCi/l, 1.2 pCi/l and 3.2 pCi/l for the contaminated, diluent, and amended soils, respectively. Comparison of the contaminated soil extraction value of radium with the radium concentration detected in monitoring wells placed within the area of contaminated soil indicated a tendency for the extraction tests to overestimate the concentration of radium which would actually be seen in groundwater associated with the soil being evaluated. The mean amended soil radium extraction value of 3.2 pCi/l, as well as its corresponding 95% upper bound of 4.1 pCi/l, was then used in a simple analytical groundwater model which incorporated only transport and dispersion. A maximum value of 1.5 pCi/l radium was predicted at a point 500 feet from a hypothetical emplacement site of the amended soil. This value, which was derived using several worst case assumptions, was well below all concentration limits deemed acceptable by present regulatory standards.

INTRODUCTION

In recent years, much attention has been focused on the disposition of contaminated soils. As landfill space has continued to become increasingly scarce, and correspondingly expensive, emphasis has shifted to treatment alternatives. Many approaches, such as soil washing and bioremediation have been extensively studied (1). Dilution of contaminated soil with clean fill has generally not been pursued. In the case of synthetic lipophilic organics which can be reconcentrated in the biosphere, this is a sensible proscription. The same caveat however need not apply when the contamination present is from naturally occurring inorganic contaminants which with appropriate treatment can be made to approximate background concentrations. Land spreading of soils with low levels of radioactivity to approximate natural background radiation levels has been cited by EPA as a possible treatment option, while land spreading of radium sludge from drinking water treatment system has been carried out in Illinois since 1984 (2).

In 1986, following the loss of access to a preplanned disposal site, the State of New Jersey was faced with the need to get rid of approximately 4,100 yd^3 of soil which was contaminated with radium-226 at a mean value of approximately 60 pCi/gram. To facilitate in-State disposal of this material, a bench-scale demonstration was undertaken to evaluate the technical feasibility of blending this material to a pseudo-background target concentration of ≤ 3 pCi/gm. Technically, such amended product material, which would be less than the EPA soil standard of 5 pCi/gm in the first 15 cm, and 15 pCi/g in any subsequent 15 cm increment (40 CFR 192.12a), would constitute clean fill and would be potentially available for unrestricted use.

The contaminated soil originated from a pilot project in which soil was excavated from under and around a number of single-family residences that had been constructed over contaminated fill, thus leading to elevated levels of radon-222 and progeny in indoor air, as well as elevated gamma levels both indoors and out. The houses chosen were taken to be representative of a much larger group of contaminated structures. Removal of the contaminant source from this subgroup was evaluated in 1985 as a potential remedial alternative for general implementation. As noted, loss of the originally planned disposal site produced a need to consider other alternatives.

SAMPLE PREPARATION

Ten sub-samples were gathered from drummed soils representing each of the three contaminated neighborhoods (Virginia-Franklin, Carteret, Lorraine) and from the proposed diluent soil site. The sub-samples were then mixed to yield a large representative composite sample for each location. In the case of the contaminated samples, mixing was monitored via gamma spectroscopy to insure that the resulting composites were in the 55-75 pCi/g range, in correspondence with the estimated weighted site-wide average Ra-226 activity of the contaminated soils. Each contaminated composite was then amended with the diluent composite in a cement-type mixer, at a ratio so as to produce an amended soil of ≤ 3 pCi/g Ra-226. Ratios of 30:1, 35:1, and 40:1 were utilized.

Five 100-gm replicates were drawn from each contaminated composite and each amended mix, and batch extracted for 48 hours in accord with ASTM D 3987-81 Standard Test Method for Shake Extraction of Solid Waste with Water (3). In a modification to the standard method, 400 ml solutions of pH 3 (60/40 H_2SO_4/HNO_3) and pH 5 (0.1N sodium acetate) were shaken with the soil replicates for 48 hours. The extracts were paper filtered to remove gross solids and then passed through a 0.45 um filter. Three 40 ml aliquots were drawn from each filtered replicate, placed in tubes, flame-sealed, and set aside for radon in-growth. Radon was de-emanated (degassed) from the solutions containing radium and quantitated in a counting cell. A fourth aliquot was taken and utilized as a matrix spike. Spiked blanks and reagent blanks were also deemanated in conjunction with each group of composite replicates at each pH. Parent radium concentration was then determined from the radon value (4, 5).

FINDINGS

A. Leachability Testing

Extraction results along with soil radium concentrations are presented in Table 1. Statistical comparisons of data sets are given in Table 2. All references to statistical significance refer to the 5% significance level. Examination of these Tables along with Tables 3a and 3b yields a number of observations.

1. In all cases, contaminated soil leachate grand means were significantly greater than those of the amended or diluent soil.

2. For a given soil no significant differences were seen between the leachate means at pH 3 and 5, with the exception of the contaminated Lorraine composite (Table 2).

3. The mean values of amended soil leachates ranged from 1.3 pCi/l to 4.8 pCi/l (Table 1), and averaged 2.7 pCi/l (Table 3). All of these values are below the EPA Primary Drinking Water Standard for radium-226 of 5 pCi/l.

4. The mean values of contaminated soil leachate replicates ranged from 7.4 to 13 pCi/l (Table 1), with a mean leachate value of 10.6 pCi/l (Table 3).

5. Under these same experimental conditions, the diluent soil yielded a mean leachate value of 1.2 pCi/l (Table 3).

6. The mean percentage radium extracted from the contaminated composited soils was 0.065%. This is 10 times less than the average percent extracted from the amended and diluent soils (0.6%, cf. Table 3).

Discussion

The observation noted in item 1 above, proportionality between the amount of radium in solution and the amount in the soil is consistent with observations in the literature (6). Implicit in the leachate concentrations observed however is that strict solubility concerns are not the controlling influence on radium mobility in these soils. Simple solubility alone would allow concentrations of aqueous radium to be present at many orders of magnitude beyond those encountered here. For example, in the presence of equimolar concentrations of sulfate, radium could be soluble at 7.4×10^{-6} M (K_{sp} $RaSO_4 = 5.5 \times 10^{-11}$)(4). This solubility potential would allow quantitative extraction to occur at the soil concentrations encountered in the present work. That this is not seen is clear evidence that additional mechanisms are at work to limit the aqueous concentration of radium. Substantial affinity for ion-exchange, adsorption, and co-precipitation reactions have been noted for radium (5, 7, 8).

The lack of differentiation in radium leachate concentrations with pH for a given soil indicates that under the conditions studied, with a volume/mass (V/M) ratio of 4, the soil buffer complex dominates the reaction and levels the potential effects of extractants of differing pH values. As the amending soil displays effervescence, and therefore contains free carbonate, in-situ buffer capacity is effectively infinite with respect to a dilute extractant. This same leveling effect would function in the environment as well, i.e., infiltrating water would be rapidly buffered to the pH of the soil. The anomalous behavior of contaminated Lorraine is indicative of differing leachabilities due to sample heterogeneity rather than a true pH effect, as all amended samples displayed post-extraction pH values of 7.4 ± 0.2.

To a substantial extent, the results obtained from a leaching test, are a function of how that test was designed and conducted. In the present case a low V/M ratio allowed the soil buffer to control the pH of the leaching process, which occurred during 48 hours of batch agitation. Altering V/M or agitation time sufficiently would have produced different results, as would have sequential extraction with fresh leachant, as would have the execution of a column or field lysimeter study. Variations in sample preparation leachant composition, temperature, and manner of leachate separation may also produce varying results (9).

Agitated tests, such as the one here employed, provide a type of acceleration and thus rapidly achieve a degree of steady-state behavior which is indicative of the contributions of relatively short term equilibria phenomena. The chemical properties of the system independent of short term kinetic limitations may thus be evaluated. Assessment of the ultimate impact of long term release requires either a field study in real time, or more practically, more intensive acceleration, e.g., elevated temperature, stronger leachant, sequential extraction, particle size reduction. Implicit in the conduction of an accelerated test is that the actual leaching mechanisms which occur under natural conditions are not altered by the acceleration process. As this is not necessarily true, caution should be exercised in the interpretation of results.

When conducting a leaching experiment, it is vital to keep in mind the ultimate goal of the experiment. Very often, that goal is the prediction of the behavior of the studied material in the environment. Often however, it is merely the comparison of the leaching behavior of a substance relative to another substance, or to a standard. Most tests however presume mimicry of the environment to some degree. Even regulatory tests such as EP Toxicity (40 CFR 261) or the newer TCLP (FR 51, (114), 21648, June 13, 1986), which contain standards to which the behavior of tested materials is compared, incorporate within their protocols assumptions indicative of certain environmental conditions, i.e., leaching by organic acid in conjunction with presumed co-disposal of the analyzed material with municipal solid waste. The standardization of this procedure, which may or may not mimic actual environmental behavior, does implicitly allow the comparison of the various materials tested relative to one another. When modelling a particular phenomenon however, e.g., long term releases, the requirements of data quality and appropriateness are correspondingly greater as the goal is an accurate prediction of actual environmental behavior. Unfortunately, there exists no single standardized leach test methodology for producing high quality enviromimetic data. Coté, et. al., have recently compiled a detailed review of current procedures (9).

In the present work, the experimental conditions do not necessarily mimic actual environmental behavior. They do however allow for comparison of relative behavior of the different materials, which have been tested under the same conditions. Amended soil leachate means were significantly lower than their corresponding contaminated soil means (Table 1). These values are presented as overall means by soil classification in Tables 3a and 3b. The pH 3 and pH 5 leachate data have been combined. Radium concentrations in the amended soil averaged 3.0 times greater than that from the diluent composites (Table 3b). Amended soil leachate means, averaged 2.3 times greater than those of the leachate from the diluent soil. These ratios are essentially equivalent. The diluent soil, which is present within the amended soil to great excess, provided a volumetric solid phase dilution which effectively dominated the leaching character of the amended soils. The diluted contaminated soil proportionately released approximately the same amount of radium as did the diluent soil. Mean percentage radium extracted was rather consistent between the amended and diluent soils and averaged 0.6%. Contaminated soils yielded 10-fold less radium averaging 0.065% extracted. This is also illustrated by the high degree of correspondence between the apparent distribution coefficients (K'_d) of the amended and diluent soils and their mutual order of magnitude variation from that of the contaminated soils. The apparent distribution coefficient is so designated as distribution coefficients, K_ds, are typically determined by introducing and allowing a quantity of aqueous analyte to equilibrate in the presence of a solid phase (10). The amount taken up on the solid phase is then determined, as opposed to the present work which measures the amount of analyte released by the solid phase under the specified conditions.

Thus, while the solid phase radium concentration of contaminated soils is approximately 100 times greater than the diluent soil, the net radium leachate contribution from the contaminated soils relative to the diluent soil is only one order of magnitude greater. On a unit activity basis, the native diluent soil therefore leached approximately 10 times more radium than the contaminated soils. Differences in radium distribution between the solid and aqueous phase related to the physical forms in which it is present, are clearly indicated. This is plausible in that the contaminated soil is known to contain unreacted carnotite ore as well as ore processing residues such as $BaSO_4$, both of which would be distinct from the native diluent soil. $BaSO_4$ in particular is known to strongly retain trace quantities of radium (5).

As noted, the results achieved from a leaching test are to a large extent a function of the test that was done. Thus the observation noted in item 3 above, that amended soil leachate means are below the radium Primary Drinking Water Standard of 5 pCi/l, need not necessarily imply that this assumed standard would be met in an aquifer that was impacted by leachate emanating from this material. In order to further assess potential environmental impacts, validation of the testing protocol is required.

In the present case, the mean contaminated soil leachate concentration of 10.6 ± 2.3 pCi/l may be compared with the mean (1984-86) radium concentrations detected in shallow monitoring wells which were located in or immediately downgradient from the areas of known contamination in the affected neighborhoods, 2.4 ± 2.6 pCi/l (Table 4). While not exact, this comparison does allow the inference that the leaching tests tend to overestimate the concentration of radium which would actually be seen in the environment under present conditions. This trend is similarly supported by comparison of the diluent soil leachate mean, 1.2 ± 0.4 pCi/l, to a ground water sample taken from the vicinity of the diluent soil source material, 0.12 pCi/l. While even less exact than the previous comparison, it does serve to support the inference that the leaching test tends to overestimate actual environmental concentrations.

B. Ground Water Transport

In-situ leachate generally does not remain stationary in the environment. The potential for radium transport in ground water from an emplacement site containing the amended soils was thus evaluated by utilizing the batch extraction radium concentrations as input data to a simplified analytical model (5). Analytical models typically make a number of simplifying assumptions such as constant recharge and discharge rates, and uniform aquifer characteristics. Thus, rate of leaching and subsequent transmission through the unsaturated zone was determined by assuming a constant mass influx rate over time. Short term seasonal recharge rate variations as well as long term changes due to the chemical evolution of the amended materials were not evaluated.

Conceptually, the model assumed high potential solute mobility in the subsurface, i.e., emplacement siting was assumed to be in a permeable environmental with little capacity for chemical interaction between aquifer materials and solutes. Additionally, consistent with the presumption of the amended material to be available for unrestricted use, no controlling layers (caps, liners, etc.) were assumed to be present.

Radium would thus exit the emplaced amended soil as leachate through the unsaturated zone contributing an initial concentration to the saturated zone ground water as a function of leaching rate, radium concentration within the leachate, and the retardation factor operating in the unsaturated zone. Leached radium would then add to the radium already present in the saturated zone. For conservativeness, retardation was assumed to be negligible. This new total radium value would then be subject to attenuation via mixing and dilution through transport and dispersion along the extant downgradient flow path of the saturated zone. Retardation of the radium plume due to distribution of the elevated quantities of dissolved radium onto the solid phase of the downgradient aquifer, as above, was assumed to be negligible thus further enhancing the conservativeness of the model. That these retardation assumptions are indeed conservative is illustrated by the observations of Krishniswami, et. al., whose in-situ studies of Connecticut ground waters revealed that radium injected into the aqueous phase via alpha recoil from the adjoining soild surfaces was removed from the aqueous phase on a time scale of the order of minutes, the net result being that radium did not migrate through ground waters far from the point of injection (11).

Water budget data was derived from EPA's Hydrological Evaluation of Landfill Performance (HELP) computer program, based on inputs of New Jersey annualized climatological data (12). Calculations were done utilizing parametric values appropriate to a vegetated, loamy top soil overlying the emplaced amended soil, which was assumed to have sandy characteristics.

Model calculations were performed assuming an emplacement of amended soil occupying an area of 900 x 900 feet to a depth of 10 feet, which was then underlain by a 50 foot thick sand and gravel aquifer. Leachate concentration of Ra-226 at the bottom of the fill was assumed to be either 3.2 pCi/l or 4.1 pCi/l, which were the weighted (with respect to soil volumes represented by the composited samples) mean and 95% upper bound confidence limit for the amended soils in the batch extraction tests. Three dilution scenarios were generated based on zero downgradient recharge, a "moderate" rate of recharge, and the full recharge rate based on the HELP model analysis. Results displayed in Table 5 showed radium concentrations ranging from 0.8 pCi/l to 1.5 pCi/l, varying as a function of initial leachate concentration and distance downgradient from the site (500-5000 feet). All of these values are well below the Primary Drinking Water Standard for radium.

It should be noted that radium leachate values reported are for total aqueous radium. No effort was undertaken to distinguish between radium which was truly dissolved or which was present in a colloidal phase. The absence or presence of significant quantities of radiocolloids cannot be conclusively demonstrated here. This question is of some relevance as colloidal particles are likely to display transport behavior different from that of dissolved species. Such facilitated transport occurs when colloids move with advective ground water flow (8). While radium has been reported not to form homogeneous colloidal particles, it is known to adsorb onto other colloidal species such as iron (8, 13, 14).

Further studies to confirm the apparent utility of the soil amendment process would be desirable. A series of well designed laboratory column and/or field lysimeter studies would provide a much closer simulation of actual environmental behavior of these materials. As flow through a column inherently incorporates both dilution and retardation, it would be reasonable to anticipate radium values somewhat lower in magnitude than those demonstrated in the current batch studies.

CONCLUSIONS

1. Among amended and diluent soils, no significant differences were seen between extracts of pH 3 and pH 5, due to both the soil/water ratio used in the extraction, which allowed the soil buffer to predominate, as well as the calcareous nature of the diluent soil which provided an effectively infinite buffer capacity.

2. Amended and diluent soil leachates are significantly lower in radium concentration than those of the contaminated soils, however as percentage of total radium extracted, the contaminated soils yield 10 times less radium than the diluent or amended soils. This is reflected by the apparent distribution coefficients of 600, 780 and 6190 ml/g for the diluent, amended, and contaminated soils, respectively.

3. Comparison of mean leachate results from the diluent soil to a regional groundwater value, along with comparison of the contaminated soil leachate mean to the mean radium value from monitoring wells in contact with the contaminated materials suggests that the leaching tests, as performed, tend to overestimate the actual environmental concentration of radium that would result from contact with the tested materials.

4. Using the experimental amended soil leachate concentrations (3.2 and 4.1 pCi/l, weighted mean and 95% confidence limit, respectively) as inputs to a simplified analytical groundwater model, results in radium concentrations ranging from 0.8 pCi/l to 1.5 pCi/l varying with initial input concentration and distance from the emplacement site.

5. In consideration of the conservativeness contained in the above points (overestimate of environmental concentrations, permeable amended soil, sand and gravel aquifer, negation of solute retardation) the exceedance of the Primary Drinking Water Standard for radium of 5 pCi/l in an aquifer in receipt of leachate from this amended soil is unlikely.

6. The results presented represent a preliminary verification of the environmental acceptability of amending soil contaminated with low level radionuclides with a "clean" diluent soil. Further work to support this conclusion to a higher degree of confidence should focus on colloidal particles as no attempt was made to differentiate between radium in a truly dissolved or colloidal state, as well as actual field studies which can provide a more accurate assessment of the environmental dynamics extant at an emplacement site.

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Table 1. Results of Radium Batch Extraction. Grand Means of Replicate Determinations.

Radium Phase	Soil(b)	Virginia/Franklin	Carteret	Lorraine	Diluent
			pH 3(a)		
Soil (pCi/g)	C	63 ± 4.4	58 ± 5.9	74 ± 4.2	
Leachate (p Ci/l)	C	11 ± 2.5	12 ± 1.9	8.1 ± 0.8	
Soil	A	2.4 ± 0.4	2.0 ± 0.2	2.4 ± 0.3	
Leachate	A	2.4 ± 0.3	3.7 ± 2.9	1.3 ± 0.1	
Soil					0.7 ± 0.1
Leachate					1.5 ± 1.2
			pH 5(a)		
Soil	C	67 ± 19	56 ± 3.2	75 ± 4.7	
Leachate	C	7.4 ± 3.3	13 ± 0.9	12 ± 2.6	
Soil	A	2.3 ± 0.4	2.0 ± 0.4	1.7 ± 0.1	
Leachate	A	2.8 ± 2.2	4.8 ± 2.7	1.4 ± 0.5	
Soil					0.7 ± 0.1
Leachate					0.9 ± 0.3

(a) Initial leachant pH
(b) C = Contaminated Soil, A = Amended soil

Table 2

Comparison of Leachate by t-Test
at the 95% Confidence Limit, pH 3 vs. pH 5.

	pH Contaminated		pH Amended	
Virginia-Franklin	3		3	
		NSD		NSD
	5		5	
Carteret	3		3	
		NSD		NSD
	5		5	
Lorraine	3	-	3	
				NSD
	5	+	5	
Diluent			3	
				NSD
			5	

NSD = No Significant Difference
\+ = Significantly Greater
\- = Significantly Lesser

Table 3a. Mean Radium Values (±SD) in Soils and Leachate, Percent Radium Extracted and Apparent Distribution Coefficients.

	Leachate (pCi/l)	Soil (pCi/g)	% Extracted	K'_d (ml/g)[c]
Amended[a]	2.7 ± 1.4	2.1 ± 0.3	0.51	780
Contaminated[a]	10.6 ± 3.3	65.6 ± 8.0	0.065	6190
Diluent[b]	1.2 ± 0.4	0.7 ± 0.0	0.69	600

(a) n = 6

(b) n = 2

(c) $K'_d = C_{soil\ (Ra)}/C_{leachate\ (Ra)}$

Table 3b. Radium Concentration Ratios

	Leachate	Soil
Amendeded/Diluent	2.3	3.0
Contaminated/Diluent	8.8	93.7
Contaminated/Amended	3.9	31.2

Table 4. Radium Concentrations in Overburden Monitoring Wells Within Areas of Contaminated Soil (15). Quarterly Ground Water Monitoring Results 8/27.84-6/12/86, pCi/1 ± SD.(a)

Well	1	2	3	4	5	6	7	8
M-S-3	11.8 ± 0.6	Dry	Dry	Dry	Dry	Dry	4.2 ± 0.5	0.6 ± 0.3
M-S-1	3.8 ± 0.2	Dry	Dry	Dry	Dry	Dry	5.2 ± 0.5	1.0 ± 0.3
M-S-2	N/A	3.3 ± 0.2	1.7 ± 0.1	3.2 ± 0.2	0.5 ± 0.1	0.6 ± 0.2	0.4 ± 0.2	0.3 ± 0.2
G-S-2	N/A	1.8 ± 0.1	3.4 ± 0.2	0.0 ± 0.1	Dry	Dry	7.2 ± 0.6	0.9 ± 0.3
G-S-1	2.4 ± 0.1	4.0 ± 0.2	0.6 ± 0.1	1.8 ± 0.1	1.5 ± 0.1	0.8 ± 0.4	1.0 ± 0.4	1.3 ± 0.4

Mean Value = 2.4 ± 2.6 pCi/1
n = 26

(a) Only wells whose mean radium values exceeded background are tabulated. Background was assumed to be ≤1.0 pCi/gm Ra-226.

Table 5. Ground Water Transport Modeling Results.

	R (ft/yr)	L (ft)	C_1 (pCi/l)
C_r = 3.15 pCi/l	0	500	1.21
C_o = 1.21 pCi/l	0	1500	1.20
	0	5000	0.99
	0.5	500	1.20
	0.5	1500	1.16
	0.5	5000	0.91
	1.96	500	1.16
	1.96	1500	1.09
	1.96	5000	0.77
C_r = 4.10 pCi/l	0	500	1.45
C_o = 1.45 pCi/l	0	1500	1.44
	0	5000	1.19
	0.5	500	1.44
	0.5	1500	1.39
	0.5	5000	1.09
	1.96	500	1.39
	1.96	1500	1.31
	1.96	5000	0.93

C_r = concentration of radium in leachate as it enters the ground water.
C_o = concentration of radium in ground water after mixing.
R = downgradient recharge rate
L = distance downgradient from emplacement fill boundary
C_1 = radium concentration at distance L.

Constant Values

C_b = Background aquifer radium concentration = 0.55 pCi/l (based on weighted average of US public drinking water supplies).

Q_b = Aquifer flow = 3.6×10^5 l/d

Q_r = volumetric flow rate of recharge through the fill = 1.23×10^5 l/d

Z = fill emplacement depth = 50 feet

V_c = velocity of radium in the aquifer = 296 feet/year
($V_c = V_w$, aquifer volocity, as retardation is assumed to be zero).

INTERLABORATORY COMPARISON OF METHODS 1310, 1311 AND 1312 FOR LEAD IN SOIL

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ABSTRACT

The Extraction Procedure Toxicity Test (EP), Method 1310 and its intended replacement, the Toxicity Characteristic Leaching Procedure (TCLP), Method 1311 were both designed to simulate leaching of an industrial waste disposed in a sanitary landfill. The applicability of either one to assessment of the clean up levels of contaminated soils has been questioned. The basic objection is that the sanitary landfill codisposal scenario of Methods 1310 and 1311 does not apply to contaminated soils where organic acids like the acetic acid used in these methods are not expected to be present. If Methods 1310 or 1311 were used to assess such site clean ups, the acetic acid might solubilize certain elements like lead and incorrectly classify the soil as hazardous when, in fact, no such mobilization would actually be expected to occur.

To address the need for a predictive leaching method for contaminated soil, Method 1312, Synthetic Precipitation Leach Test for Soils has been developed. Method 1312 is designed to determine the mobility of both organic and inorganic contaminants present in soils. The Method uses the equipment and conditions of Method 1311, but instead of acetic acid, it uses an extraction fluid which is intended to model the precipitation of the region of the country where the soil site is located.

The purpose of this study was to determine the precision of Method 1312. This was accomplished by conducting an interlaboratory study involving six soils each containing lead at levels ranging from hundreds of µg/g to percent levels. In addition, comparison data were obtained using Methods 1310 and 1311. Four acid soils and two alkaline soils were collected and made as homogeneous with respect to bulk lead as possible without excessive particle size reduction. Bulk lead was determined to characterize the soils and to assess the success of the homogenization steps.

A COMPARISON OF THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) AND A MODIFIED TCLP IN AN EVALUATION OF STABILIZED OIL SLUDGE

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ABSTRACT

An acidic petroleum sludge was stabilized in a related research project which utilized a variety of products including cements, organophilic clays, pozzolanic materials, and proprietary agents. The effectiveness of the stabilization process was evaluated by using two procedures, the Toxicity Characteristic Leaching Procedure (TCLP) and a modification of that procedure. The TCLP (excluding volatile organics analysis) was performed in accordance with EPA specifications. The modified procedure used sulfuric acid (H_2SO_4) as the extraction fluid instead of acetic acid, as designated by the TCLP. Replicate stabilized (treated) sludge samples, as well as unstabilized (untreated) sludge samples, were evaluated concurrently using both testing procedures to allow comparison.

Initial findings indicate that differences exist in the results obtained from the TCLP and the modified TCLP. In a comparison of the modified and unmodified TCLP, the results indicate that more semivolatile organic compounds (in particular, straight-chain alkanes and polyaromatic hydrocarbons) are detected in the modified extract.

INTRODUCTION

An investigation is currently underway whereby an acidic petroleum sludge is stabilized using a variety of materials including cements, organophilic clays, pozzolanic materials, and proprietary agents; this methodology has been published previously (Evans, *et al.*, 1988; Pancoski, *et al.*, 1988). The effectiveness of this treatment was evaluated by physical and chemical analyses; however, only the chemical testing is discussed in this paper. The chemical testing consists of analyzing the treated and untreated oil sludge with respect to leaching potential using the Toxicity Characteristic Leaching Procedure (TCLP) as specified by the EPA (Federal Register, 1986), and a modification of that procedure. The modified procedure used sulfuric acid (H_2SO_4) as the extraction fluid instead of acetic acid, as designated by the TCLP. Acetic acid is intended to simulate landfill leachate. Because the waste used in this study will be disposed of on-site, and not in a sanitary landfill, other acids were considered for the extraction fluid. H_2SO_4 was chosen for two reasons. First, the oil sludge was acidified with H_2SO_4 in the refining process. Secondly, the oil sludge is currently stored in open pits, constantly exposed to the environment; thus, the H_2SO_4 would mimic conditions caused by acidic precipitation.

METHODS

Replicate stabilized sludge samples were evaluated concurrently using both testing procedures. The TCLP (excluding volatile organics analysis) was performed in accordance with EPA specifications. In the modified TCLP, a sample of the treated sludge was evaluated by, first, reducing the particle size using a 9.5 mm sieve, and then placing a 100 gram sample in a flint glass jar with 1600 ml of deionized water (16x the sample weight). The pH was then determined and, if the pH was greater than 5, H_2SO_4 was added until the pH was 5 or less. The sample was extracted in a rotary agitator for eighteen hours. The pH was monitored during this extraction, and adjusted (to pH 5 or less) when necessary. After the agitation period, 400 ml of deionized water (4x the sample weight) was added, and the sample was filtered under pressure using glass filter paper. The filtrate obtained was monitored for the presence of several Priority Pollutant metals, as well as other metals found in the stabilization additives, using atomic absorption spectroscopy; in addition, a one liter subsample of the filtrate was extracted with methylene chloride following the TCLP base/acid extraction procedure. An internal standard (d10-acenaphthene) was then added to the resulting sample (at a concentration of 85 ppb). A 1 ul portion of this sample was then analyzed for semivolatile organic compounds, including several Priority Pollutants and straight-chain hydrocarbons from C_{10} to C_{24}, using a Hewlett Packard gas chromatograph/mass selective detector equipped with HP-UX Chemstation software. Untreated sludge samples were also evaluated using both the TCLP and modified TCLP to provide a basis for comparison.

Another parameter investigated was the relative hydrocarbon concentration, which was a measurement devised to compare the relative amount of unresolved material under the gas chromatograph "hump" (area of unresolved peaks) to the area under the internal standard peak (See Figure 1). Specifically, the area of unresolved peaks was determined using a digitizer, and this number was divided by the area under the internal standard, reported in digital counts.

This value was then multiplied by $1x10^5$ and termed the relative hydrocarbon concentration.

RESULTS

In this laboratory investigation, the untreated oil sludge was tested five times: three times using the modified (sulfuric acid) procedure and two times using the unmodified (acetic acid) TCLP. It should be noted that the untreated sludge contained free liquids along with a viscous petroleum sludge material. For both leaching procedures, only the viscous sludge material was analyzed. For the treated, or stabilized, material, thirteen different samples were analyzed, once with sulfuric acid and once with acetic acid. Results of these analyses are presented in Table 1 (metals analysis data and RHC values) and Tables 2a and 2b (semivolatile organics analysis data).

For the untreated sludge, the test results differed with regard to the two leaching procedures. In the metals analysis, higher concentrations were reported for calcium and sodium when acetic acid was used. In the case of nickel, higher concentrations were reported for the leach tests in which sulfuric acid was employed. Regarding the organic analysis, higher concentrations of dibutyl phthalate and benzyl alcohol were found in the acetic acid procedure. For the samples leached in sulfuric acid, the concentrations of the following semivolatile organic compounds were one to two orders of magnitude higher than the same samples leached with acetic acid: decane, undecane, dodecane, tetradecane, hexadecane, octadecane, eicosane, tetracosane, naphthalene, fluorene, phenanthrene, pyrene, methyl naphthalene, and dimethyl naphthalene. The first eight compounds in the list above are straight-chain alkanes, and the latter six compounds are polyaromatic hydrocarbons.

For the thirteen treated sludge samples, some differences in chemical concentrations between the two leach procedures existed. With regard to the metals analysis, calcium concentrations were higher in all thirteen of the samples tested with sulfuric acid. No apparent differences existed in overall comparisons among the other metals which were analyzed. In the organic analysis, dibutyl phthalate concentrations were higher in eight of the thirteen samples, and phenol concentrations were higher in ten of the thirteen samples when acetic acid was used. In seven of eight samples in which fluorene was detected, sulfuric acid was the leaching fluid. In general, there were no readily apparent differences in concentrations for the other organics as evaluated by the two different leaching procedures.

The relative hydrocarbon concentration (RHC) was used as a general indicator of the amount of hydrocarbon constituents present but not quantifiable by GC/MS. Nine of the thirteen samples tested with acetic acid had higher RHC values than the same samples tested in sulfuric acid. Therefore, the unmodified TCLP (utilizing acetic acid) tended to leach greater amounts of hydrocarbon contituents (unresolvable by gas chromatography) from the stabilized petroleum sludge.

SUMMARY

Differences exist in the results obtained from the two leaching procedures, a modified TCLP (sulfuric acid leaching fluid) and the unmodified TCLP (acetic acid leaching fluid). In general, the modified procedure, using sulfuric acid, leached more semivolatile organics (in particular, straight chain alkanes and polyaromatic hydrocarbons) from the untreated oil sludge. Also, higher nickel concentrations were reported in the untreated sludge tested with sulfuric acid; however, acetic acid produced higher calcium and sodium concentrations in the untreated sludge. For the treated sludge samples, higher concentrations of dibutyl phthalate and phenol were reported when the acetic acid procedure was used, while use of the sulfuric acid procedure resulted in higher fluorene and calcium concentrations. These preliminary results suggest that acetic acid and sulfuric acid vary in their ability to leach specific metals and semivolatile organics from treated and untreated petroleum sludges. Further research is planned on this topic.

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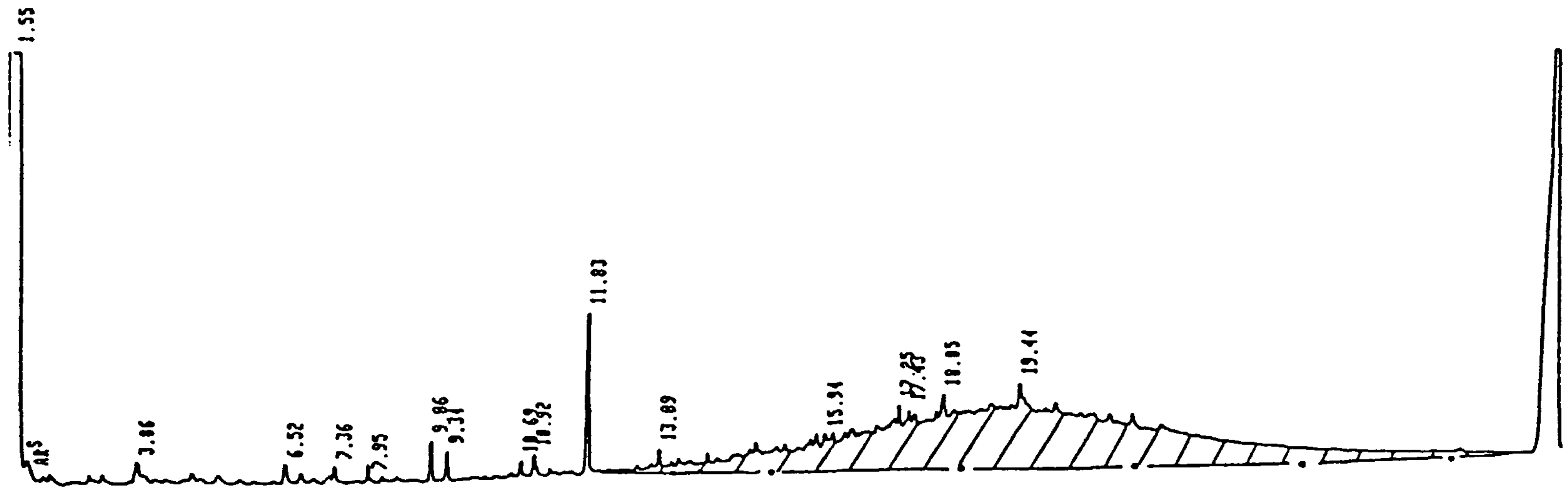

FIGURE 1: SAMPLE CHROMATOGRAM ILLUSTRATING RELATIVE HYDROCARBON CONCENTRATION

TABLE 1: METALS ANALYSIS DATA AND RHC VALUES

SAMPLE	extraction acid used	calcium ppm	sodium ppm	lead ppm	nickel ppm	copper ppm	magnesium ppm	zinc ppm	cadmium ppm	chromium ppm	relative hydrocarbon concentration
treated sludge 51	acetic	0.00	71.00	0.10	0.00	0.01	18.00	0.01	0.00	0.00	0.335
treated sludge 51	sulfuric	5.81	45.00	0.00	0.37	0.10	111.00	0.65	0.00	0.00	0.113
treated sludge 52	acetic	0.00	62.00	0.10	0.03	0.01	28.00	0.16	0.00	0.00	0.242
treated sludge 52	sulfuric	20.26	55.00	0.30	0.67	0.50	135.00	0.01	0.00	0.40	0.07
treated sludge 67	acetic	0.00	40.00	0.00	0.64	0.03	2.50	0.04	0.00	0.00	0.204
treated sludge 67	sulfuric	11.10	50.00	0.00	0.61	0.03	1.80	0.08	0.00	0.00	0.103
treated sludge 70	acetic	0.00	180.00	0.00	0.63	0.02	11.40	0.07	0.00	0.00	0.113
treated sludge 70	sulfuric	24.80	180.00	0.00	0.65	0.14	1.40	1.00	0.00	0.50	0.014
treated sludge 77	acetic	0.00	200.00	0.00	0.03	0.04	10.00	0.00	0.00	0.00	0.185
treated sludge 77	sulfuric	16.30	180.00	0.00	0.01	0.03	54.00	0.01	0.00	0.00	0.095
treated sludge 78	acetic	0.00	100.00	0.00	0.02	0.05	10.00	0.00	0.00	0.00	0.116
treated sludge 78	sulfuric	9.90	110.00	0.00	0.02	0.04	33.00	0.00	0.00	0.00	0.413
treated sludge 89	acetic	0.00	100.00	0.00	0.65	0.08	0.70	0.02	0.00	0.00	0.024
treated sludge 89	sulfuric	8.70	130.00	0.00	0.59	0.05	5.30	0.00	0.00	0.00	0.104
treated sludge 90	acetic	0.00	210.00	0.00	0.63	0.03	2.50	0.21	0.00	0.00	0.034
treated sludge 90	sulfuric	29.30	230.00	0.00	0.64	0.08	2.10	0.75	0.00	0.10	0.045
treated sludge 99	acetic	0.00	90.00	0.00	0.62	0.03	1.80	0.09	0.00	0.00	0.041
treated sludge 99	sulfuric	35.20	100.00	0.00	0.64	0.01	1.80	0.75	0.00	0.05	0.022
treated sludge 105	acetic	0.00	40.00	0.00	0.03	0.04	1.20	0.00	0.00	0.01	0.122
treated sludge 105	sulfuric	7.68	40.00	0.00	0.03	0.03	2.90	0.00	0.00	0.00	0.066
treated sludge 106	acetic	0.00	50.00	0.00	0.03	0.04	1.30	0.00	0.00	0.00	0.061
treated sludge 106	sulfuric	7.07	40.00	0.00	0.01	0.01	2.50	0.00	0.00	0.00	0.038
treated sludge 107	acetic	0.00	80.00	0.00	0.04	0.04	0.90	0.00	0.00	0.00	0.522
treated sludge 107	sulfuric	8.93	70.00	0.00	0.01	0.01	0.80	0.00	0.00	0.00	0.025
treated sludge 108	acetic	0.00	50.00	0.00	0.04	0.04	1.30	0.00	0.00	0.00	0.028
treated sludge 108	sulfuric	7.29	60.00	0.00	0.02	0.02	1.20	0.00	0.00	0.00	0.075
untreated sludge	acetic	13.90	1320.00	0.00	0.00	0.04	5.00	0.51	0.00	0.00	0.148
untreated sludge	acetic	19.57	1170.00	0.00	0.00	0.05	8.00	1.00	0.00	0.00	0.188
untreated sludge	sulfuric	12.57	21.00	0.00	0.18	0.00	8.00	1.00	0.00	0.15	0.115
untreated sludge	sulfuric	13.07	23.00	0.00	0.18	0.00	8.00	1.00	0.00	0.00	0.241
untreated sludge	sulfuric	11.45	21.00	0.00	0.07	0.00	6.00	1.00	0.00	0.00	0.16

TABLE 2a: SEMIVOLATILE ORGANICS ANALYSIS DATA

SAMPLE	extraction acid used	decane ppb	undecane ppb	dodecane ppb	tetradecane ppb	hexadecane ppb	octadecane ppb	eicosane ppb	tetracosane ppb	phenol ppb	dimethyl phenol ppb	methyl phenol ppb
treated sludge 51	acetic	ND	ND	ND	ND	ND	ND	ND	ND	1297.00	119.70	397.90
treated sludge 51	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	457.20	31.70	280.20
treated sludge 52	acetic	ND	ND	ND	ND	ND	ND	ND	ND	553.30	43.50	71.70
treated sludge 52	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	218.50	19.60	55.10
treated sludge 67	acetic	ND	ND	ND	ND	ND	ND	ND	29.60	1288.00	60.30	271.20
treated sludge 67	sulfuric	ND	ND	ND	6.20	ND	ND	ND	ND	1464.00	79.90	364.10
treated sludge 70	acetic	ND	ND	ND	ND	ND	ND	ND	ND	1855.00	39.50	229.70
treated sludge 70	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	1778.00	53.30	272.20
treated sludge 77	acetic	ND	ND	ND	ND	ND	ND	ND	ND	3499.00	206.60	757.40
treated sludge 77	sulfuric	ND	ND	ND	ND	ND	ND	ND	11.10	3389.00	156.90	646.30
treated sludge 78	acetic	ND	ND	ND	ND	ND	ND	ND	ND	2484.00	101.50	485.20
treated sludge 78	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	2166.00	57.70	355.00
treated sludge 89	acetic	ND	ND	ND	ND	3.50	ND	ND	6.00	1916.00	166.20	460.10
treated sludge 89	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	1741.00	88.00	307.40
treated sludge 90	acetic	ND	ND	ND	ND	ND	ND	ND	8.40	2211.00	57.60	303.80
treated sludge 90	sulfuric	ND	ND	ND	ND	ND	ND	ND	35.80	2479.00	58.70	333.50
treated sludge 99	acetic	ND	ND	ND	ND	ND	ND	ND	ND	2585.00	58.30	355.50
treated sludge 99	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	2203.00	73.90	372.10
treated sludge 105	acetic	ND	ND	ND	ND	ND	ND	ND	ND	2256.00	202.90	527.00
treated sludge 105	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	2281.00	193.20	547.10
treated sludge 106	acetic	ND	ND	ND	ND	ND	ND	ND	ND	2038.00	176.60	475.90
treated sludge 106	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	640.00	185.50	545.60
treated sludge 107	acetic	ND	ND	ND	ND	ND	ND	ND	ND	2260.00	201.10	567.00
treated sludge 107	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	467.00	143.50	408.90
treated sludge 108	acetic	ND	ND	ND	ND	2.30	ND	ND	ND	2527.00	241.50	650.70
treated sludge 108	sulfuric	ND	ND	ND	ND	ND	ND	ND	ND	1364.00	124.80	344.30
untreated sludge	acetic	ND	ND	27.40	14.60	19.00	14.30	25.50	131.20	1106.00	189.50	242.30
untreated sludge	acetic	ND	9.00	10.20	7.10	11.80	12.10	17.20	11.00	823.70	129.00	151.60
untreated sludge	sulfuric	81.00	291.00	553.00	1923.00	2616.00	2069.00	3502.00	3829.00	1845.00	218.00	716.00
untreated sludge	sulfuric	177.00	435.00	686.00	1790.00	2626.00	1843.00	2895.00	3381.00	3928.00	250.00	242.00
untreated sludge	sulfuric	289.00	141.00	592.00	1878.00	2396.00	1701.00	2725.00	2731.00	620.00	186.00	361.00

ND - Not Detected

TABLE 2b: SEMIVOLATILE ORGANICS ANALYSIS DATA

SAMPLE	extraction acid used	dibutyl phthalate ppb	diethylhexyl phthalate ppb	naphthalene ppb	fluorene ppb	phenanthrene ppb	pyrene ppb	methyl naphthalene ppb	dimethyl naphthalene ppb	diethyl phthalate ppb	benzyl alcohol ppb
treated sludge 51	acetic	6.20	174.60	27.40	ND	3.60	ND	40.00	11.40	ND	243.60
treated sludge 51	sulfuric	4.70	133.70	21.90	ND	2.20	ND	33.80	10.80	ND	259.70
treated sludge 52	acetic	7.70	205.10	14.00	ND	1.30	ND	20.80	5.80	ND	13.40
treated sludge 52	sulfuric	6.20	143.80	9.20	ND	0.90	ND	15.20	4.10	ND	ND
treated sludge 67	acetic	3.10	124.00	17.80	ND	4.40	ND	27.50	9.90	ND	19.70
treated sludge 67	sulfuric	2.10	106.70	21.20	2.20	4.30	ND	35.60	12.50	ND	27.00
treated sludge 70	acetic	4.50	44.40	18.10	ND	1.30	ND	25.00	ND	ND	ND
treated sludge 70	sulfuric	2.80	60.70	13.90	ND	1.30	ND	21.60	6.80	ND	12.80
treated sludge 77	acetic	2.30	239.00	25.30	ND	2.40	ND	38.10	12.10	ND	26.00
treated sludge 77	sulfuric	2.10	296.40	26.30	2.20	4.00	ND	41.50	13.10	ND	63.40
treated sludge 78	acetic	1.70	106.40	15.20	ND	1.50	ND	25.40	10.70	ND	13.40
treated sludge 78	sulfuric	ND	78.60	15.80	ND	1.70	ND	23.10	ND	ND	ND
treated sludge 89	acetic	2.80	1916.00	15.00	2.10	3.60	ND	27.00	10.50	ND	46.70
treated sludge 89	sulfuric	3.50	192.00	20.90	ND	3.80	ND	33.70	11.60	ND	9.70
treated sludge 90	acetic	2.20	34.50	15.30	ND	2.20	ND	26.10	9.30	ND	865.90
treated sludge 90	sulfuric	2.80	1525.00	16.40	ND	2.30	ND	26.20	9.60	ND	947.20
treated sludge 99	acetic	2.10	44.10	11.30	ND	2.50	ND	27.70	10.60	ND	666.60
treated sludge 99	sulfuric	2.50	35.30	21.60	1.90	3.50	ND	36.00	12.80	ND	749.90
treated sludge 105	acetic	2.50	125.50	22.80	ND	4.60	ND	34.20	12.20	ND	729.70
treated sludge 105	sulfuric	4.90	199.30	24.80	2.50	4.30	ND	38.10	14.70	1.20	612.40
treated sludge 106	acetic	3.00	127.90	20.70	ND	2.10	ND	28.70	10.80	ND	18.60
treated sludge 106	sulfuric	1.30	144.10	26.90	2.10	3.50	ND	42.20	14.20	ND	3.00
treated sludge 107	acetic	3.60	1032.00	22.40	ND	2.20	ND	34.60	10.10	ND	65.60
treated sludge 107	sulfuric	1.40	1156.00	21.40	1.90	2.30	ND	32.20	9.80	ND	14.20
treated sludge 108	acetic	4.20	2566.00	24.70	ND	3.60	ND	39.10	12.60	ND	21.40
treated sludge 108	sulfuric	3.30	170.80	16.30	2.10	3.60	ND	25.00	8.60	ND	34.60
untreated sludge	acetic	2.70	135.20	80.20	9.40	30.50	5.00	172.00	82.30	ND	70.10
untreated sludge	acetic	12.00	35.40	54.60	8.80	22.10	2.20	122.50	67.20	ND	17.50
untreated sludge	sulfuric	ND	ND	162.00	91.00	353.00	114.00	732.00	842.00	ND	ND
untreated sludge	sulfuric	ND	ND	165.00	84.00	312.00	111.00	702.00	762.00	ND	ND
untreated sludge	sulfuric	ND	68.00	143.00	72.00	243.00	85.00	666.00	780.00	ND	ND

ND - Not Detected

TCLP EXTRACTION OF REFERENCE WASTE SAMPLES STORED OVER TIME

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ABSTRACT

Four sets of reference samples were prepared and stored at 4°C for 24 months. The materials used to prepare the samples were a metal plating waste, an API separator sludge, a creosote-contaminated soil, and a smelter dust. Immediately following preparation of each set, a sample was withdrawn at random and tested using the Toxicity Characteristic Leaching Procedure (TCLP). Periodically during their storage, additional random samples were selected from each set and tested by the TCLP. The average elemental concentrations determined in the TCLP extracts generated over time for each set of samples were compared. Although in many cases the data are limited due to elemental concentrations being below analytical detection limits, they provide information on TCLP reproducibility, sample stability, and sample variability. The results in general suggest that (1) the TCLP shows good reproducibility for inorganic analytes; (2) based on TCLP characterization of their inorganic constituents, the samples have remained stable; and (3) based on the quantity of sample used in the TCLP and the inorganic data available, there is interbottle homogeneity among samples of the metal plating waste, creosote-contaminated soil, and smelter dust. However, the data indicate that the API separator sludge samples are poorly homogenized.

INTRODUCTION

Public Law 94-580, the Resource Conservation and Recovery Act (RCRA), requires that all wastes destined for land disposal be evaluated for their potential hazard to the environment. Wastes are deemed hazardous by a series of four classification tests that assess reactivity, ignitability, corrosivity, and toxicity.

Introduced in 1980, the Extraction Procedure Toxicity Characteristic (EPTC) is currently used to assess the toxicity of wastes destined for land disposal (1). However, in 1984, Congress amended RCRA requiring the EPA to develop a more accurate leaching test (2). A new test procedure was officially proposed in the January 1986 Land Disposal Restrictions (3), in a further modified version as a proposed replacement to the EPTC in June 1986 (4), and in still another version in the November 1986 final rule making on the Land Disposal Restrictions (5). It has not yet appeared in a final version that replaces the EPTC, but is expected to do so in the near future. The new test is known as the Toxicity Characteristic Leaching Procedure (TCLP).

In satisfying the requirements of the regulations under RCRA, analyzing wastes using the TCLP will account for a significant volume of analytical testing by the regulatory community. As a result, standard reference samples prepared from wastes for use as performance evaluation and/or quality assurance samples for the TCLP will be very beneficial. For this reason, a study was undertaken to prepare reference solid waste samples for the TCLP and to evaluate the stability of the samples stored over time based on TCLP characterization of their inorganic constituents. Data generated in this study provide information on TCLP reproducibility, sample stability, and sample variability.

EXPERIMENTAL

A metal plating waste, an API separator sludge, a creosote-contaminated soil, and a smelter dust were obtained for preparation of TCLP reference samples. Each waste material was homogenized in a batch mixer equipped with paddle-style blades. Homogeneity was determined by visual inspection. Following homogenization, the material was added to commercially precleaned bottles (6). Each bottled sample was placed in a poly bag, sealed with a twist tie, and placed in a metal can, which was then filled with vermiculite and sealed with a lid. A crimp overseal was placed on the can to prevent accidental opening. A label was placed on the outside of the can corresponding to the label on the sample bottle identifying the waste, the container size and type, the position in the sequence in which it was packaged, and the mass of material in the container. The sample cans were then placed in cardboard boxes in sequence and stored at 4°C.

Immediately following preparation of the sets of metal plating waste samples, creosote-contaminated soil samples, and smelter dust samples, a container was selected at random from each set and its contents tested using the TCLP (4). Due to an oversight a sample of the API separator sludge was not tested by the TCLP prior to storage. The TCLP was applied in duplicate to the metal plating waste and smelter dust, whereas a single TCLP extraction was performed on the creosote-contaminated soil.

Periodically during their storage, additional random samples were selected from each set and tested by the TCLP. During the period between sample preparation and the first stability testing episode, the November 1986 version of the TCLP was published in the Federal Register (5). The TCLP as specified in this publication was followed for all stability testing.

The metal plating waste samples were tested for stability after six months, 18 months, and 24 months of storage. The API separator sludge samples were tested after five months, 17 months, and 23 months of storage. The creosote-contaminated soil samples were tested for stability after 4.5 months, 17 months, and 23 months of storage, and the smelter dust samples were tested after 10 months and 16 months of storage.

For each set of samples, stability testing involved randomly selecting five sample containers from each set and applying the TCLP to a 100-gram sample of material from each container. In addition, single alkalinity determinations were performed on a portion of sample from each bottle. The TCLP was also applied to a blank consisting of extraction fluid from the same batch used to extract the five samples. The pH values of the TCLP slurries prior to filtration and of the TCLP leachates following filtration were recorded. The leachates were analyzed for inorganic elements, generally including the eight metals currently regulated under RCRA and three to four additional elements selected as indicators of matrix stability. Inductively coupled plasma (ICP) spectroscopy and atomic absorption spectroscopy (AAS) were used to analyze the extracts (7). Specific methods used and the elements determined for each waste type are given in the data tables presented in the results section.

RESULTS AND DISCUSSION

Metal Plating Waste

The time zero, six-month, 18-month, and 24-month leachates of the metal plating waste samples had pH values ranging from 5.6 to 5.9. In addition, the extraction slurries generated at each of the testing times had pH values ranging from 5.7 to 5.9.

Listed in Tables 1 through 4 are the elemental concentrations determined in the TCLP leachates of the metal plating waste samples. Leachate concentration values determined for silver, arsenic, cadmium, chromium, lead, selenium, and mercury are all below instrumental detection limits, whereas barium concentrations range from approximately 0.2 mg/L to less than 0.10 mg/L. The concentrations of copper, magnesium, and nickel in the leachates are all above detection limits, and as a result, can be more closely compared in Tables 5 through 7.

Listed in these tables are the elemental concentrations in the 15 TCLP leachates that have been generated over time. The average concentrations for the six-month, 18-month, and 24-month testing times; the percent standard deviation of the values for each testing time; and the 90% confidence interval for each data set are also presented. In addition, the values from the three testing times have also been treated as a single data set, and the overall average, percent standard deviation, and 90% confidence interval calculated from the 15 values are listed.

The data presented in Tables 5 through 7 indicate that the TCLP results for copper, magnesium, and nickel have been reproducible over 24 months, and based on the concentrations of these elements, the samples appear to have remained stable. For each of these elements, the variability between data generated for each testing time is approximately the same as the overall variability, and the average elemental concentrations determined at each testing time for each of the elements are similar. Based on the overall percent standard deviations and the percent standard deviations at each testing time, the samples are homogeneous in their distributions of magnesium and nickel; however, they do not appear to be homogeneous with respect to their copper concentrations. This may be due to the chemical speciation of copper in the metal plating waste matrix.

API Separator Sludge

The pH values of the five-month, 17-month, and 23-month extraction slurries ranged from 5.3 to 5.8. The pH values of the five-month, 17-month, and 23-month final leachates ranged from 5.3 to 6.0.

Tables 8 through 10 list the elemental concentrations determined in the TCLP leachates of the API separator sludge samples. Leachate concentration values determined for silver, arsenic, cadmium, lead, selenium, nickel, and mercury are all below instrumental detection limits, whereas chromium concentrations range from 0.11 mg/L to less than 0.10 mg/L. The concentrations of barium, iron, and magnesium are all above detection limits, and as a result, can be compared more closely in Tables 11 through 13.

These tables present data similar to the data in Tables 5 through 9 for the metal plating waste; however, interpretation of the API separator sludge data is more difficult. The percent standard deviations between the five-month concentration values for all three elements are low, whereas variability between the 17-month values and variability between the 23-month values for the three elements are very high. This does not appear to be due to sample instability or poor TCLP precision. For barium, the percent standard deviation between the average values calculated at five months, 17 months, and 23 months is 21%, for iron it is 11%, and for magnesium it is 7%. This indicates that although the concentration values vary considerably overall and within the 17-month and 23-month testing times, the average values do not.

The API separator sludge was obtained from a petroleum refining facility. The material had been withdrawn from a sludge pit that had been used as a collection area for other sludges, plant slops, debris, and soil. The API separator sludge was also contaminated with fragments of metal, wire, and cloth.

Based on the nonuniformity of the API separator sludge material used to prepare the samples and the data presented in Tables 11 through 13, it appears that the samples were poorly homogenized, but they have remained stable, and their TCLP results are reproducible.

Creosote-Contaminated Soil

The pH value of the time zero extraction slurry and final leachate was 5.1. In addition, the pH values of the 4.5-month, 17-month, and 23-month extraction slurries and final leachates were also 5.1.

Tables 14 through 17 list the elemental concentrations determined in the TCLP leachates of the creosote-contaminated soil samples. Mercury was not determined in the 4.5-month leachate (Table 15) because of its high ICP detection limit. Iron was added to the list of analytes at the 17-month testing time (Table 16) to provide additional data because so many of the previously determined concentration values were below instrumental detection limits. Leachate concentration values determined for silver, arsenic, cadmium, chromium, lead, selenium, and mercury are all below instrumental detection limits, whereas nickel concentrations range from 0.15 mg/L to less than 0.10 mg/L. The concentrations of barium, iron, and magnesium are all above detection limits, and as a result, can be compared more closely in Tables 18 through 20.

These tables present the elemental concentrations determined in the TCLP leachates that have been generated over 23 months. The average concentrations for the 4.5-month, 17-month, and 23-month testing times; the percent standard deviation of the values for each testing time; and the 90% confidence interval for each data set are also listed. In addition, the values from the three testing times have been treated as a single data set and the overall average, percent standard deviation, and 90% confidence interval calculated from the values are listed.

The data presented in Tables 18 and 20 show that the TCLP results for barium and magnesium are reproducible over 23 months, and based on the concentrations of these elements, the samples appear to have remained stable. Not only is the variability between the data generated for each testing time very similar to the overall variability, but the averages for each of the testing times are also very similar and many of the confidence intervals overlap. Because the 4.5-month data for iron were not determined, it is difficult to make conclusions based on the data presented in Table 19; however, it appears that the samples may not be homogeneous in their distribution of iron.

Smelter Dust

Comparison of the pH values of the extraction slurries and final leachates generated during each extraction of the smelter dust samples shows close correlation among the data. The pH values of the time zero extraction slurries and final leachates were 4.4, whereas the pH values of the 10-month and 16-month extraction slurries and final leachates ranged from 4.6 to 4.7.

Tables 21 through 23 list the elemental concentrations determined in the TCLP leachates of the smelter dust samples. Leachate concentration values determined for mercury are all below the instrumental detection limit, whereas chromium values range from 0.15 mg/L to less than 0.10 mg/L, and silver values range from 0.18 mg/L to less than 0.10 mg/L. The concentrations of barium, cadmium, copper, iron, lead, arsenic, magnesium, and nickel are all above instrumental detection limits, and as a result, can be compared more closely in Tables 24 through 31. In addition, because selenium was analyzed by furnace AAS in the 10-month and 16-month extracts, concentration values for that element are also compared in Table 32.

These tables list the elemental concentrations determined in the 10 TCLP leachates that have been generated over 16 months. Although there are only two data sets that can be compared for each element, it is advantageous that there are data for nine elements. The average concentrations for the 10-month and 16-month testing times are listed along with the percent standard deviation of the values, and the 90% confidence interval for each data set. In addition, the values from the two testing times are treated as a single data set and the overall average, percent standard deviation, and 90% confidence interval calculated from the 10 values are listed.

The data presented for barium, cadmium, copper, lead, magnesium, nickel, and selenium in Tables 24, 25, 26, 28, 30, 31, and 32, respectively, show similar averages for the two testing times, similar overall variability compared to the variability within the two data sets, and overlap of the 90% confidence intervals calculated from the 10-month and 16-month data. The data indicate that with respect to these elements, the samples have remained stable over 16 months and that their TCLP results are reproducible. In addition, sample homogeneity in terms of the distribution of these elements also appears to be good. However, it should be noted that comparing the time zero values listed for cadmium in Table 25 with the 10-month and 16-month data shows that the time zero values are higher. Also, a comparison of the time zero values listed for lead in Table 28 with the 10-month and 16-month data shows that the time zero values are lower. It is difficult to make any conclusions based on these comparisons because the time zero data are limited in that only one sample was tested. Interpretation of the data for iron in Table 27 is difficult. The time zero values from the testing of one sample in duplicate are similar to those values determined at 10-months; however, all of the values determined in the 16-month extracts are much lower. The same is true of the data for arsenic in Table 29. Possible explanations are that the samples are not homogeneous in their distributions of iron and arsenic, and by chance, random samples were selected at each testing time with similar distributions; that error was made in analyzing the sets of leachates; or that the samples have not remained stable with respect to iron and arsenic. It is not possible to determine if any of these explanations are correct based on the limited data available. Additional testing is required to make any conclusions concerning the concentrations of these elements in the TCLP leachates of the smelter dust samples.

As previously mentioned, the sample labels contain information concerning sample position in the preparation sequence. Examining the positions of the smelter dust samples selected for testing showed no correlation between elemental concentrations in the TCLP leachates and sample position in the preparation sequence. This was also true for the metal plating waste samples, API separator sludge samples, and creosote-contaminated soil samples.

CONCLUSIONS

Recognizing that the data are limited because many elemental concentrations are below analytical detection limits, the results to date suggest that (1) the TCLP shows good reproducibility for inorganic analytes; (2) based on TCLP characterization of their inorganic constituents, the samples have remained stable; and (3) based on the quantity of sample used in the TCLP and the inorganic data available, there is interbottle homogeneity among samples of the metal plating waste, creosote-contaminated soil, and smelter dust. However, the data indicate that the API separator sludge samples are poorly homogenized. The metal plating waste and creosote-contaminated soil could have been better homogenized prior to sample preparation. This is indicated by the concentrations of copper determined in the metal plating waste leachates and the iron concentrations in the creosote-contaminated soil TCLP leachates. The TCLP data for iron and arsenic in the smelter dust samples are too limited to base any conclusions concerning sample stability, homogeneity, or TCLP reproducibility. However, they do emphasize the need for further testing to determine why the 10-month values vary so much from those determined at 16 months.

Table 1. Metal Plating Waste TCLP Leachate Analysis Time Zero

	Elemental Concentrations,[1] mg/L								
Duplicate Leachates	Ag	As	Ba	Cd	Cr	Pb	Se	Cu	Mg[2]	Ni
1	<.10	<1.0	0.22	<.10	<.10	<.50	<1.0	73.0	---	0.64
2	<.10	<1.0	0.21	<.10	<.10	<.50	<1.0	55.0	---	0.62
Ave	<.10	<1.0	0.21	<.10	<.10	<.50	<1.0	64.0	---	0.63
% Std Dev	---	---	4%	---	---	---	---	8%	---	4%
Method Blk	<.10	<1.0	0.06	<.10	<.10	<.50	<1.0	0.9	---	<.10

Table 2. Metal Plating Waste TCLP Leachate Analysis Six-Month Storage Time

	Elemental Concentrations,[1] mg/L									
Leachate	Ag	As	Ba	Cd	Cr	Pb	Se	Cu	Mg	Ni
A	<.10	<1.0	0.22	<.10	<.10	<.50	<1.0	17.8	119	0.45
B	<.10	<1.0	0.12	<.10	<.10	<.50	<1.0	54.5	116	0.59
C	<.10	<1.0	0.13	<.10	<.10	<.50	<1.0	50.1	120	0.64
D	<.10	<1.0	0.13	<.10	<.10	<.50	<1.0	58.0	120	0.50
E	<.10	<1.0	0.16	<.10	<.10	<.50	<1.0	23.6	121	0.59
Ave	<.10	<1.0	0.15	<.10	<.10	<.50	<1.0	40.8	119	0.55
% Std Dev	---	---	27%	---	---	---	---	46%	2%	14%
Method Blk	<.10	<1.0	<.10	<.10	<.10	<.50	<1.0	<.10	<.05	<.10

Table 3. Metal Plating Waste TCLP Leachate Analysis 18-Month Storage Time

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As[3]	Ba	Cd	Cr	Pb	Se[3]	Cu	Mg	Ni	Hg[4]
A	<.10	<.05	0.13	<.10	<.10	<.50	<.05	40.9	112	0.48	<.0004
B	<.10	<.05	<.10	<.10	<.10	<.50	<.05	59.0	109	0.49	<.0004
C	<.10	<.05	0.12	<.10	<.10	<.50	<.05	64.9	105	0.42	<.0004
D	<.10	<.05	0.16	<.10	<.10	<.50	<.05	30.7	106	0.45	<.0004
E	<.10	<.05	<.10	<.10	<.10	<.50	<.05	42.0	109	0.43	<.0004
Ave	<.10	<.05	---	<.10	<.10	<.50	<.05	47.5	108	0.45	<.0004
% Std Dev	---	---	---	---	---	---	---	30%	3%	7%	---
Meth Blk	<.10	<.05	<.10	<.10	<.10	<.50	<.05	<.10	<.05	<.10	<.0004

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[1] Determined by ICP spectroscopy unless otherwise noted
[2] No data available
[3] Determined by furnace AAS
[4] Determined by cold vapor AAS

Table 4. Metal Plating Waste TCLP Leachate Analysis 24-Month Storage Time

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As[2]	Ba	Cd	Cr	Pb	Se[2]	Cu	Mg	Ni	Hg[3]
A	<.10	<.10	0.16	<.10	<.10	<.50	<.05	56.3	112	0.61	<.002
B	<.10	<.10	<.10	<.10	<.10	<.50	<.05	52.6	114	0.57	<.002
C	<.10	<.10	<.10	<.10	<.10	<.50	<.05	23.7	112	0.43	<.002
D	<.10	<.10	<.10	<.10	<.10	<.50	<.05	66.6	111	0.57	<.002
E	<.10	<.10	<.10	<.10	<.10	<.50	<.05	57.7	115	0.57	<.002
Ave	<.10	<.10	---	<.10	<.10	<.50	<.05	50.8	113	0.55	<.002
% Std Dev	---	---	---	---	---	---	---	32%	1%	13%	---
Meth Blk	<.10	<.10	<.10	<.10	<.10	<.50	<.05	<.10	<.05	<.10	<.002

Table 5. Copper Concentrations in Metal Plating Waste TCLP Leachates, mg/L

Time Zero Duplicate Values: 73.0, 55.0

After Six Months of Storage	17.8 54.5 50.1 58.0 23.6	Ave: 40.8 % Std Dev: 46% 90% CI[4]: 23.0-58.6
After 18 Months of Storage	40.9 59.0 64.9 30.7 42.0	Ave: 47.5 % Std Dev: 30% 90% CI: 34.1-60.9
After 24 Months of Storage	56.3 52.6 23.7 66.6 57.7	Ave: 50.8 % Std Dev: 32% 90% CI: 35.5-66.1

Overall Ave: 46.4
Overall % Std Dev: 34%
Overall 90% CI: 37.7-55.1

Table 6. Magnesium Concentrations in Metal Plating Waste TCLP Leachates, mg/L

Time zero data were not determined.

After Six Months of Storage	119 116 120 120 121	Ave: 119 % Std Dev: 2% 90% CI[4]: 117-121
After 18 Months of Storage	112 109 105 106 109	Ave: 108 % Std Dev: 3% 90% CI: 105-111
After 24 Months of Storage	112 114 112 111 115	Ave: 113 % Std Dev: 1% 90% CI: 111-115

Overall Ave: 113
Overall % Std Dev: 4%
Overall 90% CI: 110-116

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[1] Determined by ICP spectroscopy unless otherwise noted
[2] Determined by furnace AAS
[3] Determined by cold vapor AAS
[4] 90% confidence interval determined using t distribution

Table 7. Nickel Concentrations in Metal Plating Waste TCLP Leachates, mg/L

Time Zero Duplicate Values: 0.64, 0.62

After Six Months of Storage	0.45 0.59 0.64 0.50 0.59	Ave: 0.55 % Std Dev: 14% 90% CI[1]: 0.48-0.63
After 18 Months of Storage	0.48 0.49 0.42 0.45 0.43	Ave: 0.45 % Std Dev: 7% 90% CI: 0.42-0.48
After 24 Months of Storage	0.61 0.57 0.43 0.57 0.57	Ave: 0.55 % Std Dev: 13% 90% CI: 0.48-0.62

Overall Ave: 0.52
Overall % Std Dev: 14%
Overall 90% CI: 0.48-0.52

Table 8. API Separator Sludge TCLP Leachate Analysis Five-Month Storage Time

Elemental Concentrations,[2] mg/L

Leachate	Ag	As	Ba	Cd	Cr	Pb	Se	Fe	Mg	Ni
A	<.10	<1.0	0.46	<.10	<.10	<.50	<1.0	175	14.1	<.10
B	<.10	<1.0	0.51	<.10	<.10	<.50	<1.0	188	15.0	<.10
C	<.10	<1.0	0.50	<.10	<.10	<.50	<1.0	219	14.5	<.10
D	<.10	<1.0	0.49	<.10	<.10	<.50	<1.0	211	14.3	<.10
E	<.10	<1.0	0.46	<.10	<.10	<.50	<1.0	175	15.4	<.10
Ave	<.10	<1.0	0.48	<.10	<.10	<.50	<1.0	194	14.7	<.10
% Std Dev	---	---	5%	---	---	---	---	10%	4%	---
Method Blk	<.10	<1.0	<.10	<.10	<.10	<.50	<1.0	0.15	<.05	<.10

Table 9. API Separator Sludge TCLP Leachate Analysis 17-Month Storage Time

Elemental Concentrations,[2] mg/L

Leachate	Ag	As[3]	Ba	Cd	Cr	Pb	Se[3]	Fe	Mg	Ni	Hg[4]
A	<.10	<.05	0.12	<.10	<.10	<.50	<.05	220	14.1	<.10	<.002
B	<.10	<.05	0.25	<.10	0.11	<.50	<.05	334	18.4	<.10	<.002
C	<.10	<.05	0.52	<.10	<.10	<.50	<.05	263	12.2	<.10	<.002
D	<.10	<.05	0.66	<.10	<.10	<.50	<.05	202	24.1	<.10	<.002
E	<.10	<.05	0.33	<.10	<.10	<.50	<.05	188	15.6	<.10	<.002
Ave	<.10	<.05	0.38	<.10	---	<.50	<.05	241	16.9	<.10	<.002
% Std Dev	---	---	57%	---	---	---	---	24%	27%	---	---
Meth Blk	<.10	<.05	<.10	<.10	<.10	<.50	<.05	0.19	<.05	<.10	<.002

Table 10. API Separator Sludge TCLP Leachate Analysis 23-Month Storage Time

Elemental Concentrations,[2] mg/L

Leachate	Ag	As[3]	Ba	Cd	Cr	Pb	Se[3]	Fe	Mg	Ni	Hg[4]
A	<.10	<.10	0.55	<.10	<.10	<.50	<.05	162	12.7	<.10	<.002
B	<.10	<.10	0.69	<.10	<.10	<.50	<.05	203	13.8	<.10	<.002
C	<.10	<.10	0.86	<.10	<.10	<.50	<.05	369	24.0	<.10	<.002
D	<.10	<.10	0.12	<.10	<.10	<.50	<.05	175	19.1	<.10	<.002
E	<.10	<.10	0.69	<.10	<.10	<.50	<.05	270	13.3	<.10	<.002
Ave	<.10	<.10	0.58	<.10	<.10	<.50	<.05	236	16.6	<.10	<.002
% Std Dev	---	---	48%	---	---	---	---	36%	29%	---	---
Meth Blk	<.10	<.10	<.10	<.10	<.10	<.50	<.05	<.10	<.05	<.10	<.002

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[1] 90% confidence interval determined using t distribution
[2] Determined by ICP spectroscopy unless otherwise noted
[3] Determined by furnace AAS
[4] Determined by cold vapor AAS

Table 11. Barium Concentrations in API Separator Sludge TCLP Leachates, mg/L

After Five Months of Storage	0.46	
	0.51	Ave: 0.48
	0.50	% Std Dev: 5%
	0.49	90% CI[1]: 0.46-0.50
	0.46	
After 17 Months of Storage	0.12	
	0.25	Ave: 0.38
	0.52	% Std Dev: 57%
	0.66	90% CI: 0.18-0.58
	0.33	
After 23 Months of Storage	0.55	
	0.69	Ave: 0.58
	0.86	% Std Dev: 48%
	0.12	90% CI: 0.31-0.85
	0.69	

Overall Ave: 0.48
Overall % Std Dev: 43%
Overall 90% CI: 0.37-0.59

Table 12. Iron Concentrations in API Separator Sludge TCLP Leachates, mg/L

After Five Months of Storage	175	
	188	Ave: 194
	219	% Std Dev: 10%
	211	90% CI[1]: 175-213
	175	
After 17 Months of Storage	220	
	334	Ave: 241
	263	% Std Dev: 24%
	202	90% CI: 185-297
	188	
After 23 Months of Storage	162	
	203	Ave: 236
	369	% Std Dev: 36%
	175	90% CI: 155-317
	270	

Overall Ave: 224
Overall % Std Dev: 27%
Overall 90% CI: 191-257

Table 13. Magnesium Concentrations in API Separator Sludge TCLP Leachates, mg/L

After Five Months of Storage	14.1	
	15.0	Ave: 14.7
	14.5	% Std Dev: 4%
	14.3	90% CI[1]: 14.2-15.2
	15.4	
After 17 Months of Storage	14.1	
	18.4	Ave: 16.9
	12.2	% Std Dev: 27%
	24.1	90% CI: 12.5-21.3
	15.6	
After 23 Months of Storage	12.7	
	13.8	Ave: 16.6
	24.0	% Std Dev: 29%
	19.1	90% CI: 12.0-21.2
	13.3	

Overall Ave: 16.0
Overall % Std Dev: 23%
Overall 90% CI: 13.9-18.1

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[1] 90% confidence interval determined using t distribution

Table 14. Creosote-Contaminated Soil TCLP Leachate Analysis Time Zero

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As	Ba	Cd	Cr	Pb	Se	Fe[2]	Mg[2]	Ni	Hg
1	<.10	<1.0	1.16	<.10	<.10	<.50	<1.0	---	---	0.15	<.20
Method Blk	<.10	<1.0	<.10	<.10	<.10	<.50	<1.0	---	---	<.10	<.20

Table 15. Creosote-Contaminated Soil TCLP Leachate Analysis 4.5-Month Storage Time

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As	Ba	Cd	Cr	Pb	Se	Fe[2]	Mg	Ni	Hg[2]
A	<.10	<1.0	1.22	<.10	<.10	<.50	<1.0	---	20.9	<.10	---
B	<.10	<1.0	1.26	<.10	<.10	<.50	<1.0	---	20.6	<.10	---
C	<.10	<1.0	1.27	<.10	<.10	<.50	<1.0	---	19.6	<.10	---
D	<.10	<1.0	1.19	<.10	<.10	<.50	<1.0	---	19.7	<.10	---
E	<.10	<1.0	1.22	<.10	<.10	<.50	<1.0	---	19.4	<.10	---
Ave	<.10	<1.0	1.23	<.10	<.10	<.50	<1.0	---	20.0	<.10	---
% Std Dev	---	---	3%	---	---	---	---	---	3%	---	---
Method Blk	<.10	<1.0	<.10	<.10	<.10	<.50	<1.0	<.05	<.10	---	---

Table 16. Creosote-Contaminated Soil TCLP Leachate Analysis 17-Month Storage Time

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As[3]	Ba	Cd	Cr	Pb	Se[3]	Fe	Mg	Ni	Hg[4]
A	<.10	<.05	1.37	<.10	<.10	<.50	<.05	1.06	21.4	<.10	<.002
B	<.10	<.05	1.25	<.10	<.10	<.50	<.05	1.54	21.6	<.10	<.002
C	<.10	<.05	1.32	<.10	<.10	<.50	<.05	1.50	21.6	<.10	<.002
D	<.10	<.05	1.22	<.10	<.10	<.50	<.05	0.82	21.8	<.10	<.002
E	<.10	<.05	1.27	<.10	<.10	<.50	<.05	0.96	21.4	<.10	<.002
Ave	<.10	<.05	1.29	<.10	<.10	<.50	<.05	1.18	21.6	<.10	<.002
% Std Dev	---	---	5%	---	---	---	---	28%	1%	---	---
Meth Blk	<.10	<.05	<.10	<.10	<.10	<.50	<.05	<.10	<.05	<.10	<.002

Table 17. Creosote-Contaminated Soil TCLP Leachate Analysis 23-Month Storage Time

	Elemental Concentrations,[1] mg/L										
Leachate	Ag	As[3]	Ba	Cd	Cr	Pb	Se[3]	Fe	Mg	Ni	Hg[4]
A	<.10	<.05	1.27	<.10	<.10	<.50	<.05	0.64	20.2	<.10	<.002
B	<.10	<.05	1.29	<.10	<.10	<.50	<.05	0.65	22.3	<.10	<.002
C	<.10	<.05	1.15	<.10	<.10	<.50	<.05	0.72	20.9	0.13	<.002
D	<.10	<.05	1.28	<.10	<.10	<.50	<.05	0.78	21.8	<.10	<.002
E	<.10	<.05	1.15	<.10	<.10	<.50	<.05	0.78	22.2	0.13	<.002
Ave	<.10	<.05	1.23	<.10	<.10	<.50	<.05	0.75	21.5	---	<.002
% Std Dev	---	---	6%	---	---	---	---	10%	4%	---	---
Meth Blk	<.10	<.05	<.10	<.10	<.10	<.50	<.05	<.10	0.15	<.10	<.002

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[1] Determined by ICP spectroscopy unless otherwise noted
[2] No data available
[3] Determined by furnace AAS
[4] Determined by cold vapor AAS

Table 18. Barium Concentrations in Creosote-Contaminated Soil TCLP Leachates, mg/L

Time Zero Single Value:	1.16	
	1.22	
After 4.5 Months of Storage	1.26	Ave: 1.23
	1.27	% Std Dev: 3%
	1.19	90% CI[1]: 1.20-1.26
	1.22	
	1.37	
After 17 Months of Storage	1.25	Ave: 1.29
	1.32	% Std Dev: 5%
	1.22	90% CI: 1.23-1.35
	1.27	
	1.27	
After 23 Months of Storage	1.29	Ave: 1.23
	1.15	% Std Dev: 6%
	1.28	90% CI: 1.16-1.30
	1.15	

Overall Ave: 1.26
Overall % Std Dev: 5%
Overall 90% CI: 1.23-1.29

Table 19. Iron Concentrations in Creosote-Contaminated Soil TCLP Leachates, mg/L

Time zero and 4.5-Month data were not determined.

	1.06	
After 17 Months of Storage	1.54	Ave: 1.18
	1.50	% Std Dev: 28%
	0.82	90% CI[1]: 0.87-1.49
	0.96	
	0.64	
After 23 Months of Storage	0.85	Ave: 0.75
	0.72	% Std Dev: 10%
	0.78	90% CI: 0.68-0.82
	0.78	

Overall Ave: 0.96
Overall % Std Dev: 32%
Overall 90% CI: 0.75-1.17

Table 20. Magnesium Concentrations in Creosote-Contaminated Soil TCLP Leachates, mg/L

Time zero data were not determined.

	20.9	
After 4.5 Months of Storage	20.9	Ave: 20.0
	19.6	% Std Dev: 3%
	19.7	90% CI[1]: 19.4-20.6
	19.4	
	21.4	
After 17 Months of Storage	21.6	Ave: 21.6
	21.6	% Std Dev: 1%
	21.8	90% CI: 21.4-21.8
	21.4	
	20.2	
After 23 Months of Storage	22.3	Ave: 21.5
	20.9	% Std Dev: 4%
	21.8	90% CI: 20.6-22.4
	22.2	

Overall Ave: 21.0
Overall % Std Dev: 4%
Overall 90% CI: 20.5-21.5

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[1] 90% confidence interval determined using t distribution

Table 21. Smelter Dust TCLP Leachate Analysis Time Zero

Duplicate Leachates	Elemental Concentrations,[1] mg/L Ag	As	Ba	Cd	Cr	Pb	Se	Cu	Fe	Mg	Ni
1	0.18	2.70	0.21	7.12	0.15	4.66	<1.0	1580	317	74.9	1.78
2	o.15	1.49	0.20	6.62	<.10	4.57	<1.0	1661	296	68.3	1.82
Ave	0.17	2.09	0.20	6.87	---	4.61	<1.0	1620	306	71.6	1.80
% Std Dev	11%	41%	3%	5%	---	1%	---	3%	5%	6%	2%
Method Blk	<.10	<1.0	<.10	<.10	<.10	<.50	<1.0	1.18	<.10	0.21	<.10

Table 22. Smelter Dust TCLP Leachate Analysis 10-Month Storage Time

Leachate	Elemental Concentrations,[1] mg/L Ag	As[2]	Ba	Cd	Cr	Pb	Se[2]	Cu	Fe	Mg	Ni	Hg[3]
A	0.11	2.50	0.22	6.30	<.10	5.94	0.09	1850	296	76.1	1.96	<.002
B	0.14	2.50	0.15	6.00	0.11	6.44	0.15	1890	265	81.8	2.02	<.002
C	<.10	2.10	0.13	4.98	<.10	5.17	0.11	1600	219	65.0	1.65	<.002
D	0.12	2.30	0.17	6.17	0.14	5.48	0.09	1720	292	66.9	1.84	<.002
E	0.13	1.90	0.16	5.87	<.10	6.23	0.11	1830	275	77.9	1.84	<.002
Ave	---	2.26	0.17	5.86	---	5.85	0.11	1778	269	73.5	1.86	<.002
% Std Dev	---	9%	20%	9%	---	9%	22%	7%	11%	10%	8%	---
Meth Blk	<.10	<.25	<.10	<.10	<.10	<.50	<.05	1.03	0.12	<.05	<.10	<.002

Table 23. Smelter Dust TCLP Leachate Analysis 16-Month Storage Time

Leachate	Elemental Concentrations,[1] mg/L Ag	As[2]	Ba	Cd	Cr	Pb	Se[2]	Cu	Fe	Mg	Ni	Hg[3]
A	0.12	0.65	0.17	5.67	<.10	6.70	0.19	1760	177	74.3	1.73	<.002
B	<.10	0.63	0.16	5.48	<.10	6.75	0.20	1750	167	75.0	1.70	<.002
C	<.10	0.58	0.14	5.20	<.10	6.43	0.11	1570	158	71.5	1.76	<.002
D	<.10	0.72	0.14	5.38	<.10	5.65	0.12	1593	191	68.2	1.55	<.002
E	<.10	0.90	0.16	6.12	<.10	5.09	0.11	1641	229	67.2	1.64	<.002
Ave	---	0.70	0.15	5.57	---	6.12	0.15	1663	184	71.2	1.68	<.002
% Std Dev	---	18%	9%	6%	---	12%	30%	5%	15%	5%	5%	---
Meth Blk	<.10	<.10	<.10	<.10	<.10	<.50	<.05	1.07	<.10	<.05	<.10	<.002

Table 24. Barium Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: *0.21, 0.20*

After 10 Months of Storage	0.22 0.15 0.13 0.17 0.16	Ave: 0.17 % Std Dev: 20% 90% CI[4]: 0.14-0.20
After 16 Months of Storage	0.17 0.16 0.14 0.14 0.16	Ave: 0.15 % Std Dev: 9% 90% CI: 0.14-0.16

Overall Ave: 0.16
Overall % Std Dev: 16%
Overall 90% CI: 0.14-0.18

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[1] Determined by ICP spectroscopy unless otherwise noted
[2] Determined by furnace AAS
[3] Determined by cold vapor AAS
[4] 90% confidence interval determined using t distribution

Table 25. Cadmium Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 7.12, 6.62

After 10 Months of Storage	6.30 6.00 4.98 6.17 5.87	Ave: 5.86 % Std Dev: 9% 90% CI[1]: 5.36-6.36
After 16 Months of Storage	5.67 5.48 5.20 5.38 6.12	Ave: 5.57 % Std Dev: 6% 90% CI: 5.24-5.90

Overall Ave: 5.72
Overall % Std Dev: 8%
Overall 90% CI: 5.42-6.02

Table 26. Copper Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 1580, 1661

After 10 Months of Storage	1850 1890 1600 1720 1830	Ave: 1778 % Std Dev: 7% 90% CI[1]: 1666-1890
After 16 Months of Storage	1760 1750 1570 1593 1641	Ave: 1663 % Std Dev: 5% 90% CI: 1579-1747

Overall Ave: 1720
Overall % Std Dev: 7%
Overall 90% CI: 1642-1798

Table 27. Iron Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 317, 296

After 10 Months of Storage	296 265 219 292 275	Ave: 269 % Std Dev: 11% 90% CI[1]: 240-298
After 16 Months of Storage	177 167 158 191 229	Ave: 184 % Std Dev: 15% 90% CI: 158-210

Overall Ave: 227
Overall % Std Dev: 23%
Overall 90% CI: 192-262

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[1] 90% confidence interval determined using t distribution

Table 28. Lead Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 4.66, 4.57

After 10 Months of Storage	5.94	
	6.44	Ave: 5.85
	5.17	% Std Dev: 9%
	5.48	90% CI[1]: 5.35-6.35
	6.23	
After 16 Months of Storage	6.70	
	6.75	Ave: 6.12
	6.43	% Std Dev: 12%
	5.65	90% CI: 5.43-6.81
	5.09	

Overall Ave: 5.99
Overall % Std Dev: 10%
Overall 90% CI: 5.57-6.40

Table 29. Arsenic Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 2.70, 1.49

After 10 Months of Storage	2.50	
	2.50	Ave: 2.26
	2.10	% Std Dev: 9%
	2.30	90% CI[1]: 2.06-2.46
	1.90	
After 16 Months of Storage	0.65	
	0.63	Ave: 0.70
	0.58	% Std Dev: 18%
	0.72	90% CI: 0.58-0.82
	0.90	

Overall Ave: 1.48
Overall % Std Dev: 57%
Overall 90% CI: 0.91-2.05

Table 30. Magnesium Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 74.9, 68.3

After 10 Months of Storage	76.1	
	81.8	Ave: 73.5
	65.0	% Std Dev: 10%
	66.9	90% CI[1]: 66.6-80.4
	77.9	
After 16 Months of Storage	74.3	
	75.0	Ave: 71.2
	71.5	% Std Dev: 5%
	68.2	90% CI: 67.9-74.5
	67.2	

Overall Ave: 72.4
Overall % Std Dev: 8%
Overall 90% CI: 68.7-76.1

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[1] 90% confidence interval determined using t distribution

Table 31. Nickel Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: 1.78, 1.82

After 10 Months of Storage	1.96	
	2.02	Ave: 1.86
	1.65	% Std Dev: 8%
	1.84	90% CI[1]: 1.73-1.99
	1.84	
After 16 Months of Storage	1.73	
	1.70	Ave: 1.68
	1.76	% Std Dev: 5%
	1.55	90% CI: 1.60-1.76
	1.64	

Overall Ave: 1.77
Overall % Std Dev: 8%
Overall 90% CI: 1.67-1.87

Table 32. Selenium Concentrations in Smelter Dust TCLP Leachates, mg/L

Time Zero Duplicate Values: <1.0, <1.0

After 10 Months of Storage	0.09	
	0.15	Ave: 0.11
	0.11	% Std Dev: 22%
	0.09	90% CI[1]: 0.09-0.13
	0.11	
After 16 Months of Storage	0.19	
	0.20	Ave: 0.15
	0.11	% Std Dev: 30%
	0.12	90% CI: 0.11-0.19
	0.11	

Overall Ave: 0.13
Overall % Std Dev: 30%
Overall 90% CI: 0.10-0.16

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[1] 90% confidence interval determined using t distribution

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MODIFICATION OF THE TCLP PROCEDURE TO ACCOMMODATE MONOLITHIC WASTES

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ABSTRACT

The current EPA Toxicity Characteristic Leaching Procedure (TCLP), SW 846 Method 1311(1), requires that all wastes be milled into smaller particles prior to being placed into the extractor. A multi-laboratory study has been conducted to determine if milling is necessary or if the tumbling action of the TCLP procedure will cause monolithic wastes, which are not strong enough to survive in environment, to fall apart in the extractor. Multiple plugs of eight different solidified waste samples of variable strength were prepared. The unconfined compressive strength of a plug of each sample was measured and the environmental survivability was evaluted in two separate laboratories using the ASTM Freeze/Thaw (D4842-89) and Wet/Dry (D4843-88) testing procedures. Identical plugs of each sample were tumbled in glass bottles, equipped with a stainless cage as proposed by EPA.(2) Additional identical plugs were tumbled in unbreakable plastic bottles following the same protocol used with the stainless steel cage. Five separate laboratories performed the stainless steel cage experiments in duplicate while three laboratories performed the plastic cage tumble; also in duplicate. No chemical analysis was performed; each laboratory simply weighed the amount of material which would not pass through a 9.5 mm sieve after the 18-hour tumble was complete. This weight compared to the initial plug weight was compared with the freeze/thaw, wet/dry and unconfined compressive strength results.

All samples that had low strength and failed the wet/dry tests fell apart when tumbled in either type of container. Comparison of the cage and plastic bottle results clearly showed the plastic bottle to be superior. The results better matched the strength data, the data was more reproducible on both an intra- and inter-laboratory basis, and a plastic bottle is easier to clean. ASTM D-34 is drafting a leaching procedure similar to the TCLP which will use a nonbreakable bottle and will not require particle size reduction of the waste prior to tumbling in the extractor.

INTRODUCTION

Section 3001 of the Resource Conservation and Recovery Act (RCRA) has charged the U.S. Environmental Protection Agency (EPA) with the task of developing methodology for identifying wastes which may pose a hazard to human health and the environment. EPA accomplishes this task by identifying RCRA regulated wastes in two ways. They have developed four lists of wastes from specific and non-specific sources which must be managed as hazardous by virtue of their listing. Wastes must also be managed as hazardous if they meet one or more of four characteristics. The testing procedure required for one of these characteristics, extraction procedure toxicity, is the subject of this paper.

When RCRA was initially promulgated a procedure called the Extraction Procedure Toxicity (EP) was the required procedure of testing the characteristic of a waste to leach toxic constituents at hazardous concentrations. This procedure required that the waste be leached in an acetate solution (essentially at pH 5) for 24 hours. Following leaching the resulting solution was tested for fourteen components to determine if it was to be managed as a RCRA hazardous waste. The test further required a Structural Integrity Procedure (SIP) to see if the wastes were of sufficient strength to remain intact in the environment. If they failed they were to be milled to pass through a 9.5 mm screen prior to being leached.

Subsequent to the EP procedure, the EPA developed a new leaching procedure, the Toxicity Characteristic Leaching Procedure (TCLP), designed to facilitate analyzing leachate for a more extensive list of components. To date the TCLP has only been promulgated as a part of the Land Disposal Restriction Rule(1), but not for its original purpose, i.e., characteristic testing. Since its promulgation for Land Disposal Restrictions, EPA has proposed(2) some modifications to the test.

One of the modifications to the TCLP proposed by EPA involved eliminating the SIP and the resulting requirement to grind wastes prior to TCLP tumbling. The modified procedure would simply allow wastes to be tumbled in the extraction vessel without particle size reduction. It should be noted that wastes which were to be tested for volatiles in the Zero Headspace Extractor (ZHE) still would require particle size reduction since the method of leachate expression in the consolidated device could not accommodate large residual pieces of material. The simplifying procedure which EPA proposed for wastes tumbled in a bottle was based on an EPA contractor study by Phillips and Marsden(3) showing that wastes which were not of sufficient strength to survive in the environment also fell apart during the tumbling. Although the reverse was not always true, this result is conservative in that wastes of insufficient strength are tested in a finely divided state while many wastes which are sufficiently strong to remain intact in the environment are leached more nearly as they would be in a landfill containing the waste.

The work of Phillips and Marsden used a stainless steel cage placed inside a glass bottle to keep the bottle from breaking as the monolithic wastes were tumbled. A subcommittee of ASTM committee D-34 on Waste Disposal reviewed the EPA proposed modification and agreed to conduct a more extensive multi-laboratory evaluation of the "cage" modification. During the review of the Phillips and Marsden results, it was noted that tumbling in the stainless steel cage seemed to be too severe in that many samples that were of sufficient strength to survive in the environment were seriously degraded in the cage. Consequently the ASTM D-34 subcommittee decided to test, along with the cage, a tumbling container which would be less severe; i.e., a plastic bottle. It was deemed that a number of plastic materials would be suitable for testing for metals while TFE containers would be suitable even if the leachate were to be tested for organics. This paper describes these tests designed to compare the structural integrity of monolithic waste in the environment to their ability to survive tumbling in plastic bottles or cage modified glass bottles. If the comparison is good and the procedure is reproducible, neither the structural integrity testing nor particle size reduction should be required for TCLP testing. This will in a sense give high strength materials credit for their strength. It will eliminate the rather foolish practice of solidifying or encapsulating wastes to reduce their leachability and then testing the effectiveness of the procedure on the solidified waste after it has been milled.

EXPERIMENTAL PROCEDURE

Multiple plugs of six waste/solidification agent mixture were prepared at the Waterways Experiment Station for use in this study. Wastes used were RCRA listed waste F006 (spent solvent) and bag house dust. The wastes were solidified with either cement, cement and fly ash mixtures, kiln dust and fly ash mixtures or lime and fly ash mixture. Each waste/agent combination was solidified such that plugs of widely varying strength resulted; i.e., both high and low strength plugs were prepared. Table I identifies the waste/solidification agent used for each of the eight plug types tested.

Unconfined compressive strength tests were run in quadruplicate by Waterways Experiment Station on each type of plug following ASTM D309. The results are shown in Table 2.

Freeze/Thaw (ASTM D4842-89) and Wet/Dry (ASTM 4843-88) tests were run in triplicate (as prescribed by the method) by Waterways Experiment Station and Alberta Environmental Centre (Peter Hannak). The results of these studies are shown in Table 3. The table shows the total percent of mass lost in twelve cycles of the tests and the number of cycles which the waste passed (i.e., specimen has lost less than 30 percent of its initial weight). The results show that the wet/dry data correlates best with unconfined compressive strength. The best correlation between both tests and unconfined compressive strength seems to be the number of cycles passed rather than the cumulative mass lost.

Identical plugs of each of the solidified wastes were tumbled in a glass bottle containing a stainless steel cage following the EPA proposed procedure.(2) Since the purpose of this study was only to compare the survivability of the sample to the tumble compared to its predicted survivability in a landfill, no chemical analysis was performed on the leachate. After the tumble was complete each laboratory simply weighed the amount of sample which would not pass through a 9.5 mm sieve. Experiments were conducted in duplicate at five laboratories; Waterways Experiment Station, Alberta Environmental Centre, S-Cubed, Alcoa and Resource Consultants. The results of this data are shown in Table 4.

Much of the inter-laboratory variability in the cage tumbling can be attributed to the different size of bottles used. All laboratories used cages of the same diameter (2.5"); the Waterways cage was 6.2" high, the Alberta cage was 8.0" high and all of the others were 10.5" high. However, Waterways and Alberta used large enough bottles to allow the entire 150 g specimen to be tumbled. The other laboratories were forced to break the plug to get a small enough sample to allow a 20:1 dilution. Breaking the plugs could have weakened them leading to a greater weight loss when the smaller bottle was used. The larger plug size to cage size ratio resulting from the use of a larger bottle somewhat restricted the tumbling which could also have biased the results in the direction observed.

Identical plugs of each of the solidified wastes were also tumbled in two liter wide mouth plastic bottles following the same procedures used in the cage tumble. All laboratories had to break the plugs to obtain a small enough sample to allow for the 20:1 dilution. Experiments were conducted in duplicate at three laboratories; Dow, Monsanto and Union Carbide. The results are shown in Table 5.

CONCLUSIONS AND SUMMARY

Tables 6 and 7 compare the unconfined compressive strength, freeze/thaw and wet/dry results with the percent of speciment retained by a 9.5 mm sieve after tumbling in the cage (Table 6) and the plastic bottle (Table 7). The survivability in both cage and the plastic bottle matched the unconfined compressive strength reasonably well, although the match with the plastic bottle was better. The tumbling results did not match the freeze/thaw and wet/dry results as well, but it is important to note that, with the possible exception of waste E, plugs which do not have enough structural integrity to survive in the environment also did not survive the tumble in the TCLP bottle. Consequently it should not be necessary to grind any wastes prior to running this TCLP procedure. Conversely, some of the wastes which are probably strong enough to survive in the environment did not survive the tumble. However, the plastic bottle appears to be less severe and the results match the strength and environmental survivability better. This is particularly true if the plastic bottle results (where tumbling is not restricted) are compared to the cage results where the tumbling was not restricted by the cage; i.e., the results from Labs 6, 7 and 8.

The results of this study indicate that the plastic bottle is superior to a stainless steel cage in a glass bottle for testing the leachability of monolithic wastes which have not been subjected to particle size reduction. The results are less scattered and they match the strength data better. The plastic bottles are much easier to clean than the cage and are, of course, unbreakable. Even with use of the cage several glass bottles were broken during the course of this study.

These results have been reviewed by a subcommittee of ASTM Committee D-34, leading to the conclusion to ballot a TCLP procedure which would not require particle size reduction, strength testing or environmental structural integrity testing. All wastes would simply be tumbled in a plastic bottle in the structural form in which they are to be disposed. The procedure would otherwise be identical to EPA Method 1311. This method would not address TCLP testing for volatiles.

REFERENCES

1. Federal Register, November 7, 1986, 51, 216, 40572ff.
2. Federal Register, May 24, 1988, 53, 18792.
3. Phillips, R. B. and Marsden, P. J., S-Cubed, "Modification of TCLP to Accommodate Solidified Wastes", U.S. EPA Contract No. 68-03-1958, 1987.

TABLE 1

SOLIDIFIED WASTE SAMPLE IDENTIFICATION

Code	Waste	Solidification Agent	Relative Strength	Percent Moisture
A	F006	Cement	High	34
B	F006	Cement	Low	47
C	Bag House Dust	Cement	High	10
D	Bag House Dust	Kiln dust/fly ash	Low	17
E	F006	Lime/fly ash	High	35
F	F006	Lime/fly ash	Low	35
G	F006	Cement/fly ash	High	35
H	F006	Cement/fly ash	Low	32

TABLE 2
SOLIDIFIED WASTE UNCONFINED COMPRESSIVE STRENGTH

Waste Code	Age (days)	Avg. UCS* (psi)
A	7.00	37.0
A	14.00	62.0
A	20.96	77.0
A	28.04	54.7
A	35.04	71.1
B	7.00	8.1
B	13.96	8.1
B	21.00	14.8
B	27.96	25.3
C	6.92	303.4
C	14.04	334.1
C	20.96	354.9
C	27.96	383.6
C	35.00	468.8
D	6.88	919.7
D	13.96	1,177.1
D	20.88	1,261.9
D	27.88	1,759.2
D	35.00	1,312.3
E	7.04	58.4
E	13.96	413.4
E	20.96	636.8
E	28.00	998.6
F	7.00	6.1
F	13.96	86.5
F	21.00	251.4
F	28.00	299.7
G	6.00	106.3
G	13.04	290.3
G	20.00	411.9
G	26.96	485.3
G	34.04	439.9
H	6.00	27.5
H	13.04	99.5
H	20.00	129.5
H	26.96	172.6
H	33.92	186.6

* Unconfined Compressive Strength, ASTM Method D309; average of four broken cubes

TABLE 3

PREDICTION OF WASTE SURVIVABILITY IN THE ENVIRONMENT FREEZE/THAW:WET/DRY RESULTS

	Freeze/Thaw				Wet/Dry				
	Waterways		Alberta Env		Waterways		Alberta Env		UCS
Code	L	C	L	C	L	C	L	C	(psi)
A	95	1.7	100	2	98	8	100	2	54
B	33	5.7	100	6	43	12	100	5	25
C	3.2	12	100	4	3.1	12	2.9	12	380
D	2.8	12	21	12	2.6	12	1.7	12	1760
E	100	7.3	100	3	53	12	96	6	1000
F	78	12	100	9	26	12	31	12	300
G	97	12	85	8	25	12	33	12	490
H	100	5	100	3	100	2	100	4	173

L = Percent of the mass loss in the Wet/Dry or Freeze/Thaw test.
C = Number of cycles passed
UCS = Unconfined compressive strength at 28 days

TABLE 4

SAMPLE SURVIVABILITY IN STAINLESS STEEL CAGE TUMBLE

Code	Laboratory	% of Specimen Retained on a 9.5 mm sieve*
A	Waterways	0.00/0.00
	Alberta	0.00/0.00
	S-Cubed	0.00/0.00
	Alcoa	0.00/0.00
	Resource Consultants	0.00/0.00
B	Waterways	0.00/0.00
	Alberta	0.00/0.00
	S-Cubed	0.00/0.00
	Alcoa	0.00/0.00
	Resource Consultants	0.00/0.00
C	Waterways	0.00/0.00
	Alberta	0.00/0.00
	S-Cubed	0.00/0.00
	Alcoa	0.00/0.00
	Resource Consultants	0.00/0.00
D	Waterways	19.75/21.60
	Alberta	17.41/32.46
	S-Cubed	24.08/22.28
	Alcoa	22.46/22.53
	Resource Consultants	32.44/31.01
E	Waterways	44.31/43.71
	Alberta	113.94/115.27
	S-Cubed	12.02/13.48
	Alcoa	10.97/11.23
	Resource Consultants	15.03/14.72
F	Waterways	52.85/52.65
	Alberta	95.99/96.61
	S-Cubed	4.83/5.12
	Alcoa	5.98/7.66
	Resource Consultants	5.91/25.76
G	Waterways	37.89/38.1
	Alberta	89.34/91.16
	S-Cubed	4.22/4.19
	Alcoa	5.59/5.75
	Resource Consultants	5.56/7.08

Code	Laboratory	% of Specimen Retained on a 9.5 mm sieve*
H	Waterways	0.00/0.00
	Alberta	0.00/0.00
	S-Cubed	0.00/0.00
	Alcoa	0.00/0.00
	Resource Consultants	0.00/0.00

* Samples run in duplicate.

TABLE 5

SAMPLE SURVIVABILITY IN PLASTIC BOTTLE TUMBLE

Code	Laboratory	% of Specimen Retained on a 9.5 mm sieve*
A	Dow	0.00/0.00
	Monsanto	0.00/0.00
	Union Carbide	0.00/0.00
B	Dow	0.00/0.00
	Monsanto	0.00/0.00
	Union Carbide	0.00/0.00
C	Dow	0.00/0.00
	Monsanto	0.00/0.00
	Union Carbide	0.00/0.00
D	Dow	51.80/52.28
	Monsanto	50.10/51.99
	Union Carbide	40.63/43.62
E	Dow	27.96/29.11
	Monsanto	26.70/33.41
	Union Carbide	26.96/27.28
F	Dow	11.37/13.88
	Monsanto	15.87/12.76
	Union Carbide	8.67/9.96
G	Dow	10.78/7.02
	Monsanto	7.12/9.02
	Union Carbide	5.86/12.33
H	Dow	0.00/0.00
	Monsanto	0.00/0.00
	Union Carbide	0.00/0.00

* Samples run in duplicate.

TABLE 6

SURVIVABILITY OF SAMPLES OF SOLIDIFIED WASTE STRENGTH VS. CAGE TUMBLE

Sample No.	Freeze/Thaw Cycles Passed*	Wet/Dry Cycles Passed*	Unconfined Comp Strength	% of Specimen Retained on a 9.5 mm Sieve**				
				Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
A-h	2	5	54	0.00	0.00	0.00	0.00	0.00
B-l	6	9	25	0.00	0.00	0.00	0.00	0.00
C-l	8	12	470	0.00	0.00	0.00	0.00	0.00
D-h	12	12	1800	20.7	24.9	23.2	22.5	31.8
E-h	5	9	1000	44.0	115	12.8	11.1	14.9
F-l	11	12	300	52.8	96.3	5.0	6.8	15.8
G-h	10	12	490	38.0	90.2	4.2	5.7	6.3
H-l	4	3	173	0.00	0.00	0.00	0.00	0.00

h = high strength
l = low strength
* average of two laboratories
** average of duplicate samples

TABLE 7

SURVIVABILITY OF SAMPLES OF SOLIDIFIED WASTE STRENGTH VS. PLASTIC BOTTLE TUMBLE

Sample No.	Freeze/Thaw Cycles Passed*	Wet/Dry Cycles Passed*	Unconfined Comp Strength	% of Sample Retained on a 9.5 mm Sieve**		
				Lab 1	Lab 2	Lab 3
A-h	2	5	54	0.00	0.00	0.00
B-l	6	9	25	0.00	0.00	0.00
C-l	8	12	470	0.00	0.00	0.00
D-h	12	12	1800	52.0	51.0	42.1
E-h	5	9	1000	28.5	30.1	27.1
F-l	11	12	300	12.6	14.3	9.3
G-h	10	12	490	8.9	8.1	9.1
H-l	4	3	173	0.00	0.00	0.00

h = high strength
l = low strength
* average of two laboratories
** average of duplicate samples

THE PACIFIC BASIN CONSORTIUM FOR HAZARDOUS WASTE RESEARCH HAZARDOUS MATERIALS LEACHATE DATABASE

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BACKGROUND

The countries of the Pacific Basin are in various stages of industrial development—from well-developed industrial countries, to developing countries, and countries with essentially no development. As the industrial revolution continues or begins in these countries, clear-cut actions will be necessary to contain the hazardous wastes generated as by-products of this industrial growth. The Pacific Basin countries will be experiencing the same kinds of issues for containment of hazardous waste as are and were experienced in the more industrialized countries. Groundwater contamination will become an ever larger issue as development in the area continues, especially because significant amounts of drinking water in all of the countries comes from groundwater.

Most of the industrialized countries have been disposing of industrial wastes in landfills. Much of the information and technology needed for assuring that hazardous constituents are not leached from these wastes and enter into the groundwater has been determined by the more advanced countries. In some cases, the waste under question may be unique to the Pacific Basin country and there would be no prior experience on which to base corrective actions.

In 1987, scientists and engineers from several organizations established the Pacific Basin Consortium for Hazardous Waste Research (PBCHWR). The membership of the PBCHWR now comprises 49 member organizations from 14 different countries represented, including Australia, Canada, China, Hong Kong, Indonesia, Japan, Korea, Malaysia, Mexico, New Zealand, Philippines, Taiwan, Thailand, and the United States. The purpose of the Consortium is to address the special needs of the Pacific area with respect to hazardous wastes. The objectives of the PBCHWR are as follows:

- Identify and assess hazardous waste management problems common to the Pacific Basin,
- Foster and, where appropriate and possible, initiate research, engineering development, and pilot-scale testing of hazardous waste treatment equipment and processes,

- Create a forum for information exchange and technology transfer, and
- Provide training opportunities for technical personnel.

Other information regarding the Consortium is presented at the end of this paper.

One of the goals of the PBCHWR is to develop a systematic database which (1) contains prior information, (2) is easily accessible by researchers, and (3) can serve as a starting point for new definitive research with a specific waste in mind. To that end, the Methods Development Section of the Office of Solid Waste has assisted the PBCHWR in initiating the development of a hazardous materials leachate database. The development of a model for leaching of hazardous constituents from landfills is a goal of both EPA and PBCHWR. One of the essential steps in establishing such a model is to test the validity of the model compared to existing experimental results.

Over the years, a considerable amount of experimental information regarding leaching from landfills and in simulated laboratory studies has been generated. Unfortunately, much of this information is not readily retrievable. The objective of this project is aimed at developing a comprehensive leachability database to make the information readily available for (1) validating future landfill leaching models as well as (2) serving as a database in solving landfill disposal problems. It is vital to provide some facile means for the developed countries to share their environmental knowledge with developing countries. Such sharing will provide to the developing countries the benefit of solutions to early mistakes discovered by the developed countries.

DATABASE DEVELOPMENT

Many of the early studies were performed for a variety of purposes and incomplete information was reported. A key element of this project was to establish a recommended reporting format (1) to aid in documenting and characterizing leaching studies and (2) to be used in future leachability studies. This reporting format covers details of the conditions of the experimental studies regarding the nature of the wastes, location and type of sampling system, soil type, periods of sampling, leachate flow rate, analytes and constituents measured, temperature of waste and sampling system, analytical chemistry procedures used, and other pertinent parameters. The name of the study, geographic location, and researchers are also documented.

Because such information is now currently being generated in both the United States and in Pacific Basin countries, it is important that this information be reported in a consistent, uniform, recommended format and included in the database. This project provides an excellent mechanism for collaborative activities among all Pacific Basin countries.

The initial candidate reporting format shown in Figure 1 was distributed to EPA contractors, cognizant EPA officials, PBCHWR members, and ASTM Committee D34 on Waste Disposal participants for their comments and suggestions for modifications/ improvement. A key part of this information transmittal was a request for user interest and anticipated participation to provide leaching study results for inclusion in the database.

A separate leaching database was constructed using a dBASEIII+ compatible structure on a MS-DOS-based personal computer. This structure was selected because it is as close to an industry standard database as can be found. The revised/modified recommended reporting format was converted to a user-input form for implementation of the database.

Selected leachate studies performed under EPA contract were incorporated into the database. The initial data loading was used to test the report formats (which were designed to meet both consortium member's and EPA's needs). Hard copies of the reports were evaluated by project participants for ease of use, appropriateness, and value. Attendees at this symposium may participate in a leachate database demonstration. Interest in the use and future participation by symposium attendees will be solicited.

Future phases of this project consist of transferring database software and input forms to EPA and Consortium participants that desire to use the database. Participation by many users will facilitate the development of a comprehensive leachate database. A PC-based database data access system will be set up in later phases of the project. A bulletin-board type system will be installed for use by participants to access the database information. A program will be developed which will automatically call the database system and log each individual user onto the system. The user may then leave mail to others, upload or download database information, or chat with users on line. Ultimately, it may be necessary to transfer the database to a mainframe environment, but that step can be delayed by adding extra PCs to the system as required by increase in usage.

It is possible that eventually the volume of information will be too great for a personal computer-based system to handle. If that happens, the mainframe host could then satisfy the requirements. Development, initial testing, and initial implementation of the concept is less expensive when performed on a personal computer. The database developed and the code written will be easily transported to the mainframe system if required. Users will be able to dial up either the PC- or mainframe-based system from any telephone and upload and download data as their needs dictate.

This project has established a database which will serve both the EPA and all countries of the Pacific Basin. The easily available information will help prevent the duplication of research efforts in the leachate data field by making the results of research already conducted readily available. The information will also assist the developing countries by making available the experience of the developed countries which would otherwise be

HAZARDOUS WASTE LEACHING REPORT INFORMATION

Identifier

Project Title ____________________ Identifying No. ________

Investigator(s) ____________________ Institution ________

Date ________ Reference ____________________

Test Configuration

Waste Identity ________ Source ______ Leaching Test Method ____________

Pre-Test Characterization of Waste ____________________

____________________ Soil Type ________

Leaching Configuration ____________ Leaching Location: Lab ☐ Field Site ________

Waste/Leachate Contact Method ____________________ Waste Weight ________

Leaching Fluid: Composition ________ Volume ____________ Initial pH _____

Testing Duration ____________ Sampling Period ____________ Test Temp. _____

Leachate Flow Rate ____________ Leachate Sampling Method ____________

Analysis Procedures Used ____________________

Other Information ____________________

____

Findings

Leachate (1): Date/Time Sampled ________ Leachate Volume ________ Leachate pH _____

Composition ____________________

____

Leachate (2): Date/Time Sampled ________ Leachate Volume ________ Leachate pH _____

Composition ____________________

____

Etc. ....

Other

Post-Test Characterization (Observations) of Waste ____________________

____

____

Figure 1. Candidate Reporting Format

unavailable. This is especially important because the environment and its protection must be high on the list of priorities for developing nations. The information will be available simply by making a telephone call. The user cost will be little more than the cost of a telephone call. The use of the personal computer as a smart terminal facilities downloading and use of the information. Hard copies of the various reports will also be available to system users who do not have access to a PC.

PACIFIC BASIN CONSORTIUM FOR HAZARDOUS WASTE RESEARCH

Role of the Consortium

Production and use of hazardous materials are increasing rapidly throughout the Pacific Basin. These hazardous materials include wastes but also many useful, though toxic, chemicals. The more industrialized Pacific Basin nations have begun to assess their hazardous waste problems and to improve their site remediation and waste management practices. Because the basin is being industrialized more rapidly than any other part of the world, treatment and safe disposal of hazardous wastes are especially acute problems.

Scientists and engineers from several organizations have established the Pacific Basin Consortium for Hazardous Waste Research. The purpose of the Consortium is to address the special needs of the Pacific area with respect to hazardous waste. Its objectives are as follows:

- Identify and assess hazardous waste management problems common to the Pacific Basin.
- Foster and, where appropriate and possible, initiate research, engineering development, and pilot-scale testing of hazardous waste treatment equipment and processes.
- Create a forum for information exchange and technology transfer.
- Provide training opportunities for technical personnel.

The Consortium augments, rather than replaces or duplicates, the hazardous waste research, development, and training currently conducted by its member organizations. Because it facilitates cooperative research programs and the sharing of non-proprietary research results, the Consortium helps speed the performance and reduce the high costs of hazardous waste research for all its members, including those now at the forefront of this field.

The Consortium has the following four areas of activity:

- *Information Exchange.* The Consortium promotes information exchange through newsletters, symposia, annual technical conferences, and workshops.
- *Training.* The Consortium provides training opportunities by conducting courses, collaborating in the training activities of other organizations, and promoting the exchange of staff among member institutions for training purposes.
- *Professional Network.* The Consortium maintains contacts with a broad spectrum of professionals in the hazardous waste research community.
- *Collaborative Research.* The Consortium promotes collaborative research on hazardous waste problems in the Pacific Basin. The collaborative efforts may take the form of staff exchange among member institutions; coordinated research programs, and special research teams.

Membership in the Consortium is open to organizations located in areas either on the rim or within the basin of the Pacific Ocean. The Consortium is not an intergovernmental activity; there is no official governmental representation. Member institutions represent their own perspectives only. For further information contact:

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