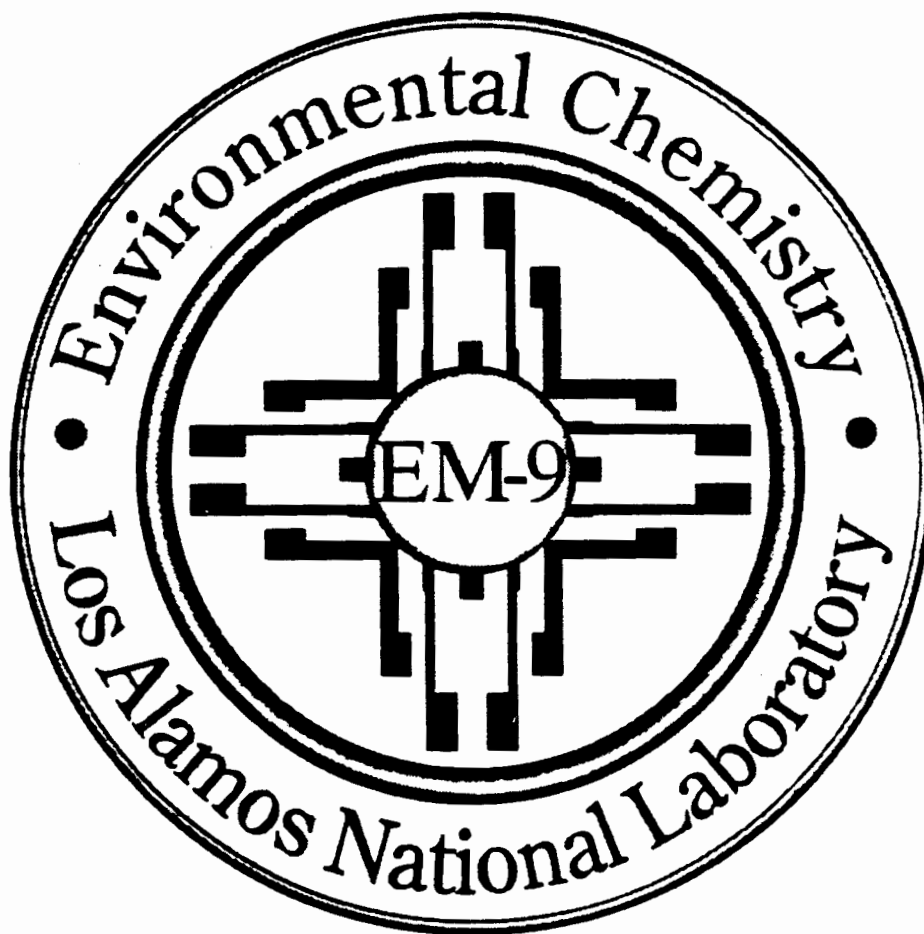


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1993

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MOBILE LABORATORY SERVICES



CHEMISTRY

RADIOCHEMISTRY

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12400

MOBILE LABORATORY SERVICES

ENVIRONMENTAL CHEMISTRY GROUP (EM-9)
ENVIRONMENTAL MANAGEMENT DIVISION
LOS ALAMOS NATIONAL LABORATORY

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MOBILE LABORATORY CONSTRUCTION AND OPERATION AT LANL

In FY91 and FY92, the Environmental Chemistry Group (EM-9) at Los Alamos constructed both a mobile radiological analysis laboratory (MRAL) and a mobile chemical analysis laboratory (MCAL) to support Los Alamos ER operations. Both mobile laboratories were tested in FY92 while supporting sampling events at Los Alamos remediation sites. The data collected during these operations were used by the Operable Unit Project Leaders for decisionmaking and by the Los Alamos Sample Coordination Facility in determining samples destination for analysis. These data did not supplant fixed laboratory analyses, but rather supported those operations. As the number of actively sampling operable units and sites at Los Alamos grow, there is a continuing need for additional mobile laboratories.

The initial MRAL was built on a bread truck-type of a base. This vehicle was obtained from GSA and was highly modified. The initial MCAL was constructed on a fifth-wheel trailer base, which was also highly modified. Since the ability to obtain GSA vehicles at Los Alamos is extremely limited, the intent will be to build the subsequent mobile laboratories strictly on fifth-wheel trailers, since they are not subject to GSA fleet allocations. Both of the next-generation mobile laboratories will share the same fifth-wheel trailer-based mechanical and electrical system. This approach should allow mass production of the laboratories. On the basic system, a specific floor plan will be prepared for both types of laboratories.

The MRAL is outfitted with a Protean Gross Alpha/Beta analyzer, which is rugged, fast, and automated. In addition, the MRAL contains a 5 inch Sodium Iodide Well Detector for gross gamma screening, an ORTEC high-purity germanium detector for gamma spectroscopy, and a Packard Liquid Scintillation Counter for tritium screening. The MRAL also contains a small hood for the limited sample preparation needed for the screening. Each screening device is automated and allows quick reports to go both to the project leader and to the sample coordination facility for sample packaging and shipment.

The MCAL is outfitted with the LANL GC/Ion Trap Detector, which runs EPA method 8260 (SW-846) for volatile organic analysis. The MCAL also contains an X-ray Fluorescence Spectrometer for metals screening. In addition, the MCAL can contain gas chromatographs with various detectors, including mass spectrometers for all types of organic screening and analysis. Also, the MCAL is equipped with a small chemical fume hood for limited sample preparation, clean water supply, dual refrigerators for samples and standards, oven for cleaning glassware, and clean air supply. Small, hand held and other screening devices have been procured and are available for support as needed. The intent with the MCAL is to provide a robust platform that can be quickly be outfitted for the specific support requested. (In essence, reaching into our toolbox for the proper tool to perform the requested job.)

Starting in FY93, a basic mobile laboratory system will be designed with two laboratory options; radiological or chemical. A package will be prepared and bids will be solicited, received, evaluated, and a company selected to construct the mobile laboratories. Also starting in FY93, instrumentation will be ordered for the laboratories since many of these are expected to have long procurement lead times. Instrumentation for many of the trailers will be dependent on Operable Unit Project Leader's needs. Since the majority of the operational documentation exists currently, little additional text will have to be prepared.

Pictures and viewgraphs of the current mobile laboratories are enclosed.

ACTION PLAN FOR LANL MOBILE LABORATORY CONSTRUCTION AND OPERATION

The following document describes LANL's proposed action plan.

A. APPROACH

The proposed approach is to use mobile laboratories to both supplement offsite analytical laboratories and to provide direct and timely support to help direct sampling activities. The mobile laboratories will be sited next to Los Alamos ER characterization sites to support sampling activities. The mobile laboratories will be used for screening samples for radioactivity or chemicals to support transportation requirements as well as contract laboratory radioactive materials license limit requirements. In addition, the mobile laboratories will be used to support directed sampling, that is, to provide near real-time data to support determination of extent of contamination or hot spots.

B. PLAN

In FY91 and FY92, the Environmental Chemistry Group (EM-9) at Los Alamos constructed both a mobile radiological analysis laboratory (MRAL) and a mobile chemical analysis laboratory (MCAL) to support Los Alamos ER operations. Both mobile laboratories were tested in FY92 while supporting sampling events at Los Alamos remediation sites. The data collected during these operations were used by the Operable Unit Project Leaders for decisionmaking and by the Los Alamos Sample Coordination Facility in determining samples destination for analysis. These data did not supplant fixed laboratory analyses, but rather supported those operations. As the number of actively sampling operable units and sites at Los Alamos grow, there is a continuing need for additional mobile laboratories. Therefore, EM-9 proposes to construct 7 new MRALs and 7 new MCALs in FY93 to support those operations. EM-9 will use the lessons learned from the previous sampling events to improve both the ruggedness and uptime of the instrumentation, while also improving the integration of the mobile laboratories into the total operation.

The initial MRAL was built on a bread truck-type of a base. This vehicle was obtained from GSA and was highly modified. The initial MCAL was constructed on a fifth-wheel trailer base, which was also highly modified. Since the ability to obtain GSA vehicles at Los Alamos is extremely limited, the intent will be to build the subsequent mobile laboratories strictly on fifth-wheel trailers, since they are not subject to GSA fleet allocations. Both of the next-generation mobile laboratories will share the same fifth-wheel trailer-based mechanical and electrical system. This approach should allow mass production of the laboratories. On the basic system, a specific floor plan will be prepared for both types of laboratories.

Starting in FY93, a basic mobile laboratory system will be designed with two laboratory options; radiological or chemical. A package will be prepared and bids will be solicited, received, evaluated, and a company selected to construct the mobile laboratories. Also starting in FY93, instrumentation will be ordered for the laboratories since many of these are

expected to have long procurement lead times. Instrumentation for many of the trailers will be dependent on Operable Unit Project Leader's needs. We expect to have the basic trailers received approximately 3 per month, starting in May and finishing in September. Once the base trailers are received, we expect that it will require approximately 4 weeks to install the equipment and another 2 weeks to shakedown each trailer. Therefore, we expect that we will have functioning laboratories 6 to 8 weeks after receipt of the base trailers. We will also need to obtain two more towing vehicles to allow timely movement of the laboratories.

Since the majority of the operational documentation exists currently, little additional text will have to be prepared. However, significant time will be required to train new mobile laboratory analysts. We will start to solicit analysts and expect to start training the first 6 analysts in January, 1993. This training will take approximately 3 months. In addition, we will use these personnel to help install and checkout instrumentation as part of their training. The second set of analysts will be obtained in May, 1993 and complete training in August, 1993. The third set of analysts will be obtained in August, 1993, and complete training in November, 1993.

The basic work breakdown structure and schedule are shown in Figure 1.

C. OUTYEARS

As the remainder of operable units are activated, it is expected that 8 mobile laboratories (5 MRAL and 3 MCAL) will be sufficient to support all operations.

D. CONTINGENCIES

Potential delays in selection of a contractor to construct the basis systems will cause slippage of the entire schedule. Since we have tested the initial design of the fifth-wheel trailer, minor changes in design are probable but are not expected to affect the schedule adversely. Delays in construction of the basic systems could also slip the schedule, however, we will work closely with the selected contractor to minimize delays. Delays in receipt of the instrumentation can also impact the schedule, but we will start procurement very early in FY93 to minimize this potential. Finally, delays in obtaining needed staffing will delay not only the start of operation, but could also delay installation of instrumentation and checkout of the laboratories, since we intend to use the new staff for the installation and checkout process.

POTENTIAL MOBILE LABORATORY FLOW

DOE HEADQUARTERS

POLICY OF MOBILE LAB USE
FUNDING FOR MOBILE LABS

VARIOUS ER PROGRAMS

SCREENING AND ANALYSIS
NEEDS AND REQUIREMENTS

LANL ENVIRONMENTAL CHEMISTRY GROUP

DESIGN AND SPECIFICATIONS
FOR MOBILE LABS

USER OR LANL ENVIRONMENTAL CHEMISTRY GROUP

PROCUREMENT AND
INSTALLATION

USER DEPLOYMENT

CHOICE OF INSTRUMENTATION
AND METHODS

MOBILE LABORATORY DETECTION LIMITS AND SCREENING ACTION LEVELS

In this section, detection limits for the instrumental methods currently available in the Mobile Chemical Analysis Laboratory (MCAL) and the Mobile Radiochemical Analysis Laboratory (MRAL) are tabulated and compared to estimates of the Los Alamos National Laboratory Screening Action Levels (SAL) for soils. It is important to make several notes:

- a) These methods are adaptations of fixed-base laboratory methods, modified to meet rapid turnaround times needed in the field. Detection limits, precision, accuracy, the level of QC and the level of data evaluation will always be better at EM-9 fixed-base laboratories.
- b) Detection limits are estimated instrument detection limits, and are based on 1992 experience. New detection limits will be obtained for 1993 and issue in the next update.
- c) Somewhat better detection limits may be obtained for these methods, if the customer requires them. This will usually be done at the cost of sample throughput, and the cost/benefit ratio will eventually make it more economical to use fixed-base laboratories.
- d) Similar arguments apply to QC frequency, data evaluation and to archival.
- e) The Screening Action Levels cited may not be up-to-date.
- f) New instruments will be added to the mobile laboratories in 1993 and 1994 (e.g. DC-ARC-CID Spectroscopy for Metals), which will result in significantly better detection limits.

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TARGET	SAL PPM	INORGANIC ANALYTES		ICPES	Laboratory	
		Field			AA	FIA
		XRF				
	PPM	PPM				
ANTIMONY	32	5	✓	3		
ARSENIC	0.4	8	✓	2	0.2	
BARIUM	5600	6	✓	0.1		
BERYLLIUM	0.16	ND	✓	0.05		
CADMIUM	0.4	4	✓	0.5	0.01	
CHROMIUM	400	9	✓	0.5		
COPPER	3000	6	✓	0.5		
LEAD	500	3	✓	4		
MANGANESE	8000	12	✓	0.1		
MERCURY	24	10	✓		0.02	
NICKEL	1600	13	✓	1.5		
SELENIUM	400	10	✓	3		
SILVER	400	8	✓	0.7		
THALLIUM	6.4	10	✓	2	0.2	
URANIUM	240	7	✓			
VANADIUM	560	10	✓	0.7		
ZINC	24000	4	✓	0.2		
CYANIDE	1600	ND				50

		ORGANIC ANALYTES					
		Field					
VOLATILES	SAL(PPM)	GC/MS(PPB)	GC/HALL/PID (ppb)				
ACETONE	8000	50	50				
BENZENE	0.67	20	10				
BROMODICHLOROMETHANE	5.4	20	10				
BROMOFORM	89	20	10				
BROMOMETHANE	0.43	20	10				
MEK	2100	50	50				
CARBON DISULFIDE	7.4	20	10				
CARBON TET	0.21	20	10				
CHLOROBENZENE	67	20	10				
CHLOROETHANE	3300	20	10				
CHLOROFORM	0.21	20	10				
CHLOROMETHANE	6.4	20	10				
DIBROMOCHLOROMETHANE	83	20	10				
1,1-DICHLOROETHANE	410	20	10				
1,1-DICHLOROETHENE	0.59	20	10				
1,2-DICHLOROETHANE	0.2	20	10				
1,2-DICHLOROETHENE	800	20	10				
1,2-DICHLOROPROPANE	6.5	20	10				
CIS-1,3-DICHLOROPROPENE	0.17	20	10				
TRANS-1,3-DICHLOROPROPENE	0.17	20	10				
ETHYL BENZENE	3100	20	10				
2-HEXANONE		20	50				
2-METHYL-2-PENTANONE	510	50	50				
METHYLENE CHLORIDE	5.6	50	10				
STYRENE	16000	20	10				
1,1,2,2-TETRACHLOROETHANE	3.9	20	10				
1,1,2,2-TETRACHLOROETHENE	5.9	20	10				
1,1,1,2-TETRACHLOROETHANE	890	20	10				
1,1,1-TRICHLOROETHANE	1000	20	10				
1,1,1,2-TRICHLOROETHANE	6.3	20	10				
1,1,2-TRICHLOROETHENE	3.2	20	10				
VINYL CHLORIDE	0.013	20	10				
XYLENES	160000	20	10				

	ORGANIC ANALYTES						
	Field						
SEMIVOLATILES	SAL(PPM)	GC/MS(PPM)	GC/ECD/FID(PPM)				
ACENAPHTHENE	4800	5	1				
ACENAPHTHYLENE		5	1				
ANTHRACENE	24000	5	1				
BENZO(a)ANTHRACENE		5	1				
BENZO(b)FLUOROANTHENE		5	1				
BENZO(k)FLUOROANTHENE		5	1				
BENZO(ghi)PERYLENE		5	1				
BENZO(a)PYRENE	0.1	5	1				
BIS(2-CHLOROETHOXY)METHANE		5	1				
BIS(2-CHLOROETHYL)ETHER	0.13	5	1				
BIS(2-ETHYLHEXYL)PHTHALATE	50	5	1				
4-BROMOPHENYL-PHENYLETHER		5	1				
BUTYL BENZYL PHTHALATE	16000	5	1				
CARBAZOLE	35	5	1				
4-CHLOROANILINE	320	5	1				
4-CHLORO-3-METHYLPHENOL	160000	5	1				
2-CHLORONAPHTHALENE	6400	5	1				
2-CHLOROPHENOL	400	5	1				
4-CHLOROPHENYL PHENYL ETHER		5	1				
CHRYSENE		5	1				
DIBENZ(a,h)ANTHRACENE		5	1				
DIBENZOFURAN		5	1				
DI-n-BUTYLPHTHALATE	8000	5	1				
1,2-DICHLOROBENZENE	1600	5	1				
1,3-DICHLOROBENZENE		5	1				
1,4-DICHLOROBENZENE	290	5	1				
1,4-DICHLOROBENZIDINE	1.6	5	1				
2,4-DICHLOROPHENOL	240	5	1				
DIETHYLPHTHALATE	64000	5	1				
2,4-DIMETHYLPHENOL	1600	5	1				
DIMETHYL PHTHALATE	80000	5	1				
4,6-DINITRO-2-METHYLPHENOL		25	1				
2,4-DINITROPHENOL	160	25	1				
2,4-DINITROTOLUENE	1	5	1				
2,6-DINITROTOLUENE	1	5	1				
DI-n-OCTYL PHTHALATE	1600	5	1				
FLUROANTHENE	3200	5	1				
FLUORENE	3200	5	1				
HEXACHLOROBENZENE	0.44	5	1				
HEXACHLOROBUTADIENE	90	5	1				
HEXACHLOROCYCLOPENTADIENE	560	5	1				
HEXACHLOROETHANE	80	5	1				
INDENO(1,2,3-cd)PYRENE		5	1				
ISOPHORONE	7400	5	1				
2-METHYLNAPHTHALENE		5	1				
2-METHYLPHENOL	4000	5	1				
4-METHYLPHENOL	4000	5	1				
NAPHTHALENE	3200	5	1				
2-NITROANILINE	4.8	25	1				
3-NITROANILINE		25	1				
4-NITROANILINE		25	1				
NITROBENZENE	5.3	5	1				
2-NITROPHENOL		25	1				
4-NITROPHENOL		25	1				
2,6-DISODIPHENYLAMINE	140	5	1				

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N-NITROSO-di-N-DIPROPYLAMINE	0.1	5	1				
OXYBIS(1-CHLOROPROPANE)	100	5	1				
1,2,4-TRICHLOROPHENOL	5.8	5	1				
PHENANTHRENE		5	1				
PHENOL	48000	5	1				
PYRENE	2400	5	1				
1,2,4-TRICHLOROBENZENE	160	5	1				
2,4,5-TRICHLOROPHENOL	8000	5	1				
2,4,6-TRICHLOROPHENOL	64	5	1				

ERSALS2.XLS

Radionuclides							
Field							
Rad	SAL (pCi/g)	SAL MESA (pCi/g)	gross a/b	gross G	LSC	GSPEC	Lab*
AM-241	18.6	22	55/24			1	0.003
C-14	244000	470000					est 0.05
CO-57	32.1	40		4			0.5
CO-60	0.72	0.9		4			0.5
CS-134	1.5	1.9		4			0.5
CS-137	3.2	4		4			0.2
H-3	7810000	15000000			5		** 0.05
I-129	2.76	41		U			est 10
MN-54	2.75	3.4		4			0.5
NA-22	1.05	1.3		4			0.5
PU-238	22.48	27	55/24				0.003
PU-239	20.15	24	55/24				0.002
RA-226	0.63	0.73		4			0.5
RU-106	11.7	15		4			5
SR-90	4.46	8.9					2
TH-232	0.72	0.88	55/24				0.01
U-233	69.9	86	55/24				0.01
U-235	14.75	18	55/24				0.01
U-238	47.81	59	55/24				0.01
*Most sensitive methods in the fixed-base laboratories at EM-9, plus extensive chemical and ion exchange concentration and much longer count times to achieve markedly better detection limits.							
** Assumes 10% soil moisture							
est Not currently done by EM-9, d.I. would need to be determined							
U Under study							

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INORGANIC ANALYTES		Proposed Field		Laboratory	
TARGET	SAL PPM	arc/cid	ICPES	AA	FIA
ANTIMONY	32	1	3		
ARSENIC	0.4	10	2	0.2	
BARIUM	5600	0.1*	0.1		
BERYLLIUM	0.16	0.1	0.06		
CADMIUM	0.4	0.1	0.5	0.01	
CHROMIUM	400	1*	0.5		
COPPER	3000	0.2*	0.5		
LEAD	500	1	4		
MANGANESE	8000	1*	0.1		
MERCURY	24	0.5		0.02	
NICKEL	1600	3*	1.5		
SELENIUM	400	2	3		
SILVER	400	0.1	0.7		
THALLIUM	6.4	0.2	2	0.2	
URANIUM	240	100*			
VANADIUM	560	1*	0.7		
ZINC	24000	0.1	0.2		
CYANIDE	1600				50

Mobile Chemical Analysis Laboratory Instrumentation Systems

1.) Purge and Trap, Gas Chromatograph/Mass Spectrometer. This instrument combines a custom designed purge and trap-gas chromatograph with a Hewlett-Packard (HP) 5971B quadrupole mass spectrometer. The instrument is capable of analyzing soil, sludge, and water matrices for volatile organic constituents. A custom designed computer system controls the hardware and data acquisition of the instrument.

2.) An HP chromatograph/mass spectrometer is deployed for the analysis of semi-volatile organic compounds. This instrument is controlled by a PC running the Hewlett-Packard Enviroquant software. A Hewlett-Packard autosampler is utilized to allow unattended analyses.

3.) An electron capture detector mounted on another HP gas chromatograph allows the detection of halogenated semi-volatile compounds such as poly-chlorinated biphenyls (PCBs). A flame ionization detector on the same gas chromatograph can also be used to identify specific classes of petroleum hydrocarbons. This instrument is also equipped with an autosampler to allow unattended operation.

4.) An infra-red spectrophotometer is in the process of being acquired to allow analysis for total petroleum hydrocarbons.

5.) Sample Hood. This hood provides space for sample preparation while providing the user with some personal protection from exposure to a variety of radiological and organic compounds that could potentially be found in the sample matrix.

6.) Sample Extraction Apparatus. A variety of apparatus are used to effect the extraction of organic compounds from the sample matrices. The laboratory is capable of effecting extractions of a variety of organic compounds from solid matrices. The extraction capabilities include sample clean-up and concentration.

7.) Uninterrupted Power Supply (UPS). This unit provides uninterrupted, highly regulated power to all of the computer control systems and the analytical instruments. In the event of a shore-based or generator power failure, the UPS minimizes damage to the instruments and prevents data loss.

8.) Temperature Control Systems. Propane heat is provided as well as two electrically powered heating systems. Furthermore, the trailer is equipped with two electrically powered air conditioners. Power is supplied either by generator, or shore-based power.

9.) Refrigeration and Oven Systems. Two refrigerators with integral freezer compartments are used, one for sample preservation and storage, and the other for analytical standard storage. The oven is used to bake the analytical and sample preparation glassware after cleaning.

10.) Water Purification System. A Millipore Milli-Q water purification system delivers ultra-pure organic free water. This water is used as a wetting agent to increase the efficiency of analyte extraction in purge and trap volatiles analysis, and is used to ensure the cleanliness of all glassware used in extraction procedures and volatiles analysis.

11.) While this van will usually be used in conjunction with the radiation van, hand-held radiation monitoring equipment is included to provide an additional measure of safety for the analysts.

12.) Emergency battery powered backup lighting is available in the event of a power failure.

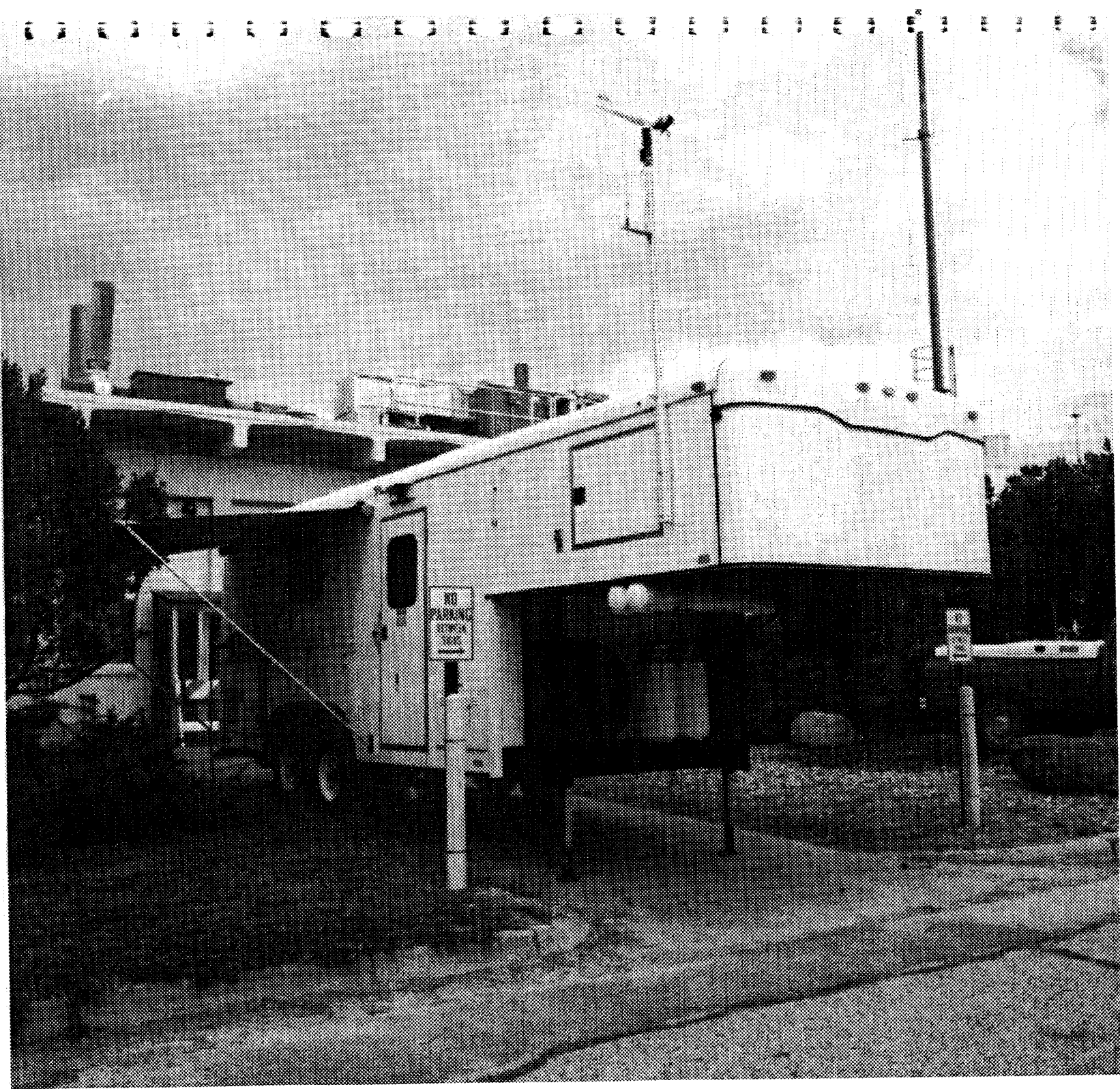
13.) Compressed air is available through a zero air compressor mounted onboard the mobile laboratory.

CHEMISTRY

CHEMISTRY

MOBILE
CHEMICAL
ANALYSIS
LAB

EQUIPMENT





VOA

**VOLATILE ORGANIC COMPOUNDS IN SOIL AND SEDIMENT:
CAPILLARY COLUMN TECHNIQUE—GC/MS
MOBLIE LABORATORY METHOD**

Analyte: Volatile organic compounds	Method No.: MLO720
Matrix: Soil or sediment	Procedure: Purge/Trap GC/MS, Capillary column
Effective Date: 02/01/90	Author: Laura Kelly Matthew Monagle

SAFETY NOTE: Before beginning this procedure, read all the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3. of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Materials 12.3 and 12.4 for proper waste disposal practices.

1. Principle of Method

- 1.1. Volatile organic compounds are purged from the sample onto a sorbent material. These analytes are then desorbed from the sorbent material into a gas chromatograph (GC). The column is temperature-programmed and analytes are separated and detected with a mass spectrometer (MS).
- 1.2. Qualitative identification is performed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriately selected ion produced by that compound to the MS response for another ion produced by an internal standard.

2. Analytes and Limit of Quantitation

Internal Standards

Surrogates

Pentafluorobenzene	1,2-Dichloroethane-d ₄
1,4-Difluorobenzene	Toluene-d ₈
1,4-Difluorobenzene-d ₄	4-Bromofluorobenzene
Chlorobenzene-d ₅	

- 2.1. Table I is a list of volatile organic compounds and their reporting limits of quantitation (LOQs). (Tables I-IV are found at the end of this procedure.)
- 2.2. Table II lists the purgeable organic compounds and their characteristic masses. The volatile internal standards with the corresponding analytes are listed in Table III.

3. Interferences

- 3.1. Impurities in the purge gas and solvent vapors in the laboratory can contaminate samples. The analytical system must be demonstrated to be free from contamination under the condition of the analysis by running laboratory reagent blanks (i.e., method blanks). The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device must be avoided.
- 3.2. Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. A trip blank, prepared from reagent water, and carried through the holding period and the analysis protocol, serves as a check on such contamination. One trip blank per request group should be analyzed.
- 3.3. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, all following samples must be reanalyzed if carryover is suspected, or a method blank should follow until the contamination has been eliminated.

4. Collection and Storage of Samples

- 4.1. Soil samples are collected in 40-mL screw-cap VOA vials with Teflon-lined silicone septa. The vials and septa should be washed with soap and water, rinsed with distilled deionized water, placed in a muffle furnace or oven, and dried at 70°C for approximately 1 h.
- 4.2. VOA vials for samples with solid or semisolid (sludges) matrices should be filled as completely as possible. The vials should be tapped lightly as they are filled to try to eliminate as much free air space as possible. Two VOA vials should be filled at each sample location.
- 4.3. All samples must be refrigerated between 0 and 4°C.
- 4.4. The holding time for soil samples is 14 days from the date of collection.

5. Apparatus

- 5.1 Purge and trap configuration.
 - 5.1.1. A purge-and-trap apparatus as detailed in SW-846 Method 5030 is used. Applicable operating parameters are determined by the analyst (adsorbent trap selection, purge time, desorb time and temperature, and bake time and temperature).

5.2. Gas chromatograph/mass spectrometer/data system.

- 5.2.1. The GC must be temperature-programmable and should be equipped with adjustable differential flow controllers so that the column flow rate will be reproducible throughout desorption and temperature program operation. The GC is interfaced to the MS with a jet separator or is directly coupled.**
- 5.2.2. Gas chromatographic column: Supelco VOCOL, 105-m x 0.53-mm x 3.0- μ m film thickness or equivalent.**
- 5.2.3. Mass spectrometer: Mass-spectral data are obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer scans from 35 to 300 amu every 1 s or less and must produce a mass spectrum that meets all criteria in Step 7.1.1 when 50 ng of 4-bromofluorobenzene is introduced into the GC.**
- 5.2.4. Data system: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundances in any EICP between NIST and/or EPA mass-spectral libraries.**

5.3. Microsyringes: 10-, 25-, 100-, and 500- μ L, for injecting the appropriate standards into the reagent water.

5.4. Syringes: 5- or 25-mL, for measuring the required aliquot of reagent water.

5.5. Balance: analytical, capable of accurately weighing 0.001 g.

5.6. Micro reaction vessels: 2- or 3-mL with Teflon-lined miniert valves, for the storage of stock or secondary standard solutions.

5.7. Disposable Pasteur pipettes: used for transferring stock or secondary standard solution from the volumetric flask to the micro reaction vessels.

6. Reagents/Standards

6.1. Methanol (CH_3OH). Pesticide quality or equivalent, demonstrated to be free of analytes. Must be stored apart from other solvents.

6.2. Reagent water. Must be purged with nitrogen for at least 30 min before use. Water must be free of interferents at the limit of quantitation (LOQ).

Alternatively, HPLC grade water may be purchased. Purity of water used must be verified by GC/MS analysis.

- 6.3. Stock solutions. All instructions for preparation of stock solutions and dilutions are in the VOA standard preparation notebook located in Room 115, TA-59. See Table IV.
- 6.4. Instructions for storage of all standards, and expiration dates are found in the VOA standards preparation notebook. Expiration dates are to be strictly enforced.
- 6.5. Surrogate standards. The surrogates used are 1,2-dichloroethane- d_4 , toluene- d_8 , and 4-bromofluorobenzene.
- 6.6. Internal standards. The internal standards used are chlorobenzene- d_5 , 1,4-difluorobenzene, 1,4-dichlorobenzene- d_4 , and pentafluorobenzene.
- 6.7. 4-Bromofluorobenzene (BFB) standard. A standard solution containing 50 ng/ μ L of BFB in methanol is used for verifying the tune of the MS.
- 6.8. Calibration standards. Secondary calibration standards are prepared from calibration stock standards. The solutions are prepared in 5- or 25-mL aliquots of reagent water.
- 6.9. Matrix spiking standards. Matrix spiking standard is prepared from volatile organic compounds which are representative of the compounds being investigated. The compounds used are 1,1-dichloroethene, benzene, trichloroethene, toluene, and chlorobenzene. A 10- μ L aliquot of the matrix spiking standard is used for 5-mL samples (50- μ L aliquot for 25-mL aqueous samples).

7. Calibration

- 7.1. See Step 9.1 for explanation of Quality Control requirements in the tiered structure.
- 7.2. Initial calibration, Tiers 2 & 3.
 - 7.2.1. Each GC/MS system must be hardware-tuned to meet the criteria listed below for a direct injection or purging of 50 ng of 4-bromofluorobenzene. Analyses can not proceed until the criteria are met.

<u>Mass</u>	<u>Relative Abundance Criteria</u>
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	≥95% but ≤101% of mass 174
177	5 to 9% of mass 176

7.2.2. Five system performance check compounds (SPCCs) are checked for a minimum average response factor (RF): chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check overall instrument performance and/or degradation caused by contaminated lines or active sites in the system.

7.2.2.1. Chloromethane. This compound is easily lost as a result of fast purge flow, or because the stock or working calibration standard (VOC #6 mix only) is degrading. The purge gas (helium) flow rate should be 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform.

7.2.2.2. Bromoform. This compound will most likely be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer line may adversely affect response.

7.2.2.3. Tetrachloroethane and 1,1-dichloroethane. These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.3. Continuing calibration check (CCC) compounds are used as a measure of the linearity of the response factors. The percent relative standard deviation (%RSD) is checked for the CCCs. These compounds are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride. The maximum %RSD for these compounds is 30%. The %RSD for all analytes should be < 30%.

7.3. Continuing daily calibration, Tiers 1, 2 & 3.

7.3.1. Before samples are analyzed, inject or purge 50 ng of the 4-bromofluorobenzene (BFB) standard (1 μ L of the 25- μ g/mL

4-bromofluorobenzene solution for direct injection and 10 μ L of the 25- μ g/mL 4-bromofluorobenzene into 5 mL of reagent water for purging). The resultant mass spectra for BFB must meet all the criteria given in Step 7.1.1. This procedure must be performed every 12 h of analysis.

- 7.3.2. Before samples are analyzed, the initial calibration curve for each compound must be checked and verified once every 12 h by analyzing a 50-ng/mL continuing calibration standard and checking the SPCCs and CCCs.
- 7.3.3. The minimum response factor for the SPCCs must be 0.300 (0.250 for bromoform). Some possible problems are standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.
- 7.3.4. The CCCs are used to check the validity of the initial calibration by calculating the percent difference between the average response factor from the initial calibration and the response factor from the current verification check standard. If the percent difference for any compound is 20%, the laboratory should consider this a warning limit. If the percent difference for each CCC is <25%, the initial calibration is assumed to be valid. If this criterion is not met (>25% difference) for any one CCC, corrective action must be taken. The percent difference for all analytes should be less than or equal to 25%. Corrective action can include, but is not limited to, reanalysis of the verification check standard, cutting a portion of the column, or using a new working calibration standard. If a source of the problem cannot be determined after corrective action has been taken, a new five-point calibration (initial calibration) must be generated. See Step 7.1. Both SPCC and CCC criteria must be met before quantitative sample analysis begins.

8. Procedure

8.1. Low- level soil analysis.

8.1.1. BFB tuning criteria and continuing calibration criteria must be met before analysis of samples can begin.

8.1.2. Parameters.

Precision Autosampler

Purge flow: 35 mL/min

Purge temp: 40°C

Soil Program for all samples

Standard: Yes

Line Heat: 100

O I Sample Concentrator

Purge time: 8-10 min

Desorb Preheat: 20°C

Desorb time: 2.00 min

Desorb temp: 180°

Trap Bake time: 14.0 min

Sample Heat: 40	Bake temp: 215
Preheat: 30 sec.	Transfer line: 135
Water volume: 5 mL	Valve temp: 125
Pre-purge: 0	
Purge time: 8.0 min	
Flushes: 1	
Soil Stir: Yes	
Desorb time: 2.0 min	
Water Trap Volume: 0	

- 8.1.3. A sample batch typically consists of a BFB, continuing calibration, reagent water blank, and samples up to the 12-h limit on BFB tune. Samples are set up as described in the following sections.
- 8.1.4. Assemble the bottom portion of the autosampler vial. Place 5 g of soil or sludge on top of the frit of the autosampler vial. Weigh the vial. Record the exact weight. Add a stirring bar and seal the vial. If percent moistures have not been done, see Section 8.3 for instructions on percent moisture determinations. All data is to be recorded on the VOA benchsheet.
- 8.1.5. For each sample analyzed, including BFB and continuing calibrations, an entry must be made in the sample injection log associated with each instrument. This entry must be made within 24 h of data acquisition. This entry includes factors such as date and time sample was run, internal standard values, and surrogate recovery.
- 8.1.6. If the initial analysis of a sample shows a concentration of analytes that exceeds the initial calibration range (higher than 200 $\mu\text{g/kg}$), the sample will need to be reanalyzed using an aliquot of <5 g but not <1 g. If compound saturation still occurs with a 1-g aliquot, a medium-level analysis is necessary (see Section 8.2). Secondary-ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, the analysis must be followed by a blank water analysis. Sample analysis may not resume until a blank can be analyzed and found free of interferences. If this occurs during an automated run, reanalyze all following samples if carryover from the saturated compound is suspected.
- 8.1.7. If one or more of the surrogate spiking compounds are not within the control limits and/or the internal standard areas are +100%/-50% of the continuing calibration in a sample, that sample should be reanalyzed. See Section 9.2 for details.
- 8.1.8. A matrix spike (MS), matrix spike duplicate (MSD), and matrix spike control (MSC) may be analyzed with every analytical batch, depending

upon which QC Tier is being used. A sample submitted by a customer will be used as the matrix medium. Ten microliters of the matrix spike mixture is injected into 5 mL of reagent water and then added to a 5-g sample. See Step 8.1.5.

- 8.1.9. If a trip, field, or holding blank is submitted with the soil samples, the sample should be prepared and analyzed as a method blank. The sample is analyzed with the associated soil samples using the same initial and continuing calibration. The surrogate recoveries for the trip, field, or holding blank should meet the control limits set for soil analysis.

8.2. Medium-level soil analysis.

- 8.2.1. The medium-level soil method is based on extracting the soil or sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the surrogate and internal standard. This method is used when saturation occurs or would occur during analysis of a 1-g sample.

NOTE: Steps 8.2.2 and 8.2.3 must be performed rapidly to avoid loss of volatile organics.

- 8.2.2. To avoid the possible loss of volatile compounds, gently mix the contents of the sample container including any supernatant liquids with a narrow metal spatula. Using a top-loading balance, weigh 5 g of sample (wet weight) into a tared 40-mL vial. Record the actual weight to the nearest 0.1 g.
- 8.2.3. Quickly add 5.0 mL of methanol to the vial. Cap and shake for 2 min.
- 8.2.4. If the initial analysis of a sample shows a concentration of analytes that exceeds the initial calibration range (higher than 200 $\mu\text{g/kg}$), the sample will need to be diluted and reanalyzed. Secondary-ion quantitation is allowed only when there are sample interferences with the primary ion. If a primary-ion saturation occurs during an automated run, all following samples should be reanalyzed if carryover from the saturated compound is suspected.
- 8.2.5. For a matrix spike in the medium-level sediment or soil samples, add 10.0 μL of matrix spike solution to the 5-mL syringe containing the methanol extract.

- 8.3. Determine percent moisture on all samples that are not radioactive, biohazards, or where an insufficient quantity of sample was submitted. If a hazard prevents this determination, document this and include in the data packet. Determine percent moisture as follows:

- 8.3.1. Weigh an empty aluminum weighing pan. Record weight.
- 8.3.2. Add approximately 5 g of sample and reweigh. Record weight.
- 8.3.3. Place in a drying oven at 80-100°C for at least 24 h. Cool and reweigh, recording dry weight.
- 8.3.4. Percent moisture is calculated by:

$$\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

9. Quality Control

- 9.1. The Quality Control requirements are defined in a tiered structure as follows:

Tier 1: 1-point calibration every day.
1 method blank every day.

Tier 2: 3-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank every day.

Tier 3: 5-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank per analytical batch.
Blind QC samples at a rate of no more than 10%.
Matrix spike and matrix spike duplicate for each analytical batch.
12-h clock for tune check and daily check standard.

- 9.2. Control limits.

9.2.1. The control limits that follow are applicable only to the QC Tier requested for each analysis.

9.2.2. The method blank must be free of any target volatile organic components at or above the limit of quantitation (LOQ) with the exception of acetone, methylene chloride, 2-butanone, and toluene. These compounds can be detected in the method blank up to 5 times their LOQ.

9.2.3. The following surrogates are spiked into each sample and analyzed as a measure of analyte recovery: 1,2-dichloroethane-d₄, toluene-d₈, and 4-bromofluorobenzene. If one or more of the surrogate spiking

compounds are not within the control limits, those samples should be reanalyzed. If the reanalysis demonstrates similar results and the surrogate recoveries in the associated method blank are within the control limits, the out-of-control situation could be attributed to matrix effect and the results from the initial analysis should be reported. If the reanalysis of the sample has surrogate recoveries within the control limits, the out-of-control condition could be due to analyst error or to a degradation of the surrogate spiking mix. In this case the results from the reanalysis should be reported.

SURROGATE RECOVERY CONTROL LIMITS

1,2-Dichloroethane-d ₄	70-121%
Toluene-d ₈	81-117%
4-Bromofluorobenzene	74-121%

9.2.4. A matrix spike and a matrix spike duplicate are analyzed under Tier 3 QC requirements. Spikes are run at a frequency of 10% for each respective matrix. The data is interpreted in terms of percent recovery and relative percent difference (RPD). The control limits for percent recovery and RPD are generated from the historical data of each respective matrix.

9.2.5. "Blind" QC samples are analyzed as required under the tier structure. Those analyses requiring blind QCs must be run at a frequency of 10% of the total samples analyzed per matrix. These samples are analyzed in exactly the same manner as submitted samples.

10. Data Interpretation

10.1. Qualitative analysis.

10.1.1. An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of the compound from a standard (standard reference spectrum). The standard reference spectrum is obtained through analysis of a calibration standard. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention time (RRT) as that component in the daily standard; and (2) correspondence of the mass spectra of the sample component and the standard component.

10.1.1.1. The sample component RRT must compare within ± 0.06 units of the RRT of the standard component in the daily calibration. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by

using extracted ion current profiles (EIPCs) for ions unique to the component of interest.

- 10.1.1.2. All ions present in the standard mass spectrum at a relative intensity >10% must be present in the sample spectrum. The relative intensities of these ions must agree within $\pm 20\%$ between the standard and sample spectra.

EXAMPLE. For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30% and 70%.

- 10.1.2. For samples containing components not associated with the calibration standards (non-target volatile organic components), a library search may be made for the purpose of tentative identification. Ten organic compounds of greatest concentration which are not identified as part of the calibration standard may be identified. Non-target volatile organic components with a response of <10% of the nearest internal standard are not required to be searched. Comparison of sample spectra with the spectra from the library searches will assign a tentative identification.

- 10.1.2.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

- 10.1.2.2. The relative intensities of the major ions should agree within $\pm 20\%$.

EXAMPLE. For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.

- 10.1.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

- 10.1.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

- 10.1.2.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination of coeluting peaks.

If the compound does not meet the identification criteria listed above, the compound shall be reported as unknown.

10.2. Quantitative analysis.

10.2.1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion (see Table II). The compound will be quantitated using an internal standard technique. The internal standard used will be the one nearest the retention time of that of a given analyte.

10.2.1.2. The concentration of each identified analyte in the sample is calculated as follows:

$$\text{concentration } (\mu\text{g/kg}) = \frac{(Ax) (Is)}{(Ais) (RF) (W_s) (D)} ,$$

where Ax = area of characteristic ion for compound being measured,

Is = amount of internal standard injected (ng),

Ais = area of characteristic ion for the internal standard,

RF = response factor for compound being measured,

W_s = weight of sample extracted (g) or purged, and

D = $\frac{100 - \% \text{ moisture}}{100}$.

10.2.2. Where applicable, an estimate of concentration for non-target volatile organic components in the sample should be made. The areas Ax and Ais (defined in Step 10.2.1.2) should be from the total ion chromatogram, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. The nearest internal standard free of interferences is used.

10.2.3. Results are reported without method blank correction. Method blanks will be reported as discrete samples.

11. Proper Waste Disposal Practices

11.1. General waste management.

11.1.1. Each analyst within the section shall be given Waste Generator Training by EM-8 within 90 days of date of hire.

11.1.2. Wherever possible, the generation of waste shall be minimized through reduction, reuse, or recycling. Wherever possible, containers should be segregated to reflect the nature of the hazardous waste and the eventual waste-disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, nonchlorinated solvents and >50-ppm PCB contaminated waste should be segregated from <50 ppm PCB contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

11.1.3. Categorize the waste using a Waste Profile Form from EM-8.

11.1.4. Upon completion of a Waste Profile Form, the waste is disposed of by completing a Waste Disposal Request Form from EM-7. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

11.2. Solid waste.

11.2.1. Solid hazardous waste, such as contaminated paper towels, pipettes, spent syringes, and glass vials, is accumulated in a covered plastic container lined with a plastic bag. The container is labeled with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

11.2.2. The waste container is opened only for the time necessary to add the waste.

11.3. Liquid waste.

11.3.1. Liquid wastes, such as spent samples and spent solvents that are not reuseable, are accumulated in glass or steel containers appropriate for the type of sample being stored. For example, caustic materials should be stored in glass containers whereas spent solvents that are not to be recycled should be stored in metal containers.

11.3.2. All containers storing hazardous liquid materials must be secondarily contained. The container is labeled with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

11.3.3. The waste container is opened only for the time necessary to add the waste.

11.4. Unused samples.

11.4.1. Return unused environmental samples to the Sample Management section for disposal.

12. Source Materials

- 12.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Laboratory Manual Vol. 1B Method 8260, report no. SW-846 (November 1986).**
- 12.2. "Statement of Work for Organics Analysis," USEPA Contract Laboratory Program (October 1986).**
- 12.3. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).**
- 12.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).**

TABLE I. VOLATILE ORGANIC COMPOUNDS

Analyte	CAS No.	LOQ μg/kg
Chloromethane	74-87-3	20
Vinyl chloride	75-01-4	20
Bromomethane	74-83-9	20
Chloroethane	75-00-3	20
Acetone	67-64-1	20
Acrolein	107-02-8	200
Acrylonitrile	107-13-1	200
2-Chloroethyl vinyl ether	110-75-8	200
Dichlorodifluoromethane	75-71-8	10
Iodomethane	74-88-4	5.0
Trichlorotrifluoroethane	76-13-1	5.0
Trichlorofluoromethane	75-69-4	5.0
Methylene chloride	75-09-2	5.0
1,1-Dichloroethene	75-35-4	5.0
Carbon disulfide	75-15-0	5.0
trans-1,2-Dichloroethene	156-60-5	5.0
1,1-Dichloroethane	75-34-3	5.0
cis-1,2-Dichloroethene	156-59-2	5.0
Bromochloromethane	74-97-5	5.0
Chloroform	67-66-3	5.0
1,2-Dichloroethane	107-06-2	5.0
1,1-Dichloropropane	563-58-6	5.0
Vinyl acetate	108-05-4	10
2-Butanone	78-93-3	20
2,2-Dichloropropane	594-20-7	5.0
1,1,1-Trichloroethane	71-55-6	5.0
Carbon tetrachloride	56-23-5	5.0
Benzene	71-43-2	5.0

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	LOQ μg/kg
1,2-Dichloropropane	78-87-5	5.0
Trichloroethene	79-01-6	5.0
Dibromomethane	74-95-3	5.0
Bromodichloromethane	75-27-4	5.0
trans-1,3-Dichloropropene	1006-10-26	5.0
cis-1,3-Dichloropropene	1006-10-15	5.0
1,1,2-Trichloroethane	79-00-5	5.0
1,3-Dichloropropane	142-28-9	5.0
Chlorodibromomethane	124-48-1	5.0
4-Methyl-2-pentanone	10-81-01	20
Toluene	108-88-3	5.0
2-Hexanone	59-17-86	20
1,2-Dibromoethane	106-93-4	5.0
Tetrachloroethene	127-18-4	5.0
Chlorobenzene	108-90-7	5.0
1,1,1,2-Tetrachloroethane	630-20-6	5.0
Ethylbenzene	100-41-4	5.0
o,m,p-Xylene (mixed)	133-020-7	5.0
Styrene	100-42-5	5.0
Bromoform	75-25-2	5.0
1,1,2,2-Tetrachloroethane	79-34-5	5.0
1,2,3-Trichloropropane	96-18-4	5.0
Isopropylbenzene	98-82-8	5.0
Bromobenzene	108-86-1	5.0
n-Propylbenzene	103-65-1	5.0
2-Chlorotoluene	95-49-8	5.0
4-Chlorotoluene	106-43-4	5.0
1,3,5-Trimethylbenzene	108-67-8	5.0

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	LOQ
		$\mu\text{g/kg}$
tert-Butylbenzene	98-06-6	5.0
1,2,4-Trimethylbenzene	95-63-6	5.0
sec-Butylbenzene	135-98-8	5.0
1,3-Dichlorobenzene	541-73-1	5.0
1,4-Dichlorobenzene	106-46-7	5.0
p-Isopropyltoluene	99-87-6	5.0
1,2-Dichlorobenzene	95-50-1	5.0
n-Butylbenzene	104-51-8	5.0
1,2-Dibromo-3-chloropropane	96-12-8	100
Hexachlorobutadiene	87683	5.0
Napthalene	91203	5.0
1,2,3-Trichlorobenzene	87616	5.0

TABLE II. CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	43	58
Acrylonitrile	53	52
Acrolein	57	56,55
Benzene	78	-
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromoethane	94	96
2-Butanone	43	72
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroethyl vinyl ether	63	65,106
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromoethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78

TABLE II. CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS (cont)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
cis-1,3-Dichloropropene	75	77,39
trans-1,3-Dichloropropene	75	77,39
Ethylbenzene	91	106
2-Hexanone	43	58,85,100
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134,91
Methylene chloride	84	86,49
4-Methyl-2-pentanone	43	58,85,100
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133,119
1,1,2,2-Tetrachloroethane	83	131,85
Tetrachloroethene	166	168,129
Toluene	92	91
1,1,1-Trichloroethane	97	99,61
1,1,2-Trichloroethane	83	97,85
Trichloroethene	95	130,132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m,p-Xylene	106	91

INTERNAL STANDARDS/SURROGATES

Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d ₅	117	
1,4-Dichlorobenzene	152	
4-Bromofluorobenzene	95	174,176
Toluene-d ₈	98	
1,2-Dichloroethane-d ₄	65	

TABLE III. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING
ANALYTES ASSIGNED FOR QUANTITATION

Pentafluorobenzene

Acetone
Acrolein
Acrylonitrile
Benzene
Bromochloromethane
Bromomethane
2-Butanone
Carbon disulfide
Carbon tetrachloride
Chloroethane
Chloroform
Chloromethane
Dichlorodifluoromethane
1,2-Dichloroethane
1,1-Dichloroethane
1,1-Dichloroethene
1,2-Dichloroethane-d₄^a
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
2,2-Dichloropropane
1,1-Dichloropropene
Iodomethane
Methylene chloride
1,1,1-Trichloroethane
Trichlorofluoromethane
Trichlorotrifluoroethane
Vinyl acetate
Vinyl chloride

1,4-Difluorobenzene

Bromodichloromethane
2-Chloroethyl vinyl ether
1,2-Dibromoethane
Dibromomethane
trans-1,3-Dichloropropene
Toluene-d₈^a
Trichloroethene

Chlorobenzene

Bromoform
Chlorodibromomethane
Chlorobenzene
1,2-Dibromoethane
1,3-Dichloropropane
cis-1,3-Dichloropropene
Ethylbenzene
2-Hexanone
4-Methyl-2-pentanone
Styrene
Toluene
1,1,2-Trichloroethane
Tetrachloroethane
1,1,1,2-Tetrachloroethane
o,m,p-Xylenes

1,4-Dichlorobenzene-d₄

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane

TABLE III. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION (cont)

1,4-Dichlorobenzene-d₄ (cont)

1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
n-Propylbenzene
1,1,2,2-Tetrachloroethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
4-Bromofluorobenzene ^a

^a Surrogate

TABLE IV. STOCK AND WORKING CALIBRATION SOLUTIONS

Chemical name/concentration	Final concentration	
	Stock ($\mu\text{g/mL}$)	Working std. ($\mu\text{g/mL}$)
<u>INTERNAL STANDARD MIX</u>		
Pentafluorobenzene (1000 $\mu\text{g/mL}$)	50	NA
Chlorobenzene- d_5 (1000 $\mu\text{g/mL}$)	50	NA
1,4-Difluorobenzene (1000 $\mu\text{g/mL}$)	50	NA
1,4-Dichlorobenzene- d_4 (1000 $\mu\text{g/mL}$)	50	NA
<u>CALIBRATION STANDARD MIX</u>		
HSL Custom standard		
Acetone (1000 $\mu\text{g/mL}$)	100	25
Methyl ethyl ketone (1000 $\mu\text{g/mL}$)	100	25
Carbon disulfide (1000 $\mu\text{g/mL}$)	100	25
4-methyl-2-pentanone (1000 $\mu\text{g/mL}$)	100	25
Vinyl acetate (1000 $\mu\text{g/mL}$)	100	25
2-Chloroethyl vinyl ether (1000 $\mu\text{g/mL}$)	100	25
2-Hexanone (1000 $\mu\text{g/mL}$)	100	25
Acrolein (1000 $\mu\text{g/mL}$)	100	25
Acrylonitrile (1000 $\mu\text{g/mL}$)	100	25
Iodomethane (1000 $\mu\text{g/mL}$)	100	25
Freon 113 (1000 $\mu\text{g/mL}$)	100	25
Purgeable Surrogate Standard Mix - CLP		
Bromofluorobenzene (250 $\mu\text{g/mL}$)	50	NA
1,2-Dichloroethane- d_4 (250 $\mu\text{g/mL}$)	50	NA
Toluene- d_8 (250 $\mu\text{g/mL}$)	50	NA

TABLE IV. STOCK AND WORKING CALIBRATION SOLUTIONS
(cont)

Chemical name/concentration	Final concentration	
	Stock ($\mu\text{g/mL}$)	Working std. ($\mu\text{g/mL}$)
Volatile Organic Compounds Mix #1		
sec-Butylbenzene (2000 $\mu\text{g/mL}$)	100	25
tert-Butylbenzene (2000 $\mu\text{g/mL}$)	100	25
Chlorobenzene (2000 $\mu\text{g/mL}$)	100	25
2-Chlorotoluene (2000 $\mu\text{g/mL}$)	100	25
4-Chlorotoluene (2000 $\mu\text{g/mL}$)	100	25
1,2-Dichlorobenzene (2000 $\mu\text{g/mL}$)	100	25
1,3-Dichlorobenzene (2000 $\mu\text{g/mL}$)	100	25
1,4-Dichlorobenzene (2000 $\mu\text{g/mL}$)	100	25
Isopropylbenzene (2000 $\mu\text{g/mL}$)	100	25
n-Propylbenzene (2000 $\mu\text{g/mL}$)	100	25
o-Xylene (2000 $\mu\text{g/mL}$)	100	25
p-Xylene (2000 $\mu\text{g/mL}$)	100	25
Volatile Organic Compounds Mix #2		
Benzene (2000 $\mu\text{g/mL}$)	100	25
Bromobenzene (2000 $\mu\text{g/mL}$)	100	25
n-Butylbenzene (2000 $\mu\text{g/mL}$)	100	25
Ethylbenzene (2000 $\mu\text{g/mL}$)	100	25
p-Isopropyltoluene (2000 $\mu\text{g/mL}$)	100	25
Naphthalene (2000 $\mu\text{g/mL}$)	100	25
Styrene (2000 $\mu\text{g/mL}$)	100	25
Toluene (2000 $\mu\text{g/mL}$)	100	25
1,2,3-Trichlorobenzene (2000 $\mu\text{g/mL}$)	100	25
1,2,4-Trichlorobenzene (2000 $\mu\text{g/mL}$)	100	25

TABLE IV. STOCK AND WORKING CALIBRATION SOLUTIONS
(cont)

Chemical name/concentration	Final concentration	
	Stock ($\mu\text{g/mL}$)	Working std. ($\mu\text{g/mL}$)
Volatile Organic Compounds Mix #2 (cont)		
1,2,4-Trimethylbenzene (2000 $\mu\text{g/mL}$)	100	25
1,2,5-Trimethylbenzene (2000 $\mu\text{g/mL}$)	100	25
m-Xylene (2000 $\mu\text{g/mL}$)	100	25
Volatile Organic Compounds Mix #3		
1,2-Dibromo-3-chloropropane (2000 $\mu\text{g/mL}$)	100	25
1,2-Dibromomethane (2000 $\mu\text{g/mL}$)	100	25
1,2-Dichloroethane (2000 $\mu\text{g/mL}$)	100	25
1,2-Dichloropropane (2000 $\mu\text{g/mL}$)	100	25
1,3-Dichloropropane (2000 $\mu\text{g/mL}$)	100	25
1,1-Dichloropropene (2000 $\mu\text{g/mL}$)	100	25
1,3-Dichloropropene (4000 $\mu\text{g/mL}$) *	400	50
Hexachlorobutadiene (2000 $\mu\text{g/mL}$)	100	25
1,1,1,2-Tetrachloroethane (2000 $\mu\text{g/mL}$)	100	25
1,1,2,2-Tetrachloroethane (2000 $\mu\text{g/mL}$)	100	25
1,1,2-Trichloroethane (2000 $\mu\text{g/mL}$)	100	25
Trichloroethene (2000 $\mu\text{g/mL}$)	100	25
1,2,3-Trichloropropane (2000 $\mu\text{g/mL}$)	100	25
Volatile Organic Compounds Mix #4		
Bromochloromethane (2000 $\mu\text{g/mL}$)	100	25
Bromoform (2000 $\mu\text{g/mL}$)	100	25
Carbon tetrachloride (2000 $\mu\text{g/mL}$)	100	25
Chloroform (2000 $\mu\text{g/mL}$)	100	25
Dibromomethane (2000 $\mu\text{g/mL}$)	100	25

TABLE IV. STOCK AND WORKING CALIBRATION SOLUTIONS
(cont)

Chemical name/concentration	Final concentration	
	Stock ($\mu\text{g/mL}$)	Working std. ($\mu\text{g/mL}$)
Volatile Organic Compounds Mix #4 (cont)		
1,1-Dichloroethane (2000 $\mu\text{g/mL}$)	100	25
2,2-Dichloropropane (2000 $\mu\text{g/mL}$)	100	25
Tetrachloroethene (2000 $\mu\text{g/mL}$)	100	25
1,1,1-Trichloroethane (2000 $\mu\text{g/mL}$)	100	25
Volatile Organic Compounds Mix #5		
Bromodichloromethane (2000 $\mu\text{g/mL}$)	100	25
Dibromochloromethane (2000 $\mu\text{g/mL}$)	100	25
1,1-Dichloroethene (2000 $\mu\text{g/mL}$)	100	25
cis-1,2-Dichloroethene (2000 $\mu\text{g/mL}$)	100	25
trans-1,2-Dichloroethene (2000 $\mu\text{g/mL}$)	100	25
Methylene chloride (2000 $\mu\text{g/mL}$)	100	25
<u>VOC #6 CALIBRATION STANDARD MIX</u>		
Volatile Organic Compounds Mix #6		
Bromomethane (2000 $\mu\text{g/mL}$)	100	25
Chloromethane (2000 $\mu\text{g/mL}$)	100	25
Chloroethane (2000 $\mu\text{g/mL}$)	100	25
Dichlorodifluoromethane (2000 $\mu\text{g/mL}$)	100	25
Trichlorofluoromethane (2000 $\mu\text{g/mL}$)	100	25
Vinyl chloride (2000 $\mu\text{g/mL}$)	100	25

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Volatile Organic Components in Soil and Sediment: Field Screening Method

Method No.: MLO720

Revision No.: 0

Section Leader

Chris Carlson

Date:

4/23/93

Group Leader

C. DL

Date:

4/23/93

QA Concurrence

Margaret A. Gantieri

Date:

4-23-93

EXTRAX=SVOA

**EXTRACTION OF SEMIVOLATILE ORGANIC ANALYTES IN
SOLID MATRICES BY GC/MS
MOBILE LABORATORY METHOD**

Analytes: Base Neutral/Acid
Extractables (BNAs)

Method No.: MLO510

Matrix: Soil, sediment, and
sludges

Minimum Detection Limit:
1.0 - 2.0 $\mu\text{g}/\text{mg}$ nominal
(matrix-dependent)

Procedure: Extraction of
analytes in the field using
appropriate solvents and
rotary table agitation. Analysis is
by a field screening GC/MS method.

Accuracy and Precision: These parameters are
analyte-dependent and are greatly influenced
by the matrix.

Effective Date: 04/03/93

Authors: Martin W. Koby
Matthew Monagle

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 13 of this procedure and Source Material 14.4 for proper waste disposal practices.

1. Principle of Method

- 1.1. Depending on the analysis required, semivolatile constituents are extracted from various solid matrices using a rotary action shaker table. Extracts are then concentrated to a small volume (typically 0.5 mL or less) and analyzed by gas chromatography/mass spectrometry.

Analytes from a wide variety of compound classes can be determined using this method. Table IV lists the compounds in the current Hazardous Substance List which are analyzed routinely. Table V contains the Appendix IX list of compounds that are not routinely analyzed. (Tables IV and V are found at the end of this procedure.)

2. Sensitivity

- 2.1. Practical limits of quantitation are generally in the range of 1.0 mg/kg to 2.0 mg/kg for low-level solid matrices. Matrices which are relatively free of interferences have lower attainable limits of detection than those having large amounts of coextractable material such as drum waste. Medium-level extracts have a nominal detection limit of 20,000 $\mu\text{g}/\text{kg}$.

- 2.2. Factors affecting sensitivity include the response factor of the compound being measured, the final volume of extract, the sample aliquot extracted, and the level of coextracted material.

3. Accuracy and Precision

- 3.1. Based upon fixed-based laboratory surrogate and spike data, analyte recoveries are typically in the 60-110% range. Recoveries can be expected to vary depending on the given analyte and matrix complexity.
- 3.2. Long-range precision data is currently based upon fixed-base laboratory matrix spike and spike duplicate percent recovery and the relative percent difference between the two. Refer to Section 11, Table III.

4. Interferences

- 4.1. Any material which will cause an increase in background signal or elevated baseline or result in discrete chromatographic peaks which are not attributable to target compounds may interfere with the identification and quantitation of a given analyte. Examples are environmental matrices containing high concentrations of humic material, oils, hydrocarbons, lipids, sulfur, or polar materials such as alcohols and carboxylic acids.
- 4.2. Excessive particulate matter in water, extreme alkalinity or acidity, reactive material, intense light, and high temperature can negatively effect analyte recovery.

5. Sample Collection and Storage

- 5.1. All sampling equipment should be free of introduced contaminants.
- 5.2. Soil or sediment samples are typically collected in amber or clear glass wide-mouth bottles. Caps should have Teflon liners; however, aluminum foil can be substituted for Teflon if necessary. Excessive headspace should be avoided.
- 5.3. Samples should be stored, unpreserved, in a refrigerator at 4°C until extraction is initiated.

6. Sample holding times

- 6.1. Soil or sediment samples must be extracted within 14 d of receipt.
- 6.2. Sample extracts must be analyzed within 40 d of extraction.

7. Apparatus

- 7.1. Electronic balance: capable of measurement to three decimal places.

- 7.2. Nitrogen evaporation apparatus with multiple sample capacity: Organomation N-EVAP, Model 111 or equivalent.
- 7.3. Beakers: glass, 100-, 150-, 250-, 400-, and 600-mL capacity.
- 7.4. Glass vials: 1.8-mL crimp cap, 1.8-, 7-, 10-, 12-, 15-, and 40-mL capacity screw cap with septa.
- 7.5. Volumetric flasks: 1-, 2-, 5-, 10-, 25-, 50-, 100-, and 250-mL with stoppers.
- 7.6. Disposable glass pipettes: 1-, 2-, 5-, and 10-mL.
- 7.7. Adjustable low-volume pipettors: 10- and 250- μ L capacity with disposable capillary tips. SMI brand or equivalent.
- 7.8. Syringes: glass, gas-tight, 10-, 25-, 50-, and 100- μ L volume.
- 7.9. Aluminum foil.

8. Reagents

- 8.1. Methylene chloride (Baker Resi-analyzed).
- 8.2. Acetone (Baker Resi-analyzed).
- 8.3. Methanol (HPLC-grade).
- 8.4. Hexane (pesticide-grade).
- 8.5. Reagent water (deionized). Charcoal filtered and/or distilled water demonstrated to be free from interferences.
- 8.6. Sodium sulfate (granular). Muffle overnight at 400°C. Alternatively, it can be Soxhlet-extracted with methylene chloride before use. Store in a covered container.

9. Analytical Standards

- 9.1. All analytical standards are refrigerated at -20°C. Working standards typically have a shelf life of three months. Stock standards are considered usable for at least six months or until degradation becomes apparent.

The following analytical standards are specified by EPA protocol to be used in the analysis of base/neutral acid extractables. They are readily available from any number of chemical suppliers as neat standards or as stock solutions. Currently, we use standard mixes formulated by Ultra Scientific, Inc.

9.2. **Surrogate compounds.** The surrogates closely resemble target compounds chemically but are not normally encountered in nature. Before extraction, each sample is fortified with a known concentration of surrogate mix. Evaluating surrogate recoveries give a measure of the method's efficiency for any given matrix.

9.2.1. **Base/Neutral Surrogate Standard Mix** (1000 $\mu\text{g/mL}$ in CH_2Cl_2). This formulation contains the following compounds:

Nitrobenzene- d_5
2-Fluorobiphenyl
Terphenyl- d_{14}

9.2.2. **Acid Surrogate Standard Mix** (2000 $\mu\text{g/mL}$ in methanol). This formulation contains the following compounds:

2-Fluorophenol
Phenol- d_5
2,4,6-Tribromophenol

9.2.3. **BNA surrogate working standards** are prepared by diluting each mix 1:20 with methanol in the same volumetric flask. This results in a final concentration of 50 or 100 ppm of base neutral/acid components, respectively.

9.3. **Matrix spike compounds.** These compounds (see Table II) are used to document analytical precision and accuracy, the objective being to identify both long-term and short-term trends in method performance. Known concentrations of spike material are added, to duplicate representative samples before extraction. Under Tier Three QC requirements, matrix spike and matrix spike duplicate data are generated once for every 20 samples analyzed.

TABLE II. BNA MATRIX SPIKE COMPOUNDS

Compound	Fraction	Amount added (μg)
1,2,4-Trichlorobenzene	BN	50
Acenaphthene	BN	50
2,4-Dinitrotoluene	BN	50
Pyrene	BN	50
N-nitroso-Di-n-propylamine	BN	50
1,4-Dichlorobenzene	BN	50
Pentachlorophenol	Acid	100

TABLE II. BNA MATRIX SPIKE COMPOUNDS
(cont)

Compound	Fraction	Amount added (μg)
Phenol	Acid	100
2-Chlorophenol	Acid	100
4-Chloro-3-methylphenol	Acid	100
4-Nitrophenol	Acid	100

- 9.3.1. Base/neutral matrix spike solution (1000 $\mu\text{g}/\text{mL}$ in CH_2Cl_2). This formulation contains the following components:

Acenaphthene
1,4-Dichlorobenzene
2,4-Dinitrophenol
N-Nitroso-di-n-propylamine
Pyrene
1,2,4-Trichlorobenzene

- 9.3.2. Acid matrix spike solution (2000 $\mu\text{g}/\text{mL}$ in methanol). This formulation contains the following components:

4-Chloro-3-methylphenol
2-Chlorophenol
4-Nitrophenol
Pentachlorophenol
Phenol

- 9.3.3. Working standards of matrix spiking solutions are made by diluting each stock 1:20 with methanol in the same volumetric flask. Final concentrations are 50/100 ppm base neutral/acid respectively.

10. Sample Extraction

- 10.1. Extracting low-level BNAs from soils, sediments, and other solid matrices using the rotary action table shaker.

10.1.1. Rinse all glassware with methylene chloride and air dry before use.

10.1.2. If any standing water is present in the sample container, decant it before homogenizing the sample. If the quantity of water is sufficient it may be treated as a separate sample, depending on the needs of the customer.

- 10.1.3. Avoiding rocks >2-mm-diam, grass, twigs, and other interfering material, weigh 10.0 g of homogenized sample into a 40-mL VOA vial. Record the sample weight in the benchsheet. Add about 10.0 g of granular sodium sulfate and mix thoroughly with a stainless-steel spatula. If the sample has significant moisture, additional Na_2SO_4 should be added. The sample should flow readily and have a grainy texture when sufficient sodium sulfate has been added.
- 10.1.4. If the sample has an oily appearance or strong organic/petroleum odor, extract a reduced aliquot. This will result in higher reported limits of quantitation.
- 10.1.5. If the analyte concentrations are to be reported on a dry-weight basis, determine the percent moisture. Tare an aluminum weigh boat or pan, add approximately 10 g of moist soil, and dry overnight at 105°C. Reweigh the samples and calculate the percent moisture from the weight loss on drying.
- 10.1.6. Add 1.0 mL of BNA surrogate standard mix directly to the surface of all samples, blanks, and matrix spikes. Similarly add 1.0 mL of BNA spike mix to the matrix spike and matrix spike duplicate samples.
- 10.1.7. Add exactly 10 mL of CH_2Cl_2 to the sample. Cap the vial and secure it to the sample shaker. Shake the vial vigorously for 30 min to thoroughly mix the sample and the solvent.
- 10.1.8. Pipette exactly 5 mL of the extract into an volumetric flask. Direct a gentle stream of dry nitrogen over the surface of the solvent. Periodically rinse the inside walls of the receiver tube with methylene chloride to prevent loss of analyte. Allow the extract to dry to an apparent volume of 0.5 mL, then remove from the bath. Occasionally an extract will not evaporate below 5.0 mL. In these instances the extract should be maintained at 5.0 mL and analyzed by GC/MS.

If the sample is to be analyzed for PCBs, pesticides, and semivolatile constituents, another 1-mL aliquot should be placed into a volumetric flask for solvent exchange. This extract is solvent-exchanged to hexane or iso-octane and analyzed for organochlorine pesticides and PCBs by GC/ECD.

11. Quality Assurance and Data Interpretation Requirements

11.1. The Quality Control requirements are defined in a tiered structure as follows:

**Tier 1: 1-point calibration every day.
1 method blank every day.**

**Tier 2: 3-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank every day.**

**Tier 3: 5-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank per analytical batch.
Blind QC samples at a rate of no more than 10%.
Matrix spike and matrix spike duplicate for each analytical batch.
12-h clock for tune check and daily check standard.**

11.2. A method blank is a volume of reagent water or a purified solid material which is taken through the entire analytical scheme. The weight or volume of the blank must approximate that of the samples being analyzed.

11.3. Under Tier 2 and Tier 3 QC requirements, blanks are analyzed at a frequency of one for every 20 samples of similar matrix, or whenever samples are extracted by the same procedure, whichever is more frequent. The following criteria are checked immediately after blank analysis:

- **The method blank should contain less than five times the practical quantitation limit (PQL) of phthalate esters in the target compound list.**
- **All other analytes on the target compound list should not be present at concentrations greater than the PQL.**
- **Recovery of all surrogate compounds must be within specified limits (see Table I). If this criterion is not met, reanalyze or reextract another blank to determine whether the incident is isolated or an out-of-control status exists.**

**TABLE I. BNA SURROGATE SPIKE
RECOVERY LIMITS IN
PERCENT**

Surrogate Compound	Water	Soil
Nitrobenzene-d ₅	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d ₁₄	33-141	18-137
Phenol-d ₅	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

11.4. Surrogate spike requirements. Each sample which is prepared and analyzed for semivolatile compounds is fortified with known amounts of base-neutral and acid extractable compounds. Evaluating their recovery, measured as a percentage, allows conclusions to be derived concerning the analytical efficiency on a sample-by-sample basis.

11.4.1. Surrogate spike recoveries are considered to be acceptable if they fall within the ranges specified in Table II.

The following conditions indicate unacceptable surrogate recovery:

- Recovery of any one surrogate in either the base-neutral or acid fraction is less than 10%.
- Recoveries of any two surrogate compounds in either base-neutral or acid fraction are out of recovery limits.

11.4.2. When surrogate spike recoveries are determined to be out of control, the analyst needs to determine if the cause is matrix- or process-dependent. Re-extraction should be requested when there is sufficient sample and holding times can be met. Whichever conclusion is reached needs to be addressed in the case narrative and/or anomaly summary. Corrective action will be implemented to alleviate the causes of the out-of-control condition.

11.5. Matrix spike and matrix spike duplicate recovery requirements. In order to evaluate the matrix effect of a sample on the analytical methodology employed, known concentrations of base/neutral and acid target compounds are added to duplicates of a given sample. See Table III for a list of spike compounds. The sample chosen to be spiked should be representative of the samples from a given project.

- 11.5.1. Under Tier Three QC requirements, matrix spike and matrix spike duplicate data are generated for every 20 samples of a given matrix type prepared by the same method.
- 11.5.2. Matrix spike/matrix spike duplicates and the original unspiked sample must be concentrated to the same final volume and analyzed at the same dilution level. If high levels of target compounds are detected that are not matrix spike compounds, the original sample only needs to be diluted to enable compound quantitation.
- 11.5.3. Spike recovery is evaluated in terms of percent recovery and the relative percent difference (RPD) between individual spike compounds in the MS and MSD. This data can be used to evaluate the long-term precision and accuracy of the method. See Table III for spike recovery limits.

TABLE III. BNA MATRIX SPIKE RECOVERY LIMITS - SOIL

Compound	Percent recovered			RPD
1,24-Trichlorobenzene	38	-	107	23
Acenaphthene	31	-	137	19
2,4-Dinitrotoluene	28	-	89	47
Pyrene	35	-	142	36
N-nitroso-Di-n-propylamine	41	-	126	38
1,4-Dichlorobenzene	28	-	104	27
Pentachlorophenol	17	-	109	47
Phenol	26	-	90	35
2-Chlorophenol	25	-	102	50
4-Chloro-3-methylphenol	26	-	103	33
4-Nitrophenol	11	-	114	50

- 11.6. Under Tier Three QC requirements, blind spikes are extracted and analyzed on a regular basis as an independent check of method accuracy. Standard reference materials resemble submitted matrices as closely as possible.
- 11.7. **Percent moisture determination.** When sample concentrations are to be reported on a dry weight basis, percent moisture is calculated using the following equation:

$$\% M = \frac{S_w - S_d}{S_w} \times 100 ,$$

where SW = wet weight of the soil aliquot less the container weight, and
Sd = dry weight of the soil aliquot after oven drying at 105°C for 24 h
less the container weight.

12. Reporting

Extraction data are recorded in a bound extraction benchsheet notebook. Nonroutine amendments to the procedure are also documented in this notebook in the amendments section at the back of the notebook.

13. Proper Waste Disposal Practices

13.1. General waste management.

13.1.1. Each analyst within the section shall be given Waste Generator Training from EM-8 within 90 days of the date of hire.

13.1.2. Wherever possible, minimize the generation of waste through reduction, reuse, or recycling. Wherever possible, segregate containers to reflect the nature of the hazardous waste and the eventual waste disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, nonchlorinated solvents and >50-ppm PCB contaminated waste should be segregated from <50-ppm PCB contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

13.1.3. Categorize the waste using an EM-8 Waste Profile Form.

13.1.4. Upon completion of the Waste Profile Form, dispose of the waste by completing a Waste Disposal Request Form from EM-7. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

13.2. Solid waste.

13.2.1. Accumulate hazardous wastes such as contaminated paper towels, pipettes, spent syringes, and glass vials in a covered plastic container lined with a plastic bag. Label the container with a hazardous waste label which identifies the hazard, type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

13.2.2. Open the waste container only for the time necessary to add the waste.

13.3. Liquid waste.

13.3.1. Accumulate liquid waste, such as spent samples and spent solvents that are not reusable, in glass or steel containers appropriate for the type of sample being stored. For example, store caustic materials in glass containers and spent solvents that are not bound for recycling in metal containers.

13.3.2. Place all containers storing hazardous liquid materials within secondary containment. Label the container with a hazardous waste label which identifies the hazard, type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

13.3.3. Open the waste container only for the time necessary to add the waste.

13.4. Unused samples.

13.4.1. Return unused environmental samples to the Sample Management section for disposal.

14. Source Materials

14.1. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis Multi-media, Multi-Concentration, 2/88.

14.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd ed., 1988.

14.3. Sorbent Extraction Technology, K.C. Van Horne, Analytical International, Inc. 1985.

14.4. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Chapter 1 of Los Alamos National Laboratory Manual (most recent edition).

**TABLE IV. HAZARDOUS SUBSTANCE LIST OF
SEMIVOLATILE ORGANIC ANALYTES
LIMIT OF QUANTITATION**

Compound	CAS number	LOQ mg/kg
Acenaphthene	83-32-9	1.0
Acenaphthylene	208-96-2	1.0
Anthracene	120-12-7	1.0
Aniline	62-53-3	1.0 *
Azobenzene	3-33-3	1.0
Benzidine	92-87-5	1.0 *,a
Benz(a)anthracene	56-55-3	1.0
Benzo(b)fluoranthene	205-99-2	1.0
Benzo(k)fluoranthene	207-88-9	1.0
Benzoic acid	65-85-0	1.0 *,c
Benzo(g,h,i)perylene	191-24-2	1.0
Benzo(a)pyrene	50-32-8	1.0
Benzyl alcohol	0-51-6	1.0
Bis(2-chloroethoxy)methane	111-91-1	1.0
Bis(2-chloroethyl) ether	111-44-4	1.0
Bis(2-chloroisopropyl) ether	8-60-1	1.0
4-Bromophenyl phenyl ether	1-55-3	1.0
Butyl benzyl phthalate	85-68-7	1.0 *
4-Chloroaniline	6-47-8	1.0 *,c
4-Chloro-3-methylphenol	59-50-7	1.0
2-Chloroanaphthalene	91-58-7	1.0
2-Chlorophenol	95-57-8	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0
Chrysene	218-01-9	1.0
Dibenz(a,h)anthracene	53-70-3	1.0
Dibenzofuran	132-64-9	1.0

TABLE IV. (cont)

Compound	CAS number	LOQ mg/kg
Di-n-butylphthalate	84-74-2	1.0 *
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	6-46-7	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0 *
2,4-Dichlorophenol	120-83-2	1.0
Diethyl phthalate	84-66-2	1.0 *
2,4-Dimethylphenol	5-67-9	1.0 *,c
Dimethyl phthalate	131-11-3	1.0 *
4,6-Dinitro-2-methylphenol	534-52-1	1.0
2,4-Dinitrophenol	51-28-5	1.0 *,c
2,4-Dinitrotoluene	121-14-2	1.0
2,6-Dinitrotoluene	606-20-2	1.0
Di-n-octyl phthalate	117-84-0	1.0
Bis(2-ethylhexyl) phthalate	117-81-7	1.0
Fluoranthene	206-44-0	1.0
Fluorene	86-73-7	1.0
Hexachlorobenzene	118-74-1	1.0
Hexachlorobutadiene	87-68-3	1.0
Hexachlorocyclopentadiene	77-47-4	1.0*,d
Hexachloroethane	67-72-1	1.0
Indeno(1,2,3-cd)pyrene	193-39-5	1.0
Isophorone	78-59-1	1.0
2-Methylnaphthalene	91-57-6	1.0
2-Methylphenol	95-48-7	1.0 *,c
4-Methylphenol	6-44-5	1.0 *,c
Naphthalene	91-20-3	1.0
2-Nitroaniline	88-74-4	1.0

TABLE IV. (cont)

Compound	CAS number	LOQ mg/kg
3-Nitroaniline	99-09-2	1.0 *,c
4-Nitroaniline	0-01-6	1.0 *,c
Nitrobenzene	98-95-3	1.0
2-Nitrophenol	88-75-5	1.0
4-Nitrophenol	0-02-7	1.0 *,c
N-nitrosodimethylamine	62-75-9	1.0 *,c
N-nitrosodiphenylamine	86-30-6	1.0
N-Nitroso-di-n-propylamine	621-64-7	1.0 *
Pentachlorophenol	87-86-5	1.0 *,c
Phenanthrene	85-01-8	1.0
Phenol	8-95-2	1.0
Pyrene	129-00-0	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
2,4,5-Trichlorophenol	95-95-4	1.0
2,4,6-Trichlorophenol	88-06-2	1.0

* = The limit of quantitation has not been verified for these analytes based upon a Method Detection Limit study. All others averaged better than 70% analyte recovery based upon seven repetitions. The amount of each analyte spiked was 330 μ g into 1.0 L.

a = Exhibits nonreproducible chromatography and oxidative loss during concentration.

c = These analytes are subject to erratic chromatographic performance and/or thermal decomposition in the gas chromatograph inlet.

d = Subject to thermal decomposition in the chromatographic inlet, chemical reaction with acetone in solution, and photochemical decomposition.

Limits of quantitation (LOQ) will be two times greater for soil/sediment matrices which have been GPC cleaned.

TABLE V. APPENDIX IX TARGET COMPOUND
LIST OF SEMIVOLATILE ORGANIC ANALYTES
LIMIT OF QUANTITATION

Compound	CAS number	LOQ mg/kg
Acenaphthene	83-32-9	1.0
Acenaphthylene	208-96-2	1.0
Acetophenone	98-86-2	ND
Anthracene	120-12-7	1.0
Aniline	62-53-3	1.0 *
Aramite	140-57-8	ND
Azobenzene	3-33-3	1.0
Benzidine	92-87-5	1.0 *,a
Benz(a)anthracene	56-55-3	1.0
Benzo(b)fluoranthene	205-99-2	1.0
Benzo(k)fluoranthene	207-88-9	1.0
Benzoic acid	65-85-0	1.0 *,c
Benzo(g,h,i)perylene	191-24-2	1.0
Benzo(a)pyrene	50-32-8	1.0
Benzyl alcohol	0-51-6	1.0
Bis(2-chloroethoxy)methane	111-91-1	1.0
Bis(2-chloroethyl) ether	111-44-4	1.0
Bis(2-chloroisopropyl) ether	108-60-1	1.0
4-Bromophenyl phenyl ether	101-55-3	1.0
Butyl enyl phthalate	85-68-7	1.0 *
4-Chloroaniline	106-47-8	1.0 *,c
Chlorobenzilate	510-15-6	ND
4-Chloro-3-methylphenol	59-50-7	1.0
2-Chloroanaphthalene	91-58-7	1.0
2-Chlorophenol	95-57-8	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0

TABLE V. (cont)

Compound	CAS number	LOQ mg/kg
Chrysene	218-01-9	1.0
Diallate	2303-16-4	ND
Dibenz(a,h)anthracene	53-70-3	1.0
Dibenzofuran	132-64-9	1.0
Di-n-butyl phthalate	84-74-2	1.0 *
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	6-46-7	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0 *
2,4-Dichlorophenol	120-83-2	1.0
Diethyl phthalate	84-66-2	1.0 *
Dimethoate	60-51-5	ND
7,12-Dimethylbenz(a)- anthracene	57-97-6	ND
2,4-Dimethylphenol	5-67-9	1.0 *,c
Dimethyl phthalate	131-11-3	1.0 *
4,6-Dinitro-2-methylphenol	534-52-1	1.0
2,4-Dinitrophenol	51-28-5	1.0 *,c
2,4-Dinitrotoluene	121-14-2	1.0
2,6-Dinitrotoluene	606-20-2	1.0
Di-n-octyl phthalate	117-84-0	1.0
Diphenylamine	122-39-4	ND
Dinoseb (DNBP)	88-85-7	ND
Disulfoton	298-04-4	ND
Bis(2-ethylhexyl) phthalate	117-81-7	1.0
Ethyl methacrylate	97-63-2	ND
Ethyl methanesulfonate	62-50-0	ND
Famphur	52-85-7	ND

TABLE V. (cont)

Compound	CAS number	LOQ mg/kg
Fluoranthene	206-44-0	1.0
Fluorene	86-73-7	1.0
Hexachlorobenzene	118-74-1	1.0
Hexachlorobutadiene	87-68-3	1.0
Hexachlorocyclopentadiene	77-47-4	1.0*,d
Hexachloroethane	67-72-1	1.0
Hexachlorophene	70-30-4	ND
Hexachloropropene	1888-71-7	ND
Indeno(1,2,3-cd)pyrene	193-39-5	1.0
Isodrin	465-73-6	ND
Isosafrole	120-58-1	ND
Isophorone	78-59-1	1.0
Kepone	143-50-0	ND
3-Methylcholanthrene	56-49-5	ND
2-Methylnaphthalene	91-57-6	1.0
2-Methylphenol	95-48-7	1.0 *,c
4-Methylphenol	106-44-5	1.0 *,c
Methapyrilene hydrochloride	91-80-5	ND
Methyl methacrylate	80-62-6	ND
Methyl methanesulfonate	66-27-3	ND
Methyl Parathion	296-00-0	ND
Naphthalene	91-20-3	1.0
2-Nitroaniline	88-74-4	1.0
3-Nitroaniline	99-09-2	1.0 *,c
4-Nitroaniline	0-01-6	1.0 *,c
Nitrobenzene	98-95-3	1.0
2-Nitrophenol	88-75-5	1.0
4-Nitrophenol	100-02-7	1.0 *,c

TABLE V. (cont)

Compound	CAS number	LOQ mg/kg
4-Nitroquinoline-1-oxide	56-57-5	ND
5-Nitro-2-methylaniline	99-55-8	ND
N-Nitrosodiethylamine	55-18-5	ND
N-Nitrosomethylethylamine	10595-95-6	ND
N-Nitroso-di-n-butylamine	924-16-3	ND
N-nitrosodimethylamine	62-75-9	1.0 *,c
N-nitrosodiphenylamine	86-30-6	1.0
N-Nitroso-di-n-propylamine	621-64-7	1.0 *
o-Toluidine	95-53-4	ND
Parathion	56-38-2	ND
Pentachloroethane	76-01-7	ND
Pentachloronitrobenzene	82-68-8	ND
Pentachlorophenol	87-86-5	1.0 *,c
Phenacetin	62-44-2	ND
Phenanthrene	85-01-8	1.0
Phenol	8-95-2	1.0
Phorate	298-02-2	ND
2-Picoline	109-06-8	ND
Pronamide	23950-58-5	ND
Pyridine	110-86-1	ND
Pyrene	129-00-0	1.0
Safrole	94-59-7	ND
2,3,4,6-Tetrachlorophenol	58-90-2	ND
1,2,4-Trichlorobenzene	120-82-1	1.0
2,4,5-Trichlorophenol	95-95-4	1.0

TABLE V. (cont)

Compound	CAS number	LOQ mg/kg
O,O,O-Triethyl phosphorate	126-68-1	ND
2,4,6-Trichlorophenol	88-06-2	1.0
sym-Trinitrobenzene	99-35-4	ND
Tetraethyl dithiophosphate	3689-24-5	ND

*** =** The limit of quantitation has not been verified for these analytes based upon a Method Detection Limit study. All others averaged better than 70% analyte recovery based upon seven repetitions. The amount of each analyte spiked was 330 μ g into 1.0 L.

a = Exhibits nonreproducible chromatography and oxidative loss during concentration.

c = These analytes are subject to erratic chromatographic performance and/or thermal decomposition in the gas chromatograph inlet.

d = Subject to thermal decomposition in the chromatographic inlet, chemical reaction with acetone in solution, and photochemical decomposition.

ND = not determined for these analytes.

Limits of quantitation (LOQ) will be two times greater for soil/sediment matrices which have been GPC cleaned.

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Extraction of Semivolatile Organic Analytes in Solid Matrices for Analysis
by GC/MS Mobile Laboratory Method

Method No.: MLO510

Revision No.: 0

Section Leader

Chris Salama

Date:

4/23/93

Group Leader

QDR

Date:

4/23/93

QA Concurrence

Margaret A. Gautier

Date:

4-23-93

SVOA

**SEMIVOLATILE ORGANICS IN SOLID MATRICES:
SOLVENT EXTRACTION - GC/MS
MOBILE LABORATORY METHOD**

Analytes: Base Neutral/Acid
Extractables (BNAs)
Refer to Table VIII

Method No.: MLO500

Matrix: Soil, sediment, and
sludges

Minimum Detection Limit:
1.0-2.0 mg/kg nominal
(matrix-dependent)

Procedure: Extraction and
concentration of analytes
with an appropriate solvent
followed by capillary-column
GC/MS analysis.

Accuracy and Precision: These parameters are
analyte-dependent and are greatly influenced
by the matrix.

Effective Date: 04/03/93

Authors: Martin W. Koby
Matthew Monagle

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 13 of this procedure and Source Material 14.4 for proper waste disposal practices.

1. Principle of Method

- 1.1. Analytes are extracted from various matrices using procedure MLO510. Extracts are then concentrated to a small volume (typically 0.3 mL) and analyzed by gas chromatography/mass spectrometry. The mass spectrometer is operated in a scanning, electron-impact (EI) ionization mode. The gas chromatograph is temperature-programmed to effectively separate the wide range of analytes.

Analytes from a wide variety of compound classes can be determined using this method. Table VIII lists the compounds in the current Hazardous Substance List which are analyzed routinely. Table IX contains the Appendix IX list of compounds that are analyzed on a non-routine basis. Table X provides a list of compounds which can be incorporated into an analysis if the need arises. (Tables VIII, IX, and X are found at the end of this procedure.)

- 1.2. Qualitative analysis is performed by comparing retention time and mass-spectral data of unknowns to those of a standard mix for which the analytical system has been calibrated. EPA-defined criteria are used to establish the validity of a compound identity.

- 1.3. Quantitation is achieved using the internal standard technique. Once the identity of a compound is determined, quantitation is based on the integrated abundance of a characteristic ion for that compound. This value is compared to the characteristic ion area of the internal standard nearest the retention time of the compound so that a ratio between the two can be determined. Additional factors taken into account include the response factor of the compound being measured, the final volume of extract, and the sample aliquot extracted.

2. Sensitivity

- 2.1. Practical limits of quantitation are generally in the range of 1 to 2 mg/kg for low-level solid matrices. Matrices that are relatively free of interferences have lower attainable limits of detection than those having large amounts of coextractable material, such as drum waste. Medium-level extracts have a nominal detection limit of 20 mg/kg.
- 2.2. The values in Step 2.1 are analyte-dependent and can be greatly influenced by matrix constituents, sample inlet conditions, and general analyte reactivity. Response factors tend to show linearity to 180 $\mu\text{g/mL}$; however, specific compounds may show decreasing chromatographic performance or detector saturation at this concentration.

3. Accuracy and Precision

- 3.1. Based upon fixed-based laboratory surrogate and spike data, analyte recoveries are typically in the 60-110% range. Recoveries can be expected to vary depending upon the analyte and matrix complexity.
- 3.2. Long-range precision data is based upon matrix spike and spike duplicate percent recovery and the relative percent difference between the two. Refer to Section 11, Table VII.

4. Interferences

- 4.1. Any material that will cause an increase in background signal or an elevated baseline or result in discrete chromatographic peaks that are not attributable to target compounds may interfere with the identification and quantitation of a given analyte. Examples are environmental matrices containing high concentrations of humic material, oils, hydrocarbons, lipids, sulfur, or polar material such as alcohols and carboxylic acids.
- 4.2. Excessive particulate matter in water, extreme alkalinity or acidity, reactive material, intense light, and high temperature can negatively effect analyte recovery.

5. Sample Collection and Storage

- 5.1. All sampling equipment should be free of introduced contaminants.
- 5.2. Soil or sediment samples are typically collected in amber or clear glass wide-mouth bottles. Caps should have Teflon liners; however, aluminum foil can be substituted for Teflon if necessary. Excessive headspace should be avoided.
- 5.3. Samples should be stored, unpreserved, in a refrigerator at 4°C until extraction is initiated.

6. Sample holding times

- 6.1. Soil or sediment samples must be extracted within 14 d of receipt.
- 6.2. Sample extracts must be analyzed within 40 d of extraction.

7. Apparatus

- 7.1. Gas chromatograph/mass spectrometer: GC capable of temperature programming from 25 to 300°C. The mass spectrometer, using electron-impact ionization, must be capable of scanning a mass range 35-500 AMU in 1.0 s or less.
- 7.2. Data system: capable of initiating and controlling data acquisition, storing spectral and chromatographic data, and performing mass-spectral library searches.
- 7.3. Chromatographic column: 5% methyl phenyl silicone, 30-m x 0.25-mm-i.d. x 0.5- μ m film thickness, J & W DB-5.625 or equivalent.
- 7.4. Glass vials: 1.8-mL crimp cap, 1.8-, 7-, 10-, 12-, 15-, and 40-mL capacity screw cap with septa.
- 7.5. Volumetric flasks: 1-, 2-, 5-, 10-, 25-, 50-, 100-, and 250-mL with stoppers.
- 7.6. Disposable glass pipettes: 1-, 2-, 5-, and 10-mL.
- 7.7. Adjustable low-volume pipettors: 10- and 250- μ L capacity with disposable capillary tips. SMI brand or equivalent.
- 7.8. Syringes: glass, gas-tight, 10-, 25-, 50-, and 100- μ L volume.

8. Reagents

- 8.1. Methylene chloride (Baker Resi-analyzed).

- 8.2. Acetone (Baker Resi-analyzed).
- 8.3. Methanol (HPLC-grade).
- 8.4. Hexane (pesticide-grade).
- 8.5. Reagent water (deionized). Charcoal filtered and/or distilled water demonstrated to be free from interferences.

9. Analytical Standards

- 9.1. All analytical standards are refrigerated at -20°C . Working standards typically have a shelf life of three months. Stock standards are considered usable for at least six months or until degradation becomes apparent.

The following analytical standards are specified by EPA protocol to be used in the analysis of base/neutral acid extractables. They are readily available from any number of chemical suppliers as neat standards or as stock solutions. Currently, we use standard mixes formulated by Ultra Scientific, Inc.

- 9.2. **Internal Standards (ISs).** The IS compounds are added to extracts immediately prior to instrumental analysis. They are used to facilitate both qualitative and quantitative analysis. Extracts are spiked with an IS mix so that a final concentration of $40\text{ }\mu\text{g/mL}$ of each component is obtained.

- 9.2.1. Internal standard mix ($4000\text{ }\mu\text{g/mL}$ or $2000\text{ }\mu\text{g/mL}$ in CH_2Cl_2) depending on the supplier. This mix is used undiluted and spiked into the samples, blanks, and all calibration standards so that a final concentration of $40\text{ }\mu\text{g/mL}$ is obtained. Internal standards are:

- 1,4-Dichlorobenzene- d_4
 - Naphthalene- d_8
 - Acenaphthene- d_{10}
 - Phenanthrene- d_{10}
 - Chrysene- d_{12}
 - Perylene- d_{12}

- 9.3. **Decafluorotriphenylphosphine (DFTPP).** DFTPP is used to verify the performance of the mass spectrometer. The DFTPP spectrum must meet established EPA ion abundance criteria before performing instrument calibration and sample analysis. The working standard DFTPP concentration is $50\text{ }\mu\text{g/mL}$ in methylene chloride.

- 9.4. **Initial calibration standards.** These standards contain all target compounds of interest at five different concentrations, typically 20.0, 50.0, 80.0, 120.0, and $160.0\text{ }\mu\text{g/mL}$ of each analyte. These standards are made by volumetric dilution

of 2000- $\mu\text{g/mL}$ stock standards with methylene chloride. Appropriate amounts of internal standards and surrogate are included.

- 9.5. **Daily calibration standards.** These standards contain 50.0 $\mu\text{g/mL}$ of all target compounds of interest in methylene chloride. This standard is used to demonstrate instrument stability in terms of analyte response (response factor) and relative retention time.

10. GC/MS Calibration

- 10.1. This application uses a slightly polar methyl silicone stationary phase bonded to a fused-silica capillary column, such as the J&W DB-5.625, Supelco SPB-5, or Quadrex 007-2. Column dimensions are nominally 30-m x 0.25-mm-id, 0.50- μm film thickness.

- 10.2. The following gas chromatographic parameters are used for data acquisition:

Initial temp.: 50°C	Carrier: He
Initial time: 0.0 min	Flow: 1.0 mL/min
Final temp.: 315°C	Inlet temp.: 280°C
Final time: 20 min	Interface temp.: 300°C
Rate: 15°C/min	

Some variations are allowed for final temperature, final time, and flow rate when they improve the chromatography or analytical performance.

- 10.3. **DFTPP tuning.**

- 10.3.1. The quadrupole mass spectrometer is operated in a scanning electron-impact ionization mode. The spectrometer is tuned with the calibration compound perfluorotributylamine (PFTBA) so that a 50-ng injection of decafluorotriphenylphosphine (DFTPP) results in a spectrum which satisfies the key ion abundance and resolution criteria outlined in Table I.

TABLE I: KEY ION ABUNDANCE AND RESOLUTION CRITERIA

Mass	Ion Abundance Criteria
51	30.0-60.0% of mass 198
68	<2.0% of mass 69
70	<2.0% of mass 69
127	40.0-60.0% of mass 198
197	<1.0% of mass 198

TABLE I (cont)	
Mass	Ion Abundance Criteria
198	base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10.0-30.0 % of mass 198
365	>1.00 % of mass 198
441	present but less than mass 443
442	>40.0% of mass 198
443	17.0-23.0% of mass 442

10.3.2. Under Tier Two QC, these tuning requirements **must** be met and documented before proceeding for each mass spectrometer used for this application. The criteria, once met, are valid for a 12-h period during which standards, samples, and blanks may be analyzed. At the end of the 12-h period, the DFTPP criteria must be met again before continued analysis.

10.4. Initial calibration.

10.4.1. Under Tier Two and Tier Three QC, once the mass spectrometer is hardware tuned it **must be initially calibrated** with a minimum of three or five standard concentrations to demonstrate response linearity. Table II lists those analytes requiring only four initial calibration points. Analyze standards at concentrations of 20, 50, and 160 $\mu\text{g/mL}$ for Tier Two, and 20, 50, 80, 120, and 160 $\mu\text{g/mL}$ for Tier Three. The five-point calibration must meet the USEPA response factor criteria listed below.

TABLE II. COMPOUNDS REQUIRING A
FOUR-POINT CALIBRATION
USEPA-CLP SOW2/88

Benzoic acid	2,4-Dinitrophenol
2,4,5-Trichlorophenol	2-Nitroaniline
3-Nitroaniline	4-Nitroaniline
4-Nitrophenol	Pentachlorophenol
4,6-Dinitro-2-methylphenol	

- 10.4.2. Calculate response factors (RF) for all individual calibration compounds. The percent relative standard deviation (%RSD) for each compound should be less than 30% and **must** be less than 30% for all calibration check compounds (CCC). See Table III.

TABLE III. CONTINUING CALIBRATION CHECK COMPOUNDS FOR WHICH %RSD MUST BE <30.0

Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

Response factors are calculated using the following equation:

$$RF = \frac{(A_x) (C_{is})}{(A_{is}) (C_x)}$$

where A_x = area of the characteristic ion for the compound being measured,

C_{is} = concentration of the internal standard (ng/ μ L),

A_{is} = area of the characteristic ion for the nearest internal standard, and

C_x = concentration of the compound being measured (ng/ μ L).

Percent relative standard deviation is calculated using the following equation:

$$\%RSD = \frac{(SD)}{(RF)} \times 100$$

- 10.4.3. The minimum average response for system performance check compounds (SPCC) **must** be 0.050 or greater.

10.4.4. Relative retention times of each compound from each standard should agree within 0.06 retention time units.

10.4.5. Under Tier Three QC requirements, if the % RSD for any CCC, or the minimum RF for any SPCC is not met, corrective action must be taken. An individual calibration point or the entire calibration curve may need reanalysis.

10.5. Continuing calibration.

On a daily basis, immediately after DFTPP criteria have been demonstrated, a continuing calibration standard containing 50 µg/mL of each target analyte is analyzed. The relative response factor for each analyte is compared with the corresponding average response factor obtained from the initial calibration.

10.5.1. Under Tier Two and Tier Three QC criteria, each continuing calibration must be evaluated for and meet the criteria listed below:

10.5.1.1. All SPCCs must have a minimum response factor not less than 0.050 (see Table IV).

TABLE IV. SYSTEM PERFORMANCE
CHECK COMPOUNDS FOR
WHICH AVERAGE RF
MUST BE >0.05

N-nitroso-di-n-propylamine

Hexachlorocyclopentadiene

2,4-Dinitrophenol

4-Nitrophenol

10.5.1.2. The percent difference between the continuing calibration relative response factor and the average relative response factor and the average relative response from the initial calibration must not be greater than 25.0% for any CCC. Table III lists these analytes. If this requirement is met, the calibration is assumed to be valid.

The percent difference is calculated using the following equation:

$$\% \text{ Difference} = \frac{RF_i - RF_c}{RF_i} \times 100 ,$$

where RF_i = average response factor from the initial calibration, and

RF_c = response factor from the current continuing calibration.

10.5.1.3. Under Tier Three QC requirements, the percent difference between the continuing calibration relative response factor and the average relative response from the initial calibration should not be greater than 20.0% for any target compound for which the instrument is calibrated. If the percent difference exceeds this value it is considered as a warning limit.

10.5.2. If the preceding calibration criteria are not met, corrective action is taken and the continuing calibration standard is reanalyzed. If the criteria are still not met, a new three- or five-point initial calibration is performed.

10.5.3. Once all continuing calibration criteria have been met, the method ID file is updated with the current relative retention times (RRTs) and response factors (RFs) before acquiring and processing sample data.

10.5.4. The method ID file contains retention-time and mass-spectral data pertinent to a given target compound list. It is defined and edited by the user and resides on the GC/MS data system.

11. Quality Assurance and Data Interpretation Requirements

11.1. The Quality Control requirements are defined in a tiered structure as follows:

Tier 1: 1-point calibration every day.
1 method blank every day.

Tier 2: 3-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank every day.

Tier 3: 5-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank per analytical batch.

Blind QC samples at a rate of no more than 10%.

Matrix spike and matrix spike duplicate for each analytical batch.

12-h clock for tune check and daily check standard.

11.2. All calibration criteria listed in the previous section must be met before analyzing samples.

11.3. **Method blank analysis.** A method blank is a volume of reagent water or a purified solid material which is taken through the entire analytical procedure. The weight or volume of the blank must approximate that of the samples being analyzed.

11.3.1. Under Tier Two and Tier Three QC requirements, blanks are analyzed at a frequency of one for every 20 samples of similar matrix or whenever samples are extracted by the same procedure, whichever is more frequent. The following criteria are checked immediately after blank analysis:

- The method blank should contain less than five times the practical quantitation limit (PQL) of phthalate esters in the target compound list.
- All other analytes present on the target compound list should not be present at concentrations greater than the PQL.
- Recovery of all surrogate compounds must be within specified limits (Table V). If this criterion is not met, reanalyze or reextract another blank to determine whether the incident is isolated or an out-of-control status exists.

TABLE V. BNA SURROGATE SPIKE
RECOVERY LIMITS IN
PERCENT

Surrogate Compound	Water	Soil
Nitrobenzene-d ₅	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d ₁₄	33-141	18-137
Phenol-d ₅	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

- 11.3. **Surrogate spike requirements.** Each sample prepared and analyzed for semivolatile compounds is fortified with known amounts of base-neutral and acid extractable compounds. By evaluating their recovery, measured as a percentage, the analyst can draw conclusions concerning the analytical efficiency on a sample-by-sample basis.

- 11.3.1. Surrogate spike recoveries are considered to be acceptable if they fall within the range specified in Table V.

The following conditions indicate unacceptable surrogate recovery: (1) Recovery of any one surrogate in either the base-neutral or acid fraction is less than 10%, and (2) recoveries of any two surrogate compounds in either base-neutral or acid fraction are out of recovery limits.

- 11.3.2. When surrogate spike recoveries are determined to be out of control the analyst needs to determine if the cause is matrix- or process-dependent. Reextraction should be requested when there is sufficient sample and holding time can be met. Whichever conclusion is reached needs to be addressed in the case narrative and/or anomaly summary. Corrective action will be implemented to alleviate the causes of the out-of-control condition.

- 11.4. **Matrix spike and matrix spike duplicate recovery requirements.** In order to evaluate the matrix effect of a sample upon the analytical methodology employed, known concentrations of base/neutral and acid target compounds are added to duplicates of a given sample (Table VI). The sample chosen to be spiked should be representative of the samples from a given project.

TABLE VI. BNA MATRIX SPIKE COMPOUNDS

Compound	Fraction	Amount added (μg)
1,2,4-Trichlorobenzene	BN	50
Acenaphthene	BN	50
2,4-Dinitrotoluene	BN	50
Pyrene	BN	50
N-nitroso-di-n-propylamine	BN	50
1,4-Dichlorobenzene	BN	50
Pentachlorophenol	Acid	100
Phenol	Acid	100

TABLE VI. (cont)

Compound	Fraction	Amount added (μg)
2-Chlorophenol	Acid	100
4-Chloro-3-methylphenol	Acid	100
4-Nitrophenol	Acid	100

- 11.4.1. Under Tier Three QC requirements, matrix spike and matrix spike duplicate data are generated for every twenty samples of a given matrix type prepared by the same method.
- 11.4.2. Matrix spike/matrix spike duplicates and the original unspiked sample must be concentrated to the same final volume and analyzed at the same dilution level. If high levels of target compounds are detected that are not matrix spike compounds, the original sample only needs to be diluted to enable compound quantitation.
- 11.4.3. Spike recovery is evaluated in terms of percent recovery and the relative percent difference (RPD) between individual spike compounds in the MS and MSD. This data can be used to evaluate the long term precision and accuracy of the method. See Table VII for spike recovery limits.

TABLE VII. BNA MATRIX SPIKE RECOVERY LIMITS - SOIL

Compound	Percent recovered			RPD
1,2,4-Trichlorobenzene	38	-	107	23
Acenaphthene	31	-	137	19
2,4-Dinitrotoluene	28	-	89	47
Pyrene	35	-	142	36
N-nitroso-di-n-propylamine	41	-	126	38
1,4-Dichlorobenzene	28	-	104	27
Pentachlorophenol	17	-	109	47

TABLE VII. (cont)				
Compound	Percent recovered			RPD
Phenol	26	-	90	35
2-Chlorophenol	25	-	102	50
4-Chloro-3-methylphenol	26	-	103	33
4-Nitrophenol	11	-	114	50

11.5. Under Tier Three QC requirements, blind spikes are regularly extracted and analyzed as an independent check of method accuracy. Standard reference materials should resemble submitted matrices as closely as possible.

11.6. **Sample analysis.** Samples must be analyzed within 40 d of sample extraction.

11.6.1. Internal standard response from each sample injection must agree by a factor of two (~50% to 200%) with the internal standard response from the most recent continuing calibration standard.

11.6.2. Sample internal standard retention times must not differ by more than 30 s from the continuing calibration standard.

11.6.3. Each analytical run is checked for detector saturation for each target compound positively identified.

11.6.4. All data is evaluated for correctness of dilution. When compounds are detected at concentrations greater than 160 ppm, the sample extracts are diluted and reanalyzed.

11.6.5. Discrete chromatographic peaks that are not identified as target compounds are treated as tentatively identified compounds (TICs). These compounds may be identified if the customer requests this service. A tentative identification is made by comparison of the unknown spectra with a mass-spectral database.

11.7. **Qualitative analysis.**

11.7.1. Target compounds detected in sample injections are positively identified on the basis of relative retention time (RRT) and mass spectral criteria. See Table VIII for a list of analytes and their corresponding characteristic ions.

11.7.1.1. The sample component's relative retention time must agree within ± 0.06 RRT units of that component in the continuing calibration standard.

11.7.1.2. Qualitative verification requires the following conditions to be met:

- All ions present in the standard mass spectrum at a relative intensity $>10\%$ must be present in the sample spectrum.
- The relative intensities of ions specified above must agree within 20%.
- Ions present at relative intensities $>10\%$ in the sample spectrum but not present in the standard spectrum must be accounted for by generating extracted ion current profiles (EICPs) for the relevant ions.
- Compounds present in samples but determined not to be target compounds are treated as TICs. A maximum of 20 discrete compounds may be identified (at customer's discretion) through comparison of unknown spectra with a mass-spectral library database. TICs will be searched only when their relative ion concentration (RIC) area is greater than 10% of the nearest internal standard RIC area.

11.8. **Quantitative analysis.** When a target compound has been positively identified, quantitation is based on the EICP of the primary characteristic ion using the internal standard technique. The internal standard used will be the one nearest the retention time of the analyte.

11.8.1. The following calculations are used to quantify target analytes:

Low level soil/sludge/sediment/waste

$$\text{conc. of analyte (ng/g)} = \frac{A_x \times I_s \times V_t}{A_s \times R_t \times W_s \times V_e \times D}$$

where A_x = area of the characteristic ion for the analyte being measured,

I_s = amount of internal standard injected (ng),

V_t = volume of total extract taking into account any dilutions,

A_{is} = area of characteristic ion for the internal standard,
 R_f = response factor for the compound being measured,
 W_s = weight of sample extracted or diluted in grams, and
 V_s = volume of extract injected (μL).

$$D = \frac{(100 - \% \text{ moisture in sample})}{100} ,$$

where $D = 1.0$ if the data will be reported on a wet-weight basis.

11.8.2. Calculation of response factors (RF).

$$RF = \frac{(Ax) (Cis)}{(Ais) (Cx)} ,$$

where Ax = area of the characteristic ion for the analyte being measured,
 Cis = concentration of the specific internal standard (40 ng/ μL),
 Ais = area of the characteristic ion of the specific internal standard, and
 Cx = concentration of the compound being measured (ng/ μL).

11.8.3. Percent moisture determination. When sample concentrations are to be reported on a dry weight basis, percent moisture is calculated using the following equation:

$$\% M = \frac{S_w - S_d}{S_w} \times 100 ,$$

where S_w = wet weight of the soil aliquot less the container weight, and
 S_d = dry weight of the soil aliquot less the container weight after oven drying at 105°C for 24 h.

12. Reporting

Analytical results are reported using one of two target compound lists (TCLs) depending on the requirements of the submitter. The Appendix IX TCL list (ground water monitoring) includes the Hazardous Substance List (HSL) plus 43 additional analytes. Table IX contains a listing of HSL target compounds while Table X lists the Appendix IX target compounds. Compounds on the HSL list are routinely analyzed for and reported. Appendix IX compounds are not routinely analyzed.

13. Proper Waste Disposal Practices

13.1. General waste management.

13.1.1. Each analyst within the section shall be given Waste Generator Training by EM-8 within 90 days of date of hire.

13.1.2. Wherever possible, the generation of waste shall be minimized through reduction, reuse, or recycling. Wherever possible, containers should be segregated to reflect the nature of the hazardous waste and the eventual waste-disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, non-chlorinated solvents and >50-ppm contaminated PCB waste should be segregated from <50-ppm PCB contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

13.1.3. Categorized the waste using a Waste Profile Form from EM-8.

13.1.4. Upon completion of a Waste Profile Form, the waste is disposed of by completing a Waste Disposal Request Form from EM-7. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

13.2. Solid waste.

13.2.1. Solid hazardous waste, such as contaminated paper towels, pipettes, spent syringes, and glass vials, is accumulated in a covered plastic container lined with a plastic bag. The container is labeled with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

13.2.2. The waste container is opened only for the time necessary to add the waste.

13.3. Liquid waste.

13.3.1. Liquid wastes, such as spent samples and spent solvents that are not reuseable, are accumulated in glass or steel containers appropriate for the type of sample being stored. For example, caustic materials should be stored in glass containers whereas spent solvents that are not to be recycled should be stored in metal containers.

13.3.2. All containers storing hazardous liquid materials must be secondarily contained. The container is labeled with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

13.3.3. The waste container is opened only for the time necessary to add the waste.

13.4. Unused samples.

13.4.1. Return unused environmental samples to the Sample Management section for disposal.

14. Source Materials

14.1. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis Multi-media, Multi-Concentration, 2/88.

14.2. Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, ed. 1988.

14.3. Sorbent Extraction Technology, K.C. Van Horne, Analytical International, Inc. 1985.

14.4. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

TABLE VIII. CHARACTERISTICS IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention time (min)	Primary ion	Secondary ion(s)
2-Picoline	3.75 ^a	93	66, 92
Aniline	5.68	93	66, 65
Phenol	5.77	94	65, 66
Bis(2-chloroethyl) ether	5.82	93	63, 95
2-Chlorophenol	5.97	128	64, 130
1,3-Dichlorobenzene	6.27	146	148, 111
1,4-Dichlorobenzene-d ₄ (I.S.)	6.35	152	150, 115
1,4-Dichlorobenzene	6.40	146	148, 111
Benzyl alcohol	6.78	108	79, 77
1,2-Dichlorobenzene	6.85	146	148, 111
N-Nitrosomethylethylamine	6.97	88	42, 88, 43, 56
Bis(2-chloroisopropyl) ether	7.22	45	77, 121
Ethyl carbamate	7.27	62	62, 44, 45, 74
Thiophenol (benzenethiol)	7.42	110	110, 66, 109, 84
Methyl methanesulfonate	7.48	80	80, 79, 65, 95
N-Nitrosodi-n-propylamine	7.55	70	42, 101, 130
Hexachloroethane	7.65	117	201, 199
Maleic anhydride	7.65	54	54, 98, 53, 44
Nitrobenzene	7.87	77	123, 65
Isophorone	8.53	82	95, 138
N-Nitrosodiethylamine	8.70	102	102, 42, 57, 44, 56
2-Nitrophenol	8.75	139	109, 65
2,4-Dimethylphenol	9.03	122	107, 121
p-Benzoquinone	9.13	108	54, 108, 82, 80
Bis(2-chloroethoxy) methane	9.23	93	95, 123
Benzoic acid	9.38	122	105, 77
2,4-Dichlorophenol	9.48	162	164, 98

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion(s)
Trimethyl phosphate	9.53	110	110, 79, 95, 109, 140
Ethyl methanesulfonate	9.62	79	79, 109, 97, 45, 65
1,2,4-Trichlorobenzene	9.67	180	182, 145
Naphthalene-d ₈ (I.S.)	9.75	136	68
Naphthalene	9.82	128	129, 127
Hexachlorobutadiene	10.43	225	223, 227
Tetraethyl pyrophosphate	11.07	99	99, 155, 127, 81, 109
Diethyl sulfate	11.37	139	139, 45, 59, 99, 111, 125
4-Chloro-3-methylphenol	11.68	107	144, 142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	107, 108, 77, 79 90
Hexachloropropene	12.45	213	213, 211, 215, 117, 106, 141
Hexachlorocyclopentadiene	12.60	237	235, 272
N-Nitrosopyrrolidine	12.65	100	100, 41, 42, 68, 69
Acetophenone	12.67	105	71, 105, 51, 120
4-Methylphenol	12.82	107	107, 108, 77, 79 90
2,4,6-Trichlorophenol	12.85	196	198, 200
o-Toluidine	12.87	106	106, 107, 77, 51, 79
3-Methylphenol	12.93	107	107, 108, 77, 79, 90
2-Chloronaphthalene	13.30	162	127, 164
N-Nitrosopiperidine	13.55	114	42, 114, 55, 56, 41
1,4-Phenylenediamine	13.62	108	108, 80, 53, 54, 52
1-Chloronaphthalene	13.65 ^a	162	127, 164
2-Nitroaniline	13.75	65	92, 138
5-Chloro-2-methylaniline	14.28	106	106, 141, 140, 77, 89
Dimethyl phthalate	14.48	163	194, 164

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Acenaphthylene	14.57	152	151, 153
2,6-Dinitrotoluene	14.62	165	63, 89
Phthalic anhydride	14.62	104	104, 76, 50, 148
o-Anisidine	15.00	108	80, 108, 123, 52
3-Nitroaniline	15.02	138	108, 92
Acenaphthene-d ₁₀ (I.S.)	15.05	164	162, 160
Acenaphthene	15.13	154	153, 152
2,4-Dinitrophenol	15.35	184	63, 154
2,6-Dinitrophenol	15.47	162	162, 164, 126, 98, 63
4-Chloroaniline	15.50	127	127, 129, 65, 92
Isosafrole	15.60	162	162, 131, 104, 77, 51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	121, 122, 94, 77, 104
2,4-Dinitrotoluene	15.80	165	63, 89
4-Nitrophenol	15.80	139	109, 65
2-Naphthylamine	16.00 ^a	143	115, 116
1,4-Naphthoquinone	16.23	158	158, 104, 102, 76, 50, 130
p-Cresidine	16.45	122	122, 94, 137, 77, 93
Dichlorovos	16.48	109	109, 185, 79, 145
Diethyl phthalate	16.70	149	177, 150
Fluorene	16.70	166	165, 167
2,4,5-Trimethylaniline	16.70	120	120, 135, 134, 91, 77
N-Nitrosodibutylamine	16.73	84	84, 57, 41, 116, 158
4-Chlorophenyl phenyl ether	16.78	204	206, 141
Hydroquinone	16.93	110	110, 81, 53, 55
4,6-Dinitro-2-methylphenol	17.05	198	51, 105

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Resorcinol	17.13	110	110, 81, 82, 53, 69
N-Nitrosodiphenylamine	17.17	169	168, 167
Safrole	17.23	162	162, 162, 104, 77, 103, 135
Hexamethyl phosphoramidate	17.33	135	135, 44, 179, 92, 42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	92, 127, 129, 65, 39
Diphenylamine	17.54 ^a	169	168, 167
1,2,4,5-Tetrachlorobenzene	17.97	216	216, 214, 179, 108, 143, 218
1-Naphthylamine	18.20	143	143, 115, 89, 63
1-Acetyl-2-thiourea	18.22	118	43, 118, 42, 76
4-Bromophenyl phenyl ether	18.27	248	250, 141
Toluene diisocyanate	18.42	174	174, 145, 173, 146, 132, 91
2,4,5-Trichlorophenol	18.47	196	196, 198, 97, 132, 99
Hexachlorobenzene	18.65	284	142, 249
Nicotine	18.70	84	84, 133, 161, 162
Pentachlorophenol	19.25	266	264, 268
5-Nitro-2-methylaniline	19.27	152,	77, 152, 79, 106, 94
Thionazine	19.35	107	96, 107, 97, 143, 79, 68
4-Nitroaniline	19.37	138	138, 65, 108, 92, 80, 39
Phenanthrene-d ₁₀ (i.s.)	19.55	188	94, 80
Phenanthrene	19.62	178	179, 176
Anthracene	19.77	178	176, 179
1,4-Dinitrobenzene	19.83	168	168, 75, 50, 76, 92, 122
Mevinphos	19.90	127	127, 192, 109, 67, 164
Naled	20.03	109	109, 145, 147, 301, 79, 189
1,3-Dinitrobenzene	20.18	168	168, 76, 50, 75, 92, 122
Diallate (cis or trans)	20.57	86	86, 234, 43, 70

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
1,2-Dinitrobenzene	20.58	168	168, 50, 63, 74
Diallate (trans or cis)	20.78	86	86, 234, 43, 70
Pentachlorobenzene	21.35	250	250, 252, 108, 248, 215, 254
5-Nitro-2-methoxyaniline	21.50	168	168, 79, 52, 138, 153, 77
Pentachloronitrobenzene	21.72	237	237, 142, 214, 249, 295, 265
4-Nitroquinoline-1-oxide	21.73	174	174, 101, 128, 75, 116
Di-n-butyl phthalate	21.78	149	150, 104
2,3,4,6-Tetrachlorophenol	21.88	232	232, 131, 230, 166, 234, 168
Demeton-o	22.72	88	88, 89, 60, 61, 115, 171
Fluoranthene	23.33	202	101, 203
1,3,5-Trinitrobenzene	23.68	75	75, 74, 213, 120, 91, 63
Dicrotophos	23.82	127	127, 67, 72, 109, 193, 237
Benzidine	23.87	184	92, 185
Trifluralin	23.88	306	306, 43, 264, 41, 290
Bromoxynil	23.90	277	277, 279, 88, 275, 168
Pyrene	24.02	202	200, 203
Monocrothophos	24.08	127	127, 192, 67, 97, 109
Phorate	24.10	75	75, 121, 97, 93, 260
Sulfallate	24.23	188	188, 88, 72, 60, 44
Demeton-s	24.30	88	88, 60, 81, 89, 114, 115
Phenacetin	24.33	108	180, 179, 109, 137, 80
Dimethoate	24.70	87	87, 93, 125, 143, 229
Phenobarbital	24.70	204	204, 117, 232, 146, 161
Carbofuran	24.90	164	164, 149, 131, 122
Octamethyl pyrophosphoramidate	24.95	135	135, 44, 199, 286, 153, 243
4-Aminobiphenyl	25.08	169	169, 168, 170, 115
Terbufos	25.35	231	231, 57, 97, 153, 103

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Pronamide	25.48	173	173, 175, 145, 109, 147
Aminoazobenzene	25.72	197	92, 197, 120, 65, 77
Dichlone	25.77	191	191, 163, 226, 228, 135, 193
Dinoseb	25.83	211	211, 163, 147, 117, 240
Disulfoton	25.83	88	88, 97, 89, 142, 186
Fluchloralin	25.88	306	306, 63, 326, 328, 264, 65
Mexacarbate	26.02	165	165, 150, 134, 164, 222
4,4'-Oxydianiline	26.08	200	200, 108, 171, 80, 65
Butyl benzyl phthalate	26.43	149	91, 206
4-Nitrobiphenyl	26.55	199	199, 152, 141, 169, 151
Phosphamidon	26.85	127	127, 264, 72, 109, 138
2-Cyclohexyl-4,6-dinitrophenol	26.87	231	231, 185, 41, 193, 266
Methyl parathion	27.03	109	109, 125, 263, 79, 93
Carbaryl	27.17	144	144, 115, 116, 201
Dimethylaminoazobenzene	27.50	225	225, 120, 77, 105, 148, 42
Propylthiouracil	27.68	170	170, 142, 114, 83
Benz(a)anthracene	27.83	228	229, 226
Chrysene-d ₁₂ (I.S.)	27.88	240	120, 236
3,3'-Dichlorobenzidine	27.88	252	254, 126
Chrysene	27.97	228	226, 229
Malathion	28.08	173	173, 125, 127, 93, 158
Kepone	28.18	272	272, 274, 237, 178, 143, 270
Fenthion	28.37	278	278, 125, 109, 169, 153
Parathion	28.40	109	109, 97, 291, 139, 155
Anilazine	28.47	239	239, 241, 143, 178, 89

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Bis(2-ethylhexyl) phthalate	28.47	149	167, 279
3,3'-Dimethylbenzidine	28.55	212	212, 106, 196, 180
Carbophenothion	28.58	157	157, 97, 121, 342, 159, 199
5-Nitroacenaphthene	28.73	199	199, 152, 169, 141, 115
Methapyrilene	28.77	97	97, 50, 191, 71
Isodrin	28.95	193	193, 66, 195, 263, 265, 147
Captan	29.47	79	79, 149, 77, 119, 117
Chlorfenvinphos	29.53	267	267, 269, 323, 325 295
Crotoxypfos	29.73	127	127, 105, 193, 166
Phosmet	30.03	160	160, 77, 93, 317, 76
EPN	30.11	157	157, 169, 185, 141, 323
Tetrachlorvinphos	30.27	329	109, 329, 331, 79, 333
Di-n-octyl phthalate	30.48	149	167, 43
2-Aminoanthraquinone	30.63	223	223, 167, 195
Barban	30.83	222	222, 51, 87, 224, 257, 153
Aramite	30.92	185	185, 191, 319, 334, 197, 321
Benzo(b)fluoranthene	31.45	252	253, 125
Nitrofen	31.48	283	283, 285, 202, 139, 253
Benzo(k)fluoranthene	31.55	252	253, 125
Chlorobenzilate	31.77	251	251, 139, 253, 111, 141
Fensulfothion	31.87	293	293, 97, 308, 125, 292
Ethion	32.08	231	231, 97, 153, 125, 121
Diethylstilbestrol	32.15	268	268, 145, 107, 239, 121, 159
Famphur	32.67	218	218, 125, 93, 109, 217
Tri-p-tolyl phosphate ^b	32.75	368	368, 367, 107, 165, 198
Benzo(a)pyrene	32.80	252	253, 125
Perylene-d ₁₂ (I.S.)	33.05	264	260, 265

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
7,12-Dimethylbenz(a)anthracene	33.25	256	256, 241, 239, 120
5,5-Diphenylhydantoin	33.40	180	180, 104, 252, 223, 209
Captafol	33.47	79	79, 77, 80, 107
Dinocap	33.47	69	69, 41, 39
Methoxychlor	33.55	227	227, 228, 152, 114, 274, 212
2-Acetylaminofluorene	33.58	181	181, 180, 223, 152
4,4'-Methylenebis-(2-chloroaniline)	34.38	231	231, 266, 268, 140, 195
3,3'-Dimethoxybenzidine	34.47	244	244, 201, 229
3-Methylcholanthrene	35.07	268	268, 252, 253, 126, 134, 113
Phosalone	35.23	182	182, 184, 367, 121, 379
Azinphos-methyl	35.25	160	160, 132, 93, 104, 105
Leptophos	35.28	171	171, 377, 375, 77, 155, 379
Mirex	35.43	272	272, 237, 274, 270 239, 235
Tris(2,3-dibromopropyl)phosphate	35.68	201	137, 201, 119, 217, 219, 199
Dibenz(a,j)acridine	36.40	279	279, 280, 277, 250
Mestranol	36.48	277	277, 310, 174, 147, 242
Coumaphos	37.08	362	362, 226, 210, 364, 97, 109
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227
Dibenz(a,h)anthracene	39.82	278	139, 279
Benzo(g,h,i)perylene	41.43	276	138, 277
1,2:4,5-Dibenzopyrene	41.60	302	302, 151, 150, 300
Strychnine	45.15	334	334, 335, 333
Piperonyl sulfoxide	46.43	162	162, 135, 105, 77
Hexachlorophene	47.98	196	196, 198, 209, 211, 406, 408

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Aldrin		66	263, 220
Aroclor-1016		222	260, 292
Aroclor-1221		190	224, 260
Aroclor-1232		190	224, 260
Aroclor-1242		222	256, 292
Aroclor-1248		292	362, 326
Aroclor-1254		292	362, 326
Aroclor-1260		360	362, 394
α -BHC		183	181, 109
β -BHC		181	183, 109
4,4'-DDD		235	237, 165
4,4'-DDE		246	248, 176
4,4'-DDT		235	237, 165
Dieldrin		79	263, 279
1,2-Diphenylhydrazine		77	105, 182
Endosulfan I		195	339, 341
Endosulfan II		337	339, 341
Endosulfan sulfate		272	387, 422
Endrin		263	82, 81
Endrin aldehyde		67	345, 250
Endrin ketone		317	67, 319
2-Fluorobiphenyl (surr.)		172	171
2-Fluorophenol (surr.)		112	64
Heptachlor		100	272, 274
Heptachlor epoxide		353	355, 351

TABLE VIII. (cont)

Compound	Retention time (min)	Primary ion	Secondary ion (s)
Nitrobenzene-d ₅ (surr.)	82	128, 54	
N-Nitrosodimethylamine	42	74, 44	
Phenol-d ₆ (surr.)	99	42, 71	
Terphenyl-d ₁₄ (surr.)	244	122, 212	
2,4,6-Tribromophenol (surr.)	330	332, 141	
Toxaphene	159	231, 233	

I.S. = internal standard.

surr. = surrogate.

^aEstimated retention times; this value depends substantially on the final chromatographic conditions.

^bSubstitute for the non-specific mixture, tricresyl phosphate.

TABLE IX. HAZARDOUS SUBSTANCE LIST OF
SEMIVOLATILE ORGANIC ANALYTES IN SOIL
LIMIT OF QUANTITATION

Compound	CAS number	LOQ mg/kg
Acenaphthene	83-32-9	1.0
Acenaphthylene	208-96-2	1.0
Anthracene	120-12-7	1.0
Aniline	62-53-3	1.0 *
Azobenzene	3-33-3	1.0
Benzidine	92-87-5	1.0 *,a
Benz(a)anthracene	56-55-3	1.0
Benzo(b)fluoranthene	205-99-2	1.0
Benzo(k)fluoranthene	207-88-9	1.0
Benzoic acid	65-85-0	1.0 *,c
Benzo(g,h,i)perylene	191-24-2	1.0
Benzo(a)pyrene	50-32-8	1.0
Benzyl alcohol	0-51-6	1.0
Bis(2-chloroethoxy)methane	111-91-1	1.0
Bis(2-chloroethyl) ether	111-44-4	1.0
Bis(2-chloroisopropyl) ether	8-60-1	1.0
4-Bromophenyl phenyl ether	1-55-3	1.0
Butyl benzyl phthalate	85-68-7	1.0 *
4-Chloroaniline	6-47-8	1.0 *,c
4-Chloro-3-methylphenol	59-50-7	1.0
2-Chloronaphthalene	91-58-7	1.0
2-Chlorophenol	95-57-8	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0
Chrysene	218-01-9	1.0
Dibenz(a,h)anthracene	53-70-3	1.0
Dibenzofuran	132-64-9	1.0

TABLE IX. (cont)

Compound	CAS number	LOQ mg/kg
Di-n-butyl phthalate	84-74-2	1.0 *
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	6-46-7	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0 *
2,4-Dichlorophenol	120-83-2	1.0
Diethyl phthalate	84-66-2	1.0 *
2,4-Dimethylphenol	5-67-9	1.0 *,c
Dimethyl phthalate	131-11-3	1.0 *
4,6-Dinitro-2-methylphenol	534-52-1	1.0
2,4-Dinitrophenol	51-28-5	1.0 *,c
2,4-Dinitrotoluene	121-14-2	1.0
2,6-Dinitrotoluene	606-20-2	1.0
Di-n-octyl phthalate	117-84-0	1.0
Bis(2-ethylhexyl) phthalate	117-81-7	1.0
Fluoranthene	206-44-0	1.0
Fluorene	86-73-7	1.0
Hexachlorobenzene	118-74-1	1.0
Hexachlorobutadiene	87-68-3	1.0
Hexachlorocyclopentadiene	77-47-4	1.0*,d
Hexachloroethane	67-72-1	1.0
Indeno(1,2,3-cd)pyrene	193-39-5	1.0
Isophorone	78-59-1	1.0
2-Methylnaphthalene	91-57-6	1.0
2-Methylphenol	95-48-7	1.0 *,c
4-Methylphenol	6-44-5	1.0 *,c
Naphthalene	91-20-3	1.0
2-Nitroaniline	88-74-4	1.0

TABLE IX. (cont)

Compound	CAS number	LOQ mg/kg
3-Nitroaniline	99-09-2	1.0 *,c
4-Nitroaniline	0-01-6	1.0 *,c
Nitrobenzene	98-95-3	1.0
2-Nitrophenol	88-75-5	1.0
4-Nitrophenol	0-02-7	1.0 *,c
N-Nitrosodimethylamine	62-75-9	1.0 *,c
N-Nitrosodiphenylamine	86-30-6	1.0
N-Nitroso-di-n-propylamine	621-64-7	1.0 *
Pentachlorophenol	87-86-5	1.0 *,c
Phenanthrene	85-01-8	1.0
Phenol	8-95-2	1.0
Pyrene	129-00-0	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
2,4,5-Trichlorophenol	95-95-4	1.0
2,4,6-Trichlorophenol	88-06-2	1.0

* = The limit of quantitation has not been verified for these analytes based upon a Method Detection Limit study. All others averaged better than 70% analyte recovery based upon seven repetitions. The amount of each analyte spiked was 1.0 μg into 1.0 L.

a = Exhibits nonreproducible chromatography and oxidative loss during concentration.

c = These analytes are subject to erratic chromatographic performance and/or thermal decomposition in the gas chromatograph inlet.

d = Subject to thermal decomposition in the chromatographic inlet, chemical reaction with acetone in solution, and photochemical decomposition.

Limits of Quantitation (LOQ) will be two times greater for soil/sediment matrices which have been GPC cleaned.

**TABLE X. APPENDIX IX TARGET COMPOUND LIST
OF SEMIVOLATILE ORGANIC ANALYTES IN SOIL
LIMIT OF QUANTITATION**

Compound	CAS number	LOQ µg/Kg
Acenaphthene	83-32-9	1.0
Acenaphthylene	208-96-2	1.0
Acetophenone	98-86-2	ND
Anthracene	120-12-7	1.0
Aniline	62-53-3	1.0 *
Aramite	140-57-8	ND
Azobenzene	3-33-3	1.0
Benzidine	92-87-5	1.0 *,a
Benz(a)anthracene	56-55-3	1.0
Benzo(b)fluoranthene	205-99-2	1.0
Benzo(k)fluoranthene	207-88-9	1.0
Benzoic acid	65-85-0	1.0 *,c
Benzo(g,h,i)perylene	191-24-2	1.0
Benzo(a)pyrene	50-32-8	1.0
Benzyl alcohol	0-51-6	1.0
Bis(2-chloroethoxy)methane	111-91-1	1.0
Bis(2-chloroethyl) ether	111-44-4	1.0
Bis(2-chloroisopropyl) ether	108-60-1	1.0
4-Bromophenyl phenyl ether	101-55-3	1.0
Butyl benzyl phthalate	85-68-7	1.0 *
4-Chloroaniline	106-47-8	1.0 *,c
Chlorobenzilate	510-15-6	ND
4-Chloro-3-methylphenol	59-50-7	1.0

TABLE X. (cont)

Compound	CAS number	LOQ µg/Kg
2-Chloroanaphthalene	91-58-7	1.0
2-Chlorophenol	95-57-8	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0
Chrysene	218-01-9	1.0
Diallate	2303-16-4	ND
Dibenz(a,h)anthracene	53-70-3	1.0
Dibenzofuran	132-64-9	1.0
Di-n-butyl phthalate	84-74-2	1.0 *
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	6-46-7	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0 *
2,4-Dichlorophenol	120-83-2	1.0
Diethyl phthalate	84-66-2	1.0 *
Dimethoate	60-51-5	ND
7,12-Dimethylbenz(a)-anthracene	57-97-6	ND
2,4-Dimethylphenol	5-67-9	1.0 *,c
Dimethyl phthalate	131-11-3	1.0 *
4,6-Dinitro-2-methylphenol	534-52-1	1.0
2,4-Dinitrophenol	51-28-5	1.0 *,c
2,4-Dinitrotoluene	121-14-2	1.0
2,6-Dinitrotoluene	606-20-2	1.0
Di-n-octyl phthalate	117-84-0	1.0
Diphenylamine	122-39-4	ND
Dinoseb (DNBP)	88-85-7	ND

TABLE X. (cont)

Compound	CAS number	LOQ μg/Kg
Disulfoton	298-04-4	ND
Bis(2-ethylhexyl) phthalate	117-81-7	1.0
Ethyl methacrylate	97-63-2	ND
Ethyl methanesulfonate	62-50-0	ND
Famphur	52-85-7	ND
Fluoranthene	206-44-0	1.0
Fluorene	86-73-7	1.0
Hexachlorobenzene	118-74-1	1.0
Hexachlorobutadiene	87-68-3	1.0
Hexachlorocyclopentadiene	77-47-4	1.0*,d
Hexachloroethane	67-72-1	1.0
Hexachlorophene	70-30-4	ND
Hexachloropropene	1888-71-7	ND
Indeno(1,2,3-cd)pyrene	193-39-5	1.0
Isodrin	465-73-6	ND
Isosafrole	120-58-1	ND
Isophorone	78-59-1	1.0
Kepone	143-50-0	ND
3-Methylcholanthrene	56-49-5	ND
2-Methylnaphthalene	91-57-6	1.0
2-Methylphenol	95-48-7	1.0 *,c
4-Methylphenol	106-44-5	1.0 *,c
Methapyrilene hydrochloride	91-80-5	ND
Methyl methacrylate	80-62-6	ND
Methyl methanesulfonate	66-27-3	ND
Methyl Parathion	296-00-0	ND
Naphthalene	91-20-3	1.0
2-Nitroaniline	88-74-4	1.0

TABLE X. (cont)

Compound	CAS number	LOQ μg/kg
3-Nitroaniline	99-09-2	1.0 *,c
4-Nitroaniline	0-01-6	1.0 *,c
Nitrobenzene	98-95-3	1.0
2-Nitrophenol	88-75-5	1.0
4-Nitrophenol	100-02-7	1.0 *,c
4-Nitroquinoline-1-oxide	56-57-5	ND
5-Nitro-2-methylaniline	99-55-8	ND
N-Nitrosodiethylamine	55-18-5	ND
N-Nitrosomethylethylamine	10595-95-6	ND
N-Nitroso-di-n-butylamine	924-16-3	ND
N-Nitrosodimethylamine	62-75-9	1.0 *,c
N-Nitrosodiphenylamine	86-30-6	1.0
N-Nitroso-di-n-propylamine	621-64-7	1.0 *
o-Toluidine	95-53-4	ND
Parathion	56-38-2	ND
Pentachloroethane	76-01-7	ND
Pentachloronitrobenzene	82-68-8	ND
Pentachlorophenol	87-86-5	1.0 *,c
Phenacetin	62-44-2	ND
Phenanthrene	85-01-8	1.0
Phenol	8-95-2	1.0
Phorate	298-02-2	ND
2-Picoline	109-06-8	ND
Pronamide	23950-58-5	ND
Pyridine	110-86-1	ND
Pyrene	129-00-0	1.0

TABLE X. (cont)		
Compound	CAS number	LOQ µg/Kg
Safrole	94-59-7	ND
2,3,4,6-Tetrachlorophenol	58-90-2	ND
1,2,4-Trichlorobenzene	120-82-1	1.0
2,4,5-Trichlorophenol	95-95-4	1.0
O,O,O-Triethyl phosphorate	126-68-1	ND
2,4,6-Trichlorophenol	88-06-2	1.0
sym-Trinitrobenzene	99-35-4	ND
Tetraethyl dithiophosphate	3689-24-5	ND

* = The limit of quantitation has not been verified for these analytes based upon a Method Detection Limit study. All others averaged better than 70% analyte recovery based upon seven repetitions. The amount of each analyte spiked was 1.0 µg into 1.0 L.

a = Exhibits nonreproducible chromatography and oxidative loss during concentration.

c = These analytes are subject to erratic chromatographic performance and/or thermal decomposition in the gas chromatograph inlet.

d = Subject to thermal decomposition in the chromatographic inlet, chemical reaction with acetone in solution, and photochemical decomposition.

ND = not determined for these analytes.

Limits of Quantitation (LOQ) will be two times greater for soil/sediment matrices which have been GPC cleaned.

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Semivolatile Organics in Solid Matrices Solvent Extraction — GC/MS, Mobile Laboratory Method.

Method No.: MLO500

Revision No.: 0

Section Leader

Chris Karlme

Date:

4/23/93

Group Leader

C. D. R.

Date:

4/26/93

QA Concurrence

Margaret A. Gautier

Date:

4/23/93

PCBs

**POLYCHLORINATED BIPHENYLS (PCBs) IN SOIL
MOBILE LABORATORY METHOD**

Analyte: Polychlorinated biphenyls

Method No.: MLO410

Matrix: Soil and miscellaneous
solids

Minimum Detection Limit: 0.06 µg/g

Procedure: Capillary gas
chromatography with electron-capture
detection.

Effective Date: 08/01/91

Author: Matthew Monagle
Jeff Roberts

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.1 for proper waste disposal practices.

1. Principle of Method

- 1.1. This method is applicable to the determination of the following analytes:

<u>Analyte</u>	<u>Chemical Abstract Service Registry Number</u>
Arochlor 1016	12674-11-2
Arochlor 1221	11104-28-2
Arochlor 1232	11141-16-5
Archolor 1242	53469-21-9
Arochlor 1248	12672-29-6
Archolor 1254	11097-69-1
Archolor 1260	11095-82-5
Archolor 1262	37324-23-5

- 1.2. The applicability of this method for the determination of analytes other than those listed above must be demonstrated by the analyst.
- 1.3. Actual detection limits may vary from that listed above because detection limits are highly dependent upon chromatographic conditions and the unique matrix of any given sample.
- 1.4. This method is restricted to use by or directly under the supervision of analysts experienced in the use of gas chromatography and the interpretation of chromatographic data.

- 1.5. Although this procedure is designed to be detailed and comprehensive, it must be understood that situations may arise that require deviation from this procedure. This is particularly true of interpretation of chromatographic data. These deviations will be made at the discretion of the analyst and his/her supervisor and must be thoroughly documented.

2. Summary of Method

- 2.1. Samples are extracted into a suitable solvent.
- 2.2. Sample are cleaned up and/or diluted as necessary.
- 2.3. Samples are analyzed using a gas chromatograph and data is reduced using the associated data system.
- 2.4. Collected data is reviewed by a qualified analyst and the Arochlor(s) are identified and quantitated.
- 2.5. Applicable work is documented according to accepted laboratory operating procedures, and must satisfy all regulatory compliance requirements.

3. Sample Collection, Preservation, and Storage

- 3.1. Soil samples are placed in clean glass bottles and sealed with Teflon-lined caps.
- 3.2. Each sample is placed in a separate sealed glass bottle.
- 3.3. No preservation is required if the samples are submitted within 2 h of collection; otherwise the samples must be kept at 4°C until extracted and analyzed.

4. Interferences

- 4.1. Interference may be caused by contaminants in solvents, reagents, glassware, and other sample-processing equipment that lead either to discrete artifacts or elevated baselines in gas chromatograms.
 - 4.1.1. The use of high-purity solvents and other chemicals will help to minimize interference.
 - 4.1.2. Scrupulous cleaning of glassware and other equipment will help to minimize interference.
 - 4.1.3. Strict adherence to standard laboratory practices will help minimize analyst-generated interferences.

- 4.2. Matrix interferences pose a significant problem in PCB analyses. Each sample may be cleaned up and/or diluted before analysis as necessary.

5. Safety

- 5.1. The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure minimized. Each person using this procedure shall know where the Material Safety Data Sheets (MSDSs) are located and shall have read them before using the chemicals.
- 5.2. PCB products have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with gloves in a fume hood.
- 5.3. Since the chemical composition of the samples is unknown, all samples shall be considered potentially hazardous, and must be handled and extracted in a fume hood.
- 5.4. All gas cylinders shall be secured and fitted with the proper regulators and fittings.
- 5.5. Two waste containers shall be available for the disposal of PCB contaminated waste: one for waste containing <500 ppm PCBs, the other for waste containing >500 ppm PCBs. These containers shall be properly labeled and shall be disposed of by EM-7.
- 5.6. The laboratory will make safety glasses available for all persons present in the laboratory, including guests. Safety glasses must be worn at all times by every person in the laboratory whenever operations requiring safety glasses are being performed by anyone in the laboratory.
- 5.7. The laboratory will make protective gloves, suitable for the chemicals used, available for employees. These are to be worn whenever contact with samples or chemicals is possible.
- 5.8. The laboratory will provide employees with protective aprons or lab coats that are suitable for the chemicals used.
- 5.9. No one is allowed to perform laboratory work unless there is at least one other person in the immediate vicinity who is aware that laboratory work is being performed.

6. Apparatus

- 6.1. Electronic balance: capable of measurement to three decimal places.

- 6.2. Nitrogen evaporation apparatus with multiple sample capacity: Organomation N-EVAP, Model 111 or equivalent.
- 6.3. Beakers: glass, 100-, 150-, 250-, 400-, and 600-mL capacity.
- 6.4. Microliter syringes: assorted sizes.
- 6.5. Volumetric flasks: 1- to 25-mL, with ground-glass stoppers.
- 6.6. Sonicator bath.
- 6.7. Automatic liquid sampler (ALS) vials: 1-mL, with Teflon-lined crimp-seal caps.
- 6.8. Capping and uncapping device for ALS vials.
- 6.9. Gas chromatography system including:
 - heated injection port,
 - temperature programming capabilities,
 - appropriate detection system,
 - electronically controlled autosampler, and
 - complete data system.

7. Reagents

- 7.1. Methylene chloride (Baker Resi-analyzed).
- 7.2. Acetone (Baker Resi-analyzed).
- 7.3. Methanol (HPLC-grade).
- 7.4. Hexane (pesticide-grade).
- 7.5. Reagent water (deionized). Charcoal filtered and/or distilled water demonstrated to be free from interferences.
- 7.6. Sodium sulfate (granular). Muffle overnight at 400°C. Alternatively, it can be Soxhlet-extracted with methylene chloride prior to use. Store in a covered container.
- 7.7. Stock standard solutions.
 - 7.7.1. Prepare stock standard solutions within a concentration range of 20-50 mg/L by dilution of a certified solution or by accurately weighing the neat material and diluting to volume with hexane or iso-octane. If the purity of the neat material is assayed to be 96% or greater, the

weight can be used without correction to calculate the concentration of the stock standard solution.

7.7.2. Transfer the stock standard solutions into Teflon-sealed screw-cap glass bottles and store at 4°C. These standards may be kept for up to one year.

7.8. Secondary (calibration, working) standards.

7.8.1. Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by dilution of the stock standards with hexane. One of the concentrations should be at or near the method detection limit. The subsequent standards should define the working linear range of the GC. Add a surrogate, 2,4,5-tribromobiphenyl, to each secondary standard at a level of 260 µg/L.

7.8.2. Transfer the secondary standards to Teflon-sealed, screw-cap glass bottles and store at 4°C. Secondary standards may be kept for up to six months.

7.9. Surrogate standard.

7.9.1. The surrogate compound in use is 2,4,5-tribromobiphenyl. The surrogate will be added to every sample run to monitor the performance of the extraction, cleanup, and analytical system. The surrogate standard will be prepared at a level of 2.6 mg/L. The surrogate will be spiked in each matrix to give a final concentration of 260 mg/L.

7.10. Matrix spike standard.

7.10.1. Matrix spikes are composed of any one of the three Arochlor mixtures. The matrix spike solution should be made to deliver a recovery amount somewhere in the middle of the calibration range of the instrument. The matrix spike solution will be made using methanol as a solvent.

8. Analytical Conditions

8.1. Gas chromatographic conditions are established in accordance with the requirements of the individual analyst. The following criteria must be met:

- Sufficient resolution to allow accurate identification and quantitation.
- Sufficient sensitivity to allow accurate quantitation to the minimum detection limit.
- Sufficient ability for the system to thermally clean itself to minimize sample carryover and/or elevated baselines.

9. Quality Assurance and Data Interpretation Requirements

9.1. The Quality Control requirements are defined in a tiered structure as follows:

**Tier 1: 1-point calibration every day.
1 method blank every day.**

**Tier 2: 3-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank every day.**

**Tier 3: 5-point initial calibration, daily check standard.
BFB tune check every day.
1 method blank per analytical batch.
Blind QC samples at a rate of no more than 10%.
Matrix spike and matrix spike duplicate for each analytical batch.
12-h clock for tune check and daily check standard.**

9.2. Under Tier 2 and Tier 3 QC requirements, blanks are analyzed at a frequency of one for every 20 samples of similar matrix, or whenever samples are extracted by the same procedure, whichever is more frequent. The method blank should contain less than the reporting limit of any Arochlor mixture, and should not contain extraneous peaks that could inhibit the accurate quantitation or identification of any Arochlor.

9.3. Matrix spike and matrix spike duplicate recovery are required for Tier 2 QC. In order to demonstrate the efficacy of the extraction procedure on any given matrix, the recovery of the spiking compound is monitored. The sample chosen to be spiked should be representative of the samples from a given project.

9.3.1. Under Tier 3 QC requirements, matrix spike and matrix spike duplicate data are generated for every 20 samples of a given matrix type prepared by the same method.

9.3.2. Matrix spike/matrix spike duplicates and the original unspiked sample must be concentrated to the same final volume and analyzed at the same dilution level. High levels of Arochlors in the matrix may cause the matrix spike and duplicate recoveries to become diluted out.

9.3.3. Spike recovery is evaluated in terms of percent recovery and the relative percent difference (RPD) between the recoveries obtained in the matrix spike and the matrix spike duplicate. Data generated by this methodology will be used to generate control limits for recoveries and RPDs.

10. Procedure

10.1. Cleaning of glassware and equipment.

10.1.1. Glassware and other equipment that will come into direct contact with samples, standards, or reagents must be scrupulously clean to minimize contamination and interferences.

10.1.2. Unused vials, glass bottles, caps, and lids do not need to be washed before use. Clean all previously used glassware and equipment immediately after use by thoroughly rinsing with hexane or with the last solvent used in the glassware. Follow this rinse by washing with hot water and detergent. Rinse thoroughly with tap water, distilled water, and then rinse generously with acetone. Allow glassware to dry in the hood, then dry in a 150°C oven for 1 h.

10.2. Sample extraction. Refer to Method MLO510 for the extraction procedure.

10.3. Identification of PCBs.

10.3.1. Compare sample chromatograms to standard Arochlor chromatograms to determine which, if any, of the Arochlors are present in the sample. Determine which Arochlor or combination of Arochlors, and in what proportion, will produce a chromatogram most similar to that of the sample.

PCBs tend to degrade with age. This may cause the loss of certain peaks, particularly the earlier-eluting peaks, which represent the lower-molecular-weight compounds. This phenomenon can make identification more difficult, particularly if the analyst is not aware of it.

Because of the difficulties involved in the identification of these multicomponent residues, final judgment should be made by an experienced analyst.

11. Quantitation

11.1. Separately quantitate each peak using the curve established earlier. Alternatively, the sum of the peak areas may be used to calculate the concentration of the compounds of interest.

11.2. Average the calculated values for each peak in a given Arochlor to give the extract concentration in $\mu\text{g/mL}$. Eliminate obvious outliers before averaging.

NOTE: If the calculated values for each peak appear to vary greatly, it may indicate that the Arochlor was incorrectly identified.

- 11.3. Multiply the resulting number by the volume of solvent used in the extraction procedure. Divide by the initial weight and adjust for dilution if necessary.

12. Proper Waste Disposal Practices

12.1. General waste management.

- 12.1.1. Each analyst in the section shall be given Waste Generator Training by EM-8 within 90 days of the date of hire.

- 12.1.2. Wherever possible, minimize the generation of waste through reduction, reuse, or recycling. Wherever possible, segregate containers to reflect the nature of the hazardous waste and the eventual waste disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, nonchlorinated solvents and >50-ppm-contaminated waste should be segregated from <50 ppm PCB contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

- 12.1.3. Categorize the waste using an EM-8 Waste Profile Form.

- 12.1.4. Upon completion of the Waste Profile Form, dispose of the waste by completing a Waste Disposal Request Form from EM-7. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

12.2. Solid waste.

- 12.2.1. Accumulate solid hazardous waste, such as contaminated paper towels, pipettes, spent syringes, and glass vials, in a covered plastic container lined with a plastic bag. Label the container with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

- 12.2.2. Open the waste container only for the time necessary to add the waste.

12.3. Liquid waste.

- 12.3.1. Accumulate liquid wastes, such as spent samples and spent solvents that are not reusable, in glass or steel containers appropriate for the type of sample being stored. For example, store caustic materials in glass containers and spent solvents that are not to be recycled in metal containers.

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identifies the hazard, type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

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12.4. Unused samples.

12.4.1. Return unused environmental samples to the Sample Management section for disposal.

13. Source Materials

13.1. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

13.2. Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, 3d ed., 1988.

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Polychlorinated Biphenyls (PCBs) in Soil: Field Screening Method.

Method No.: MLO410

Revision No.: 0

Section Leader

Chris Palmer

Date:

4/23/93

Group Leader

By [Signature]

Date:

4/23/93

QA Concurrence

Margaret A. Santori

Date:

4/23/93

TPH

**PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE IN SOIL
MOBILE LABORATORY METHOD**

Analyte: Petroleum hydrocarbons

Method No: MLO274

Matrix: Soil

Detection Limit: 500 $\mu\text{g/kg}$

Procedure: Extraction with
fluorocarbon-113 and infrared
spectrophotometry

Accuracy and Precision: Unknown

Effective Date: 04/03/93

Author: Stuart D. Nielsen
Matthew Monagle

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.2 for proper waste disposal practices.

1. Principle of Method

- 1.1. This method is a modification of EPA Method 418.1 (Storet No. 45501), which uses with a water matrix instead of a soil matrix.
- 1.2. Hydrocarbons are extracted from a known weight of soil with fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) or equivalent and the extract is analyzed by infrared spectrophotometry.
- 1.3. This method is applicable to the measurement of all types of aliphatic hydrocarbon mixtures, although significant amounts of the more volatile hydrocarbons may be lost during sample collection and manipulation.

2. Range and Detection Limit

- 2.1. With the sample diluted so that its absorbance is between 0.1 and 1.0 absorbance units, the method can detect from 0.6 μg of hydrocarbon in the sample to pure aliphatic hydrocarbon.
- 2.2. The lower limit of quantitation of this method was found to be 0.5 μg of hydrocarbon per milliliter of extract, which corresponds to 500 $\mu\text{g/kg}$ of soil.

3. Accuracy and Precision

- 3.1. Accuracy and precision data are not currently available.

**PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE IN SOIL
MOBILE LABORATORY METHOD**

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Matrix: Soil	Detection Limit: 500 $\mu\text{g/kg}$
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Effective Date: 04/03/93	Author: Stuart D. Nielsen Matthew Monagle

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3. Accuracy and Precision

- 3.1. Accuracy and precision data are not currently available.

4. Interferences

- 4.1. Any compound that contains an aliphatic carbon-hydrogen bond interferes because the method measures the aliphatic carbon-hydrogen stretch band in the infrared spectrum of the analyte.

5. Advantages and Disadvantages

- 5.1. An advantage of the method is that it automatically measures the sum of all aliphatic hydrocarbons in the soil sample with one simple measurement.
- 5.2. A disadvantage of the method is that all compounds present containing aliphatic carbon-hydrogen bonds will be counted as aliphatic hydrocarbons.

6. Apparatus

- 6.1. Infrared spectrophotometer.
- 6.2. Analytical balance: capable of weighing to at least 100 g with an accuracy of at least four decimal places.
- 6.3. "VOA" vials: 45-mL, as received from the manufacturer (I-Chem or equivalent).
- 6.4. Glass pipettes.
- 6.5. Spectrometer cells: 1- or 5-cm-path-length, quartz.

7. Reagents

- 7.1. Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane, reagent-grade) or equivalent.
- 7.2. Aliphatic hydrocarbon mixture to use as a standard. A light mineral oil is the preferred standard, although gasoline, kerosene, or diesel fuel can be used.

8. Calibration and Standards

- 8.1. Although the standard curve is theoretically linear from zero absorbance to infinite absorbance, precision and accuracy for any infrared determination are highest when the absorbance is between 0.1 and 1.0 absorbance units.
- 8.2. Calibration standards.
 - 8.2.1. Stock standard. Weigh 2-5 mg of the standard hydrocarbon mixture into a tared VOA vial. Record the weight. Add 12.0 mL of fluorocarbon-113 to the vial.

4. Interferences

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- 8.2. Calibration standards.
 - 8.2.1. Stock standard. Weigh 2-5 mg of the standard hydrocarbon mixture into a tared VOA vial. Record the weight. Add 12.0 mL of fluorocarbon-113 to the vial.

- 8.2.2. Working standards. Dilute portions of the stock standard to give at least three standards with concentrations between 40 and 400 $\mu\text{g/mL}$. This should give a standard curve between approximately 0.1 and 0.9 absorbance units.

9. Procedure

- 9.1. Weigh 10–11 g of the soil sample into a tared VOA vial. Record the weight on the benchsheet.
- 9.2. Add 10 mL of fluorocarbon-113 to the vial. Cap the jar and shake vigorously. Shake the sample on a shaker table for 30 min to completely extract the hydrocarbons.
- 9.3. Allow the soil to settle. Fill a clean infrared cell with the supernatant liquid.
- 9.4. Determine the absorbance for each sample and standard over the range from 2700 cm^{-1} through 3100 cm^{-1} using pure fluorocarbon-113 as a reference.
- 9.5. If the absorbance exceeds 0.9, prepare an appropriate dilution and redetermine the absorbance.

10. Calculations

- 10.1. Measure the peak absorbance at approximately 2930 cm^{-1} . Measure background absorbances on both sides of the peak cluster at approximately 2800 cm^{-1} and 3010 cm^{-1} .
- 10.2. Calculate the background at 2930 cm^{-1} by interpolation between the absorbances measured on both sides.
- 10.3. Calculate the absorbance due to the sample by subtracting the calculated background at 2930 cm^{-1} from the peak absorbance.
- 10.4. Plot a standard curve from the data for the standards by plotting the absorbances vs. the concentrations in $\mu\text{g/mL}$.
- 10.5. Determine the concentration of petroleum hydrocarbons in the extract by comparing the absorbance against the standard curve.
- 10.6. Calculate the petroleum hydrocarbons in the sample using the following equation.

$$\mu\text{g/g of soil} = \frac{(C \times V \times D)}{W}$$

where C = concentration determined from standard curve,
 V = volume of extractant solvent used,
 D = extract dilution factor, if necessary, and
 W = weight of soil used (g).

11. Proper Waste Disposal Practices

11.1. General waste management.

11.1.1. Each analyst within the section shall be given Waste Generator Training by EM-8 within 90 days of the date of hire.

11.1.2. Wherever possible, minimize the generation of waste through reduction, reuse, or recycling. Wherever possible, segregate containers to reflect the nature of the hazardous waste and the eventual waste disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, non-chlorinated solvents and > 50-ppm contaminated waste should be segregated from <50 ppm PCB contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

11.1.3. Categorize the waste using an EM-8 Waste Profile Form.

11.1.4. Upon completion of the Waste Profile Form, dispose of the waste by completing a Waste Disposal Request Form from EM-7. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

11.2. Solid waste.

11.2.1. Accumulate solid hazardous waste, such as contaminated paper towels, pipettes, spent syringes, and glass vials, in a covered plastic container lined with a plastic bag. Label the container with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

11.2.2. Open the waste container only for the time necessary to add the waste.

11.3. Liquid waste.

11.3.1. Accumulate liquid wastes, such as spent samples and spent solvents that are not reusable, in glass or steel containers appropriate for the type of sample being stored. For example, store caustic materials in glass containers and spent solvents that are not to be recycled in metal containers.

11.3.2. Place all containers storing hazardous liquid materials within secondary containment. Label the container with a hazardous waste label which identifies the hazard, type of material being stored (i.e., pipettes, paper towels, etc.), the accumulation start date, and the laboratory of origin.

11.3.3. Open the waste container only for the time necessary to add the waste.

11.4. Unused samples.

11.4.1. Return unused environmental samples to the Sample Management section for disposal.

12. Source Materials

12.1. "Petroleum Hydrocarbons, Total Recoverable," EPA Method 418.1 (Spectrophotometric, Infrared), Storet No. 45501 (1978).

12.2. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3 in *Environment, Safety, and Health Manual*, chapter 1 of Los Alamos National Laboratory Manual (most recent edition).

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Petroleum Hydrocarbons, Total Recoverable In Soil

Method No.: IH274

Revision No.: 0

Section Leader

Chris Palma

Date:

4/23/93

Group Leader

GDE

Date:

4/23/93

QA Concurrence

Margaret A. Gauthier

Date:

4/23/93

RADIOCHEMISTRY

RADIOCHEMISTRY

MOBILE

RADIOCHEMICAL

ANALYSIS

LAB

EQUIPMENT





Mobile Radiological Analysis Laboratory (MRAL) Instrumentation Systems

1) Gross Gamma Counting System. The cabinet, which is lined with a Pb/Cd/Cu graded shield to minimize ambient background levels, houses a 5" x 7" NaI(Tl) well counter. This system provides the first level of screening capability for probable gamma emitters within the sample matrix.

2) Counting Electronics Rack. This assembly houses the high voltage supply, timer/counter, amplifier, single channel analyzer (SCA), thermal printer, NIM power supply, multichannel analyzer (MCA), cryogenic controller unit, and ambient temperature monitoring system. This rack houses all the necessary electronics that drive the gross gamma system.

3) Cryogenic Cooling System. This cabinet houses the cryogenic cooling unit that supports the Hyperpure Germanium (HPGe) detector assembly. The unit resides within a housing that is supplied with the adequate electrical and cooling needs for the system to operate.

4) Hyperpure Germanium (HPGe) Detector. This cabinet maintains a 54% N-Type HPGe that supports the high resolution gamma spectroscopy applications for the MRAL. The system is currently calibrated for silicate matrices only; simple calibrations for other matrices can provide the required analytical capabilities.

5) NOMAD System. This system was developed by EG&G ORTEC for portable gamma spectroscopy. The zero haliburton case provides all the necessary electronics to drive the HPGe, including the laptop computer. This computer not only provides software control of all of the HPGe functions, but also can support both qualitative and quantitative sample analysis.

6) COMPUADD 325 Computer System. All of the screening data reports and miscellaneous word processing capabilities are processed on this machine. Menu capabilities are provided for the user to choose from, including the creation of data files that can be loaded on to a micro diskette and transported back to the laboratory where the information can be uploaded onto the EM-9 computer system for data storage and archival purposes.

7) Liquid Scintillation Analyzer. This system provides liquid scintillation analytical capabilities, specifically tritium (H^3) analysis in soils. Our technique extracts the sample from 15 grams of soil. The sample is then mixed with the appropriate cocktail, and counted. The calculated activities, as based on an internal algorithym, are printed on the system printer, while a data file is created for eventual integration in the laboratories computer system.

8) Sample Hood. This hood provides space for sample

preparation, while providing the user with some personal protection from probable exposure to a variety of radiological/organic compounds that might found within the sample matrix.

9) Gross Alpha/Beta Instrument. This instrument, developed by the Protean Instrument Company, is a new design which lends itself well to mobile applications. The system is a gas-flow proportional type automated counting system, run in a windowless mode for greater sensitivity for lower energy alpha emitters. The results are printed and eventually entered into the data file for transfer to the laboratory computer.

10) Uninterrupted Power Supplies (UPS). The two units provide continuous, uninterrupted, clean power for all the counting systems. This capability allows us to provide an orderly shutdown in the event of catastrophic failure of either the generator or dock power. This minimizes sample lost in analysis from electrical system failures.

11) Heating Systems. Two types of heating systems are supported within the MRAL. A standard electrical powered heating system is used when the counting lab is tied to either a generator, or dock power. A propane based system is used when the unit is away from all power supplies. This maintains adequate temperatures within the MRAL, minimizing damage from temperature extremes.

GROSS a,b

GROSS ALPHA/BETA SCREENING OF SILICATES IN A MOBILE RADIOLOGICAL LABORATORY

Analyte: Alpha- and beta-emitting nuclides

Method No.: MLR100

Matrix: Silicates

Minimum Detectable Activity:

Alpha: 60 pCi/g

Beta: 24 pCi/g

Procedure: Gas flow proportional counting

Accuracy and Precision:

Alpha: 94 \pm 16%

Beta: 111 \pm 14%

Effective Date: 05/28/92

Author: George Brooks

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.5 and 13.6 for proper waste disposal practices.

1. Principle of Method

- 1.1. Samples are mounted directly on stainless steel planchets without chemical dissolution or evaporation.
- 1.2. Samples are counted for 5 min on a low-background, gas-flow proportional counting system.

2. Sensitivity

- 2.1. The sensitivity will vary greatly for alpha activity and to a lesser degree for beta activity. The variance of the alpha activity is more than for conventional wet chemistry techniques. This is largely due to the problem of variant self-absorption from the 1 g of silicate within the plate.
- 2.2. The minimum detectable limit for alpha is 60 pCi/g and for beta 24 pCi/g, based on a 1-g sample and a 5-min count.

3. Accuracy and Precision

- 3.1. In a gas flow proportional counter the efficiency and crosstalk between the alpha and beta counts may vary greatly, depending on the energy of the alpha or beta emitter. A ^{239}Pu and a ^{137}Cs point source are used as the basis for all crosstalk and relative efficiency examinations. The accuracies of a given measurement will depend on the actual energies of the unknown nuclides.

- 3.2. The following accuracy and precision measurements were derived from a set of ^{241}Am and ^{137}Cs quality control (QC) samples examined to determine the initial instrument performance characteristics. The solutions used to make the QC samples are NIST traceable:

Water Samples:

Alpha = $94 \pm 16\%$ (N = 15)

Beta = $111 \pm 14\%$ (N = 9)

4. Interferences

- 4.1. The crosstalk correction method may not adequately protect from incorrect identification of radiation from samples containing very low-energy alpha or high-energy beta activities.
- 4.2. Moderate to high levels of gamma radiation can be misinterpreted as alpha/beta counts by the gas-flow proportional counter.
- 4.3. Because of self-absorption within the sample (especially when soils are counted directly), it must be assumed that *the activity is evenly dispersed within the sample matrix, and that the counting process is adequately measuring the average activity within the sample*. In nonhomogenous samples with low levels of alpha activity, the actual sample activity may be underestimated.
- 4.4. The addition of a thin Mylar sheet covering the planchet increases self-absorption in samples containing low-energy alpha and beta activities. This may result in an under estimation of the sample activity.

5. Collection and Storage of Samples

- 5.1. There are no special collection and storage requirements.

6. Apparatus

- 6.1. Low-level alpha/beta planchet counting instrument, Protean Instrument Corporation Model IPC 9025, run in a windowless mode. The system also integrates a 50-sample automatic sample changer within its mechanical structure.
- 6.2. P-10 (argon/methane) gas cylinder, 2000 psi.
- 6.3. Planchets: stainless steel, 2.0- \times 0.25-in., Model No. 129-021, Atomic Products Corp., Shirley, New York.
- 6.4. Mylar sheet: 0.00025 in. thick.

- 6.5. Photo mount spray adhesive: Scotch brand, catalog no. 6094.
- 6.6. Plastic weight boats: 2- x 2-in. and 4- x 4-in.
- 6.7. Infrared heating lamps: dual lamp assembly, Fischer.
- 6.8. Plastic jig holder and ring for attachment of Mylar surface film to the sample planchet.
- 6.9. Mortar and pestle.

7. Reagents

- 7.1. No reagents are used in this technique.

8. Calibration and Standards

- 8.1. Determine the ionization plateau for both alpha and beta energies. This process should be completed during the initial system setup, or when the P-10 gas cylinder is changed. This step is critical for the proper and accurate operation of the instrument.

- 8.1.1. Use the plated sources that are kept with the instrument. The alpha source is a plated ^{239}Pu stainless steel 0.5-in. plate, while the beta source is a ^{137}Cs plated source.

- 8.1.2. Load the alpha source in the sample holder. Start the calibration routine by depressing the CAL button on the console.

- 8.1.2.1. This will access the submenus under this function, Calibration Selection Determination. Use the arrow keys to mark the **DETECTOR VOLTAGE DETERMINATION** function.

- 8.1.2.2. Depress the ENTER key to start the process. Pick the **ACQUIRE PLATEAU DATA** function. This process is automatic, and will step the counter through a series of voltages (30-V increments from 500 to 1800 V). A printout will be generated that shows the counts versus the voltage applied, along with a value of percent counts per voltage step. The plateau should be set at a point 10% beyond the knee of the ionization plateau. The percent counts per voltage step provides the user with additional information for accurate determination of the ionization plateau. For more information, refer to the IPC instrument manual.

- 8.1.3. Using the beta source, repeat the above process for the beta plateau determination.

- 8.2. Generate detector efficiencies for the determination of alpha and beta activities in the silicate sample, using a NIST traceable Isotope Products Laboratory ^{241}Am standard and a NIST SRM 4233-B ^{137}Cs solution.
- 8.2.1. Prepare a series of standards (3 sets of activity levels, 100, 500, and 1000 dis/min, in duplicate using 1-g soil matrix blanks) that will give a wide range of activity levels for both the alpha and beta components. This will provide statistically significant data points.
- 8.2.2. Generate a mean value of counts for each of the duplicate sets, for both alpha and beta activities. Determine the efficiency of each set by dividing the count rate (counts/min) by the known activity added to each standard. Examine the data sets for nonlinearity between the different levels. The generated efficiency values should not be significantly different between the sets.
- 8.2.3. Enter these values into the instrument's calibration file. The menu will ask for the efficiency value and the associated error for these data points. Most gross alpha/beta systems use precipitation curves to derive the efficiency values, but this type of analysis is different. Because the mass of the sample remains constant, only one efficiency point is needed. The menu also requires information on the alpha/beta crosstalk factors. This information will be present on the hardcopy output from the standard runs.
- 8.3. Determine and track the instrument performance assessment parameters using a ^{239}Pu and a ^{137}Cs point source, a soil blank, and a blank planchet.
- 8.3.1. Load the samples into the sample holder tubes in the order described in Step 8.3.
- 8.3.2. Start the calibration by depressing the CAL button on the instrument panel.
- 8.3.2.1. This will bring up the submenu **CONTROL CHART ROUTINES**. Initiate this submenu to bring up the choices: **PU-239 STANDARD, CS-137 STANDARD, SOIL BLANK, BLANK PLANCHET, AUTO SEQUENCE ALL**. Pick the **AUTO SEQUENCE ALL** function. This will run all the samples for instrument performance assessment routine.
- 8.3.3. After counting is completed for each sample, the system will notify the user if the sample counts are within acceptable limits. If other messages appear, such as the system is out of limits, notify the Radiological Analysis Van manager. The system should also provide a hard copy of the latest sample counts and a chart displaying the trend in the data.

This information should be signed and appended to the alpha/beta notebook.

- 8.3.4. For more information concerning any of the above procedures, consult the Protean IPC Instrument Manual, Section 7.

9. Procedure

9.1 Silicates.

- 9.1.1. Obtain the sample aliquot from the cooler holding the samples.
- 9.1.2. Remove approximately 1.5 g of soil from the sample bag and place in a 4- × 4-in. plastic weigh boat.
- 9.1.3. Place the sample (in the weigh boat) under a heat lamp to remove any excess moisture that may remain. Dry until the soil seems friable.
- 9.1.4. If the sample consists of large chunks of soil and aggregate, place it in the mortar and pulverize it until the soil particles are a uniform size.
- 9.1.5. Write the sample number on the bottom of the planchet.
- 9.1.6. Spray a light film of photo mount adhesive on the inside of the planchet for the soil to adhere to.
- 9.1.7. Weigh 1.0 g (± 0.05 g) of soil in the small (2- × 2-in.) weigh boat.
- 9.1.8. Transfer the 1.0 g of soil to the prepared planchet. Spread the soil around within the planchet to disperse it evenly in the sample container.
- 9.1.9. Let the adhesive dry for 1-2 min before covering the sample.
- 9.1.10. Obtain a 3.0-in. circle of 0.00025-in. Mylar to adhere to the top of the sample planchet.
- 9.1.11. Place the prepared planchet on the plastic sample holder jig. Center the mylar circle on the sample planchet. There should be some adhesive remaining on the rim of the planchet for the Mylar to attach to. If not, apply some glue stick around the rim.
- 9.1.12. Move the plastic centering tool down over the planchet to affix the sides of the mylar sheet to the planchet. This should provide adequate adhesion of the mylar to the planchet. The sample is now ready to count.

10. Operation of the Instrument

10.1. Loading the proportional counter.

10.1.1. Place the QC samples in the sample holder assemblies. The QC samples (9 alpha and 6 beta QC's), made from various activity levels of ^{241}Am and ^{137}Cs on soils, should equal approximately 10% of the total number of samples to be analyzed. These samples should be interspersed in the sample set to adequately characterize the samples. The exact QC sample used does not matter, as long as the appropriate information is logged on the sample sheet so that the activity of that QC can be examined later.

10.1.2. Load the samples and QCs in their sample holder assemblies, using the sample loading tool provided by Protean. Place the sample holding tube on this loading tool and then place the sample holder assemblies in the tube. After all the samples have been loaded, lift the sample holding tube off the loading tool.

10.1.3. Load the holding tube on the tube receiver closest to the operator. When loading the tube within this assembly, be careful not to jar the holding tube. Excess motion will cause the sample assemblies to fall out of the holding tube inside the instrument. If this occurs, see the Mobile Radiological Analysis Van manager.

10.1.4. Record the sample position, number, type, and weight, along with other associated information on the alpha/beta sample sheet (Fig. 1).

10.2. Sample counting.

10.2.1. Sign onto the Protean instrument with the appropriate user password. This will bring up the initial software layout.

10.2.2. Depress the COUNT key.

10.2.2.1. This will bring up the Acquisition Selection Menu. Select the Menu Selected Batch mode. This selection is used for general counting of samples for routine gross alpha/beta counting. This will bring up one selection only, RADVAN*GROSS/A/B.

10.2.3. This selection will lead into the following sequence:

10.2.3.1. Preparing Sample Changer

10.2.3.2. Load Magazine 1 and Press ENTER

10.2.4. After loading the sample tube holder, depress the ENTER key. This will give a **Clearing Sample Buffer** message, followed by display of a field of data that the user can examine and change, if necessary. At this point, the user can either use the default values in the block or define the specific information needed for the system. Since this procedure is using an efficiency based on one point, there is no need to elaborate on the information within the block. To use the default information, press the ENTER key. This will initiate the next sequence:

10.2.4.1. **Accessing Sample Number 01**

10.2.4.2. **Low Gas Flow to Good Gas Flow**

10.2.4.3. **Good Gas Flow, Purging Detector, Seconds Remaining XXX**

10.2.5. The system has begun to count the samples and will print out the first data after the sample count has completed.

11. Calculations

11.1. Since the efficiency factor is calculated within the software of the Protean Instrument, the external algorithm simply converts the activity from disintegrations per minute to pCi, per sample units. In this case, the sample unit is gram per sample, so the activity is expressed as pCi/g.

11.1.1. This conversion uses the following algorithm:

$$\left(\frac{SA}{2.22} \right) = \text{pCi/sample} ,$$

where SA = sample activity in dis/min,
2.22 = conversion unit to Ci.

(In this case, the sample = 1 g, so the sample activity = pCi/g)

11.2. The Protean Instrument provides a report (Fig. 2). The data is transferred from the report to the alpha/beta sample sheet. The raw data is attached to this alpha/beta sample sheet, initialed, and stored in the alpha/beta sample analysis notebook.

11.3. The information from the alpha/beta sample sheet is entered into a "basic" program that will provide the final data analysis. The program is accessed by the following steps:

- 11.3.1. Unlock the keyboard on the Mobile Radiological Analysis Laboratory (MRAL) computer.
- 11.3.2. Type RAD to initiate the program.
- 11.3.3. The program will query the user for the number of samples to be run, the type of analysis that is requested, and sample activity (in dis/min) and associated uncertainty.
- 11.3.4. Type in the appropriate information as the program requests it. After one sample has been completed, the result and uncertainty will be displayed on the screen. A secondary file is also created that provides another hard copy of the same information. This file is called ALPHA.DAT, within the DOS file structure. This file can be printed using the standard print utility from the DOS level.
- 11.3.5. The information can then be transferred to the MRAL database for the final data report and archiving.

12. Proper Waste Disposal Practices

12.1. Solid waste.

12.1.1. Sample-contaminated waste.

- 12.1.1.1. Sample-contaminated waste includes plastic weigh boats, spatulas, used planchets, Mylar, syringes, centrifuge tubes, filter disks, and gloves. Accumulate the waste in a plastic bag on a daily basis, seal the bag, and place it within a 1- x 2- x 2-ft cardboard box kept within the van.
- 12.1.1.2. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 12.1.1.3. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 12.1.1.4. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 12.1.1.5. When the above process is completed, notify the Waste Disposal Group (EM-7) to initiate the waste disposal procedure.

12.1.2. Sample waste.

- 12.1.2.1.** The sample waste is identified as the sample after the counting process has been completed. This includes the 100-g sample from the NaI(Tl) counter, the 1-g sample from the gross alpha/beta instrument, the 15 g from the extraction for tritium analysis, and the 5-g sample for the soil moisture analysis.
- 12.1.2.2.** Accumulate the waste on a daily basis and place it within a smaller bag. Seal this bag and mark it with the date the waste was accumulated and the sample range within the bag (this is for later sample retrieval, if necessary).
- 12.1.2.3.** Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 12.1.2.4.** When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 12.1.2.5.** Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 12.1.2.6.** Once the above process is complete, notify the Waste Disposal Group (EM-7) to initiate waste disposal.

12.2. Liquid waste.

- 12.2.1.** Liquid waste is generated from the process of liquid scintillation analysis. After the samples have been counted, return them to EM-9 at TA-59, and store with the routine tritium analysis sample vials.

12.3. Waste pickup.

- 12.3.1.** Contact a radiation protection technician to monitor the surface exposure rate of the sealed box and record the information on the Radioactive Solid Waste Disposal (RSWD) Record form.
- 12.3.2.** Request pickup by the Waste Management group of the full boxes of waste using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile form (WPRF) that describes the waste is referenced on both disposal request forms.

12.3.3. The Waste Management Group picks up the waste for disposal according to Laboratory policy.

13. Source Materials

- 13.1. Instruction Manual for the IPC 9025 Low Level Alpha/Beta Counting Instrument, IPC-9025-1.1, Protean Instrument Corporation, P.O. Box 910, Oak Ridge, TN (1991).
- 13.2. Environmental Protection Agency, "Tentative Reference Method for the Measurement of Gross Alpha and Gross Beta Radioactivities in Environmental Waters," Quality Assurance Branch, Technical Support Laboratory, National Environmental Research Center, Las Vegas, NV, ROAP Number 22 ACW, EPA-680/4-75-005 (1975).
- 13.3. EML Procedures Manual, 26th ed., H. L. Volchok and G. de Planque, Eds., Environmental Measurements Laboratory, U.S. Department of Energy, New York, NY, HASL-300 (1986).
- 13.4. G. Brooks, "Data Reduction Program for the Mobile Radiological Analysis Laboratory," in progress, Environmental Chemistry Group, Los Alamos National Laboratory (1992).
- 13.5. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).
- 13.6. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EM-9 Gross Alpha/Beta Sample Sheet

Date: _____

Analyst: _____

RN: _____

Pos	Samp Num	Analysis	Result	Unc.
		Alpha		
		Beta		
		Alpha		
		Beta		
		Alpha		
		Beta		
		Alpha		
		Beta		
		Alpha		
		Beta		

Figure 1.

RADVANS:GROSS/A/B MOBILE-RAD-VAN B. LOCKHART α 3124.2 \pm 790.8
 ID: 00000000 07-27-92 11:41:44 α QC 1-1 β LMOA
 Net Wt mg: 1.00 sd: 0.00
 001 Repeat: 00 BG TIME (min): 5.00 SAMPLE TIME (min): 5.00
 Alpha to Beta cps: 60.05 sd: 5.28

	COUNTS	CPM	BG CPM	NET CPM	%EFF	DPM	LLD dpm
A	561	112.20	1.00	111.20	1.60	6935.70	129.78
sd	23.69	4.74	0.47	4.76	0.40	1753.64	
B	215	43.00	14.60	-31.65	18.60	-170.15	42.75
sd	14.66	2.93	2.48	6.53	2.50	41.91	

RADVANS:GROSS/A/B MOBILE-RAD-VAN B. LOCKHART α 123.6 \pm 44.5
 ID: 00000000 07-27-92 11:48:45 β Std #6 β 2592.3 \pm 350.3
 Net Wt mg: 1.00 sd: 0.00
 SN: 002 Repeat: 00 BG TIME (min): 5.00 SAMPLE TIME (min): 5.00
 Alpha to Beta cps: 2.38 sd: 0.64

	COUNTS	CPM	BG CPM	NET CPM	%EFF	DPM	LLD dpm
A	27	5.40	1.00	4.40	1.60	274.43	129.78
sd	5.20	1.04	0.47	1.14	0.40	98.76	
B	5437	1087.40	14.60	1070.42	18.60	5754.97	42.75
sd	73.74	14.75	2.48	14.97	2.50	777.69	

RADVANS:GROSS/A/B MOBILE-RAD-VAN B. LOCKHART
 ID: 00000000 07-27-92 12:12:13 1317 LMOA
 Net Wt mg: 1.00 sd: 0.00
 001 Repeat: 00 BG TIME (min): 5.00 SAMPLE TIME (min): 5.00
 Alpha to Beta cps: 0.00 sd: 0.00

	COUNTS	CPM	BG CPM	NET CPM	%EFF	DPM	LLD dpm
A	2	0.40	1.00	-0.60	1.60	-37.42	129.78
sd	1.41	0.28	0.47	0.55	0.40	35.54	
B	64	12.80	14.60	-1.80	18.60	-9.68	42.75
sd	8.00	1.60	2.48	2.95	2.50	15.93	

RADVANS:GROSS/A/B MOBILE-RAD-VAN B. LOCKHART
 ID: 00000000 07-27-92 12:19:15 1318 LMOA
 Net Wt mg: 1.00 sd: 0.00
 SN: 002 Repeat: 00 BG TIME (min): 5.00 SAMPLE TIME (min): 5.00
 Alpha to Beta cps: 0.00 sd: 0.00

	COUNTS	CPM	BG CPM	NET CPM	%EFF	DPM	LLD dpm
A	1	0.20	1.00	-0.80	1.60	-49.90	129.78
sd	1.00	0.20	0.47	0.51	0.40	34.28	
B	28	5.60	14.60	-9.00	18.60	-48.39	42.75
sd	2.29	1.04	2.48	2.70	2.50	15.90	

RADVANS:GROSS/A/B MOBILE-RAD-VAN B. LOCKHART
 ID: 00000000 07-27-92 12:26:18 1319 LMOA
 Net Wt mg: 1.00 sd: 0.00
 SN: 003 Repeat: 00 BG TIME (min): 5.00 SAMPLE TIME (min): 5.00
 Alpha to Beta cps: 0.00 sd: 0.00

	COUNTS	CPM	BG CPM	NET CPM	%EFF	DPM	LLD dpm
A	2	0.40	1.00	-0.60	1.60	-37.42	129.78
sd	1.41	0.28	0.47	0.55	0.40	35.54	
B	57	11.40	14.60	-3.20	18.60	-20.00	42.75

Figure 2. Example of Report from Protean Instrument

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Gross Alpha/Beta Screening of Silicates in a Mobile Radiological Laboratory

Method No.: MLR100

Revision No.: 0

Section Leader

D. Knut

Date:

2-18-93

Group Leader

C. D. R.

Date:

2/18/93

QA Concurrence

Margaret A. Houten

Date:

2-18-93

GROSS 2

GROSS GAMMA SCREENING OF SILICATES IN A MOBILE RADIOLOGICAL LABORATORY

Analyte: All gamma-emitting nuclides	Method No.: MLR200
Matrix: Silicates	Minimum Detectable Activity: 4.0 pCi/g
Procedure: Instrumental gamma-ray (NaI) counting	Accuracy and Precision: 97.7 ± 3.0 %
Effective Date: 05/12/92	Author: George Brooks

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 13 of this procedure and Source Material 14.4 and 14.5 for proper waste disposal practices.

1. Principle of Method

- 1.1. Samples are packaged in 500-mL (16-oz) Nalgene HDPE plastic bottles and are counted in a NaI(Tl) well scintillation counting system for 5 min. This procedure is completed without chemical processing.
- 1.2. The sample size for silicates is 100 g.

2. Sensitivity

- 2.1. The limits of detection for silicates in this system is 4.0 pCi/g, based on the 662-keV ^{137}Cs energy line and a 5-min count.

3. Accuracy and Precision

- 3.1. This method is intended as a qualitative assessment of gross gamma activity. The accuracy and precision have been assessed using ^{137}Cs (NIST SRM 4233B) quality assurance samples. The following represents the accuracy and precision of the NaI(Tl) counting system used to count these samples:

Silicate Samples:

Gamma = 97.7 ± 3.0 % (N = 86)

- 3.2. Samples showing a positive response (usually 3 sigma above background is indicative of a positive signal) should be submitted to further analysis to determine the exact source of the elevated activity.

4. Interferences

- 4.1. Although the method is intended to measure the gamma-emitting isotopes in the sample, the wall thickness of the detector and the detector housing assembly is such that high-energy beta particles will also be counted.

5. Collection and Storage of Samples

- 5.1. There are no special collection and storage requirements for these types of samples.

6. Apparatus

- 6.1. Bicron Model No. 5MW7Q/5, 5- x 7-in. NaI(Tl) well-type scintillation detector. The well dimensions are 3.0-in.-diam by 5.5-in.-deep. The system is set in the "NORMAL" window mode, with an active energy range of 0.2 to 2.5 MeV.
- 6.2. Photomultiplier tube base with preamplifier: EG&G Ortec Model 276.
- 6.3. Amplifier: EG&G Ortec Model No. 572 amplifier.
- 6.4. Single-channel analyzer (SCA): EG&G Ortec Model No. 550A.
- 6.5. Counter/timer: EG&G Ortec Model 776 counter/timer.
- 6.6. Printer: EG&G Ortec Model No. 777A line printer.
- 6.7. High voltage power supply: EG&G Ortec Model No. 556.
- 6.8. Standard NIM rack assembly with ± 12 and 24 V.
- 6.9. Bottles: 500-mL, HDPE polyethylene, Nalgene, catalog no. 20002-0116.
- 6.10. Analytical balance: 300-g minimum capacity.
- 6.11. Bags: clear, low-density, polyethylene bags (0.002 in. thick) sized to fit 500-mL bottles. The bags protect the detector from surface contamination on the bottles.
- 6.12. Spatula.
- 6.13. Permanent ink marker.
- 6.14. Funnel: polyethylene.

7. Reagents

- 7.1. No reagents are required for this procedure.

8. Calibration and Standards

- 8.1. Prepare all standards and quality assurance materials from a NIST SRM 4233-B ^{137}Cs solution.

8.1.2. Standards.

8.1.2.1. Prepare the soil standard by overspiking a known aliquot of the stock standard solution on 100 g of blank soil in the sample bottle and evaporating under an infrared heat lamp. The solution must not come in contact with the walls or bottom of the container when preparing the overspike.

8.1.2.2. Thoroughly blend the dry standard and cap the bottle. Additional mixing may be provided by gently shaking the sealed bottle.

8.1.2.3. Mark the bottle with the appropriate information: isotope, activity level, SRM used, date prepared, preparer, notebook number, etc. Mark the bottle with tape denoting that it is a radioactive material.

8.1.3. Quality Control Materials.

8.1.3.1. Prepare quality control (QC) materials in 3 activity levels. Repeat steps outlined in Step 8.1.2.1 and 8.1.2.2. Adjust the amount of standard added to each soil blank to create 3 levels of activity.

8.1.3.2. Mark the bottle with the appropriate information: isotope, activity level, SRM used, date prepared, preparer, notebook number, etc. Mark the bottle with tape denoting that it is a radioactive material.

8.1.4. Blank.

8.1.4.1. Prepare a blank soil sample by treating 100 g of dried, "clean" soil, as outlined in Step 8.1.2.2 and 8.1.2.3.

9. Procedure

- 9.1. Weigh 100 g of a dried soil sample into the 500-mL polyethylene bottle.

- 9.2. Tightly cap the bottle and clean off any exterior contamination.
- 9.3. Place the sample in a plastic bag.
- 9.4. Because the detector efficiency and background are to be determined for each run, count triplicate standards and blanks with each sample set.
 - 9.4.1. Place the standard in a plastic bag and insert it into the well counter.
 - 9.4.2. Perform three 5-min counts for each standard. Multiple counting of the sample provides adequate counting statistics. Record each count on the NaI(Tl) Counting Log Sheet (Fig. 1).
 - 9.4.3. Remove the standard and insert the soil blank into the well. Perform three 5-min counts on the blank soil. Record each count on the log sheet.
- 9.5. Place the sample in the well counter.
- 9.6. Count the sample for 5 min.
- 9.7. Record the counts, sample number, weight of sample, date counted, and any other distinguishing information on the NaI(Tl) counting log sheet.
- 9.8. Count a QC sample at the end of each set. QCs should equal 10% of the total number of samples that will be counted. Record this information on the sample counting log sheet.

10. Operation of the Instrument

- 10.1. Turn on the voltage to the NIM bin.
- 10.2. Turn on the high-voltage supply for the NaI(Tl) detector, usually at 1000 volts, positive. The readout on the HV supply will read 1.0.
- 10.3. Check that the timer/counter is set properly. The thumbwheel for the timer should read 5 0; the time increment is already set at 1.0 min intervals by a jumper inside the unit. The dwell time knob should be off, the timer/counter switch should be set at Count (A), and the discriminator potentiometer should be set at 0.2 V.
- 10.4. Turn the line printer on, and set the cycle switch to ONE CYCLE.
- 10.5. Proceed as follows to initiate the counter:
 - 10.5.1. Depress the STOP button to complete any counting cycle that may be in progress.

10.5.2. Depress the **RESET** button to reset the counter to the first part of the counting cycle.

10.5.3. Depress the **COUNT** button to start the counting sequence.

10.6. After the count has been completed, the line printer will print the count time and the total counts for that sample. The display on the timer/counter will also display this information.

10.7. Record the count time and the total counts on the NaI(Tl) counting log sheet.

10.8. If any of the above operations produce suspicious results, or no results, immediately contact the Rad Van manager.

11. Calculations

11.1. Since the efficiency factor is calculated for each sample set, the values obtained from counting the standard and blanks are used to determine the efficiency of the counting system for that sample set.

11.2. Determine the mean value of the triplicate counts of the standard and the soil blank. Record these values on the bottom of the counting log sheet.

11.3. The following equations are embedded within the BASIC program. This program provides the user with the vehicle by which all the final data reduction processes are accomplished. The actual steps to needed for the final data reduction process are discussed in Section 12.

11.4. Counting efficiency.

11.4.1. The mean counting efficiency of the counter for a standard run is calculated using the following equation:

$$\bar{E} = \frac{\left(\frac{\bar{C}_s}{T_s} - \bar{B} \right)}{A_s}$$

where \bar{E} = mean efficiency,

\bar{C}_s = mean gross counts of the standard ($n = 3$),

T_s = count time for the standard (min),

\bar{B} = mean background count rate (counts/min), and

A_s = activity of the standard (dis/min).

11.5. Background.

11.5.1. The mean background count rate is calculated as follows:

$$\bar{B} = \frac{C_B}{T_B} ,$$

where B = mean background count rate (counts/min),
 C_b = mean gross counts of the soil background, and
 T_b = count time of the soil background (min).

11.6. Sample activity.

11.6.1. The activity of the samples is calculated using the following formula:

$$A_x = \left(\frac{\left(\frac{C_x}{T_x} - \bar{B} \right)}{\bar{E}} \right) \times 2.22 ,$$

where A_x = sample activity,
 C_x = gross counts of the sample,
 T_x = count time of the sample (min),
 \bar{B} = mean background count rate (counts/min),
 \bar{E} = mean efficiency, and
2.22 = conversion factor.

11.7. Sample uncertainty.

11.7.1. The uncertainty associated with the sample activity is calculated using the following equation:

$$SD (A_x) = |A_x| \times \sqrt{\frac{\frac{C_x}{T_x^2}}{\left(\frac{C_x}{T_x} - \bar{B} \right)^2}} ,$$

where $SD (A_x)$ = uncertainty of the sample activity (pCi),
 $|A_x|$ = absolute value of A_x from Step 11.6.1,
 C_x = gross counts of the sample,
 T_x = sample count time (min), and
 \bar{B} = background count rate (counts/min).

12. Data Reduction

12.1. The raw data logged into the NaI(Tl) counting log sheet is now ready to be entered into the system for the final data reduction process. Access the program as follows:

12.1.1. Unlock the keyboard of the Mobile Radiological Analysis Laboratory (MRAL) computer.

12.1.2. Type **RAD** to initiate the program.

12.1.3. The program will query the user for the number of samples to be run, the type of analysis requested, the mean gross counts for the standard, the mean gross counts for the sample blank, and the gross counts associated with the sample.

12.1.4. Type in the information as the program requests it. After the first sample result has been calculated, the result and uncertainty will be displayed on the screen. A secondary ASCII file is created that can provide hardcopy of the data, or the data can be uploaded directly into EM-9's database. This file is called **GAMMA.DAT**, within the DOS file structure. This file can be printed using the standard print utility from the DOS level.

12.1.5. Transfet the information to the MRAL database for final data reporting and archiving.

12.1.6. The final report is signed and dated by the analyst and placed in the **GROSS GAMMA** logbook. Send copies of the report with the aliquoted samples to provide the necessary radiological screening information requested by the Sample Management Section.

12.1.7. Transfer the final data into the EM-9 database for final data storage and record archiving.

13. Proper Waste Disposal Practices

13.1. Solid waste.

13.1.1. Sample-contaminated waste.

13.1.1.1. Sample-contaminated waste includes plastic weigh boats, spatulas, used planchets, Mylar, syringes, centrifuge tubes, filter disks, and gloves. Accumulate the waste in a plastic bag on a daily basis, seal the bag, and place it within a 1- x 2- x 2-ft cardboard box kept within the van.

- 13.1.1.2. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 13.1.1.3. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 13.1.1.4. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 13.1.1.5. When the above process is completed, notify the Waste Disposal Group (EM-7) to initiate the waste disposal procedure.

13.1.2. Sample waste.

- 13.1.2.1. The sample waste is identified as the sample after the counting process has been completed. This includes the 100-g sample from the NaI(Tl) counter, the 1-g sample from the gross alpha/beta instrument, the 15 g from the extraction for tritium analysis, and the 5-g sample for the soil moisture analysis.
- 13.1.2.2. Accumulate the waste on a daily basis and place it within a smaller bag. Seal this bag and mark it with the date the waste was accumulated and the sample range within the bag (this is for later sample retrieval, if necessary).
- 13.1.2.3. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 13.1.2.4. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 13.1.2.5. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 13.1.2.6. Once the above process is complete, notify the Waste Disposal Group (EM-7) to initiate waste disposal.

13.2. Liquid waste.

- 13.2.1. Liquid waste is generated from the process of liquid scintillation analysis. After the samples have been counted,

return them to EM-9 at TA-59, and store with the routine tritium analysis sample vials.

13.3. Waste pickup.

- 13.3.1. Contact a radiation protection technician to monitor the surface exposure rate of the sealed box and record the information on the Radioactive Solid Waste Disposal (RSWD) Record form.
- 13.3.2. Request pickup by the Waste Management group of the full boxes of waste using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile form (WPRF) that describes the waste is referenced on both disposal request forms.
- 13.3.3. The Waste Management Group picks up the waste for disposal according to Laboratory policy.

14. Source Materials

- 14.1. Method No. ER150, "Gross Gamma in Environmental Matrices," *Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance*, M. A. Gautier, Ed., Los Alamos National Laboratory Manual LA-10300-M, Vol. I (1987).
- 14.2. EML Procedures Manual, 26th ed., H.L. Volchok and G. de Planque, Eds., Environmental Measurements Laboratory, U.S. Department of Energy, New York, HASL-300 (1986).
- 14.3. G. Brooks, "Data Reduction Program for the Mobile Radiological Analysis Laboratory," in progress, Environmental Chemistry Group, EM-9, Los Alamos National Laboratory, (1992).
- 14.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).
- 14.5. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

NaI(Tl) Counting Log Sheet

Sample Set TP-21 (Rau-Ten)
 Count Time 5 min
 ROI's _____
 Sample Owner _____
 Date 7/30/92

Sample	Vol/Wt	Counts	D/M	Comments
<u>Std Blk</u>		35803		
		35822		
		35551		
<u>Std #2</u>		155808		
		156094		
		155203		
<u>1399</u>		34761		<u>LMDA</u>
<u>1400</u>		35054		"
<u>1401</u>		35115		"
<u>1402</u>		35113		"
<u>1403</u>		34957		"
<u>1404</u>		35260		"
<u>1405</u>		35519		"
<u>1406</u>		35310		"
<u>1408</u>		35687		"
<u>1409</u>		35434		"
<u>1410</u>		35743		
<u>1413</u>		35985		
<u>Std Blk</u>		35893		
		35743		
		35766		
<u>1414</u>		35604		<u>LMDA</u>
<u>1415</u>		36125		"
<u>1416</u>		36253		"
<u>1417</u>		35397		"
<u>1418</u>		35676		"
<u>1419</u>		35622		"
<u>1420</u>		35884		"

LMDA 7.1 ± 0.5
 5.8 ± 0.4

Figure 1. Gross Gamma Log Sheet

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Gross Gamma Screening of Silicates in a Mobile Radiological Laboratory

Method No.: MLR200

Revision No.: 0

Section Leader	<u>D. Knell</u>	Date:	<u>2-18-93</u>
Group Leader	<u>[Signature]</u>	Date:	<u>2/18/93</u>
QA Concurrence	<u>Margaret A. Gantier</u>	Date:	<u>2-18-93</u>

MOISTURE

GROSS MOISTURE ANALYSIS OF SILICATES IN A MOBILE RADIOLOGICAL LABORATORY

Analyte: Percent moisture

Method No.: MLR400

Matrix: Silicates

Drying Options:

Time: 1 to 60 min

Slope: 0.1 to 60 min

0.01 to 9.99% change

Procedure: Moisture determination
system

Effective Date: 10/10/92

Author: Bret Lockhart

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.3 and 12.4 for proper waste disposal practices.

1. Principal of Method

- 1.1. Ten- to 15-g soil samples are loaded directly on aluminum plates without chemical dissolution or evaporation.
- 1.2. Samples are heated at 200°C for 5 min on a moisture analyzer.

2. Sensitivity

- 2.1. The sensitivity varies with the percent change in soil moisture.
- 2.2. The minimum detectable limit for moisture is 0.01% in 0.1 min, based on any given sample weight, counted until percent change is not met.

3. Accuracy and Precision

- 3.1. The accuracy is 100% with a precision of $\pm 0.1\%$

4. Collection and Storage of Samples

- 4.1. There are no special collection and storage requirements.

5. Apparatus

- 5.1. Moisture analysis instrument: Denver Instrument Company, model no. IR-100.

5.2. Disposable aluminum pans: 4.0-in.-diam., 0.25-in.-deep, part no. 900274.1, Denver Instrument Co.

5.3. Plastic weight boat: 4- x 4-in.

6. Reagents

6.1. No reagents are used in this technique.

7. Calibration

7.1. Since the instrument determines the weight loss in percent of the initial weight, routine calibration of the system is not necessary for accurate results. Periodic calibration is suggested if the instrument is used as a standard electronic balance.

7.1.1. Use a Class I 50-g weight to calibrate the analyzer.

7.1.2. Lift the heater hood and place an empty disposable aluminum pan on the pan support. Scroll through the Setup Menu by continuously pressing the mode key until the display shows **CALIBRATION**.

7.1.2.1. Press the enter key to access the calibration procedure. Message prompts guide the operator through this procedure.

CALIBRATION - - - -
PRESS TARE NOW

7.1.2.2. Press the tare key and the display shows:

CALIBRATION - - - -
PLACE 50 g WEIGHT

7.1.2.3. Place a 50-g weight on a disposable pan; display shows:

CALIBRATION - - - -
PRESS ENTER NOW

7.1.2.4. Press the enter key and the display shows:

CALIBRATION - - - -
CALIBRATING

7.1.3. When the calibration is complete, the display shows that the calibration is done. Remove the weight and the main screen returns.

8. Procedure

8.1. Silicates.

8.1.1. Obtain the sample aliquot from the cooler holding the samples.

8.1.2. Remove 10-15 g of soil from the sample bag and place it in a 4- x 4-in. plastic weigh boat.

9. Operation of the Instrument

9.1. Initialize moisture analyzer.

9.1.1. After the unit is turned on, recall the slope for the percent moisture change. Program #1 is set at a 0.10% change in 0.5 min at 200°C. Use this program.

9.1.1.1. Press the recall key and the display will ask for the program you wish to run.

9.2. Drying a sample.

9.2.1. Lift the heater hood and place an empty disposable pan on the pan support. Press the start key and the display shows:

**SAMPLE NUMBER
NUMBER ******

9.2.2. If a different sample number is desired, use the numerical keys to select the desired sample number. Any number of 1 to 8 digits can be used. After a few seconds the display shows:

WT = **.*
TARE PAN WEIGHT**

9.2.3. Press the tare key and the display shows:

**WT = 0.000*
PLACE SAMPLE ON**

9.2.4. Place the sample on the disposable pan, spreading it evenly over the surface. Close the hood. The display shows:

**WT = 3.002
PRESS START**

- 9.2.5 Wait approximately 3 s for the unit to stabilize. Press the start key and the display shows:

WT = 3.002
WORKING
then
P1 TIME = 00.01
200 C 0:00%M

- 9.2.6 The printer automatically prints out initial data when the drying cycle begins.

- 9.2.7 When the drying cycle ends, the display shows:

I. WT = 3.002
F. WT = 2.91
then
DIFF = 0.86
PERC = 2.86

- 9.2.8 The printer automatically prints final results when the drying cycle ends or the stop key is pressed.

10. Calculations

- 10.1. When the operator selects one of the six options, the analyzer automatically changes to the appropriate calculation mode. During a drying procedure, the display always shows the selected mode. The final printout includes the calculation mode with the results.

<u>OPTION</u>	<u>DISPLAY SHOWS</u>
---------------	----------------------

MOISTURE	% M
----------	-----

$$\frac{\text{moisture weight}}{\text{wet weight}} \times 100$$

11. Proper Waste Disposal Practices

- 11.1. Solid waste.

- 11.1.1. Sample-contaminated waste.

- 11.1.1.1. Sample-contaminated waste includes plastic weigh boats, spatulas, used planchets, Mylar, syringes, centrifuge tubes,

filter disks, and gloves. Accumulate the waste in a plastic bag on a daily basis, seal the bag, and place it within a 1- x 2- x 2-ft cardboard box kept within the van.

- 11.1.1.2. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 11.1.1.3. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 11.1.1.4. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 11.1.1.5. When the above process is completed, notify the Waste Disposal Group (EM-7) to initiate the waste disposal procedure.

11.1.2. Sample waste.

- 11.1.2.1. The sample waste is identified as the sample after the counting process has been completed. This includes the 100-g sample from the NaI(Tl) counter, the 1-g sample from the gross alpha/beta instrument, the 15 g from the extraction for tritium analysis, and the 5-g sample for the soil moisture analysis.
- 11.1.2.2. Accumulate the waste on a daily basis and place it within a smaller bag. Seal this bag and mark it with the date the waste was accumulated and the sample range within the bag (this is for later sample retrieval, if necessary).
- 11.1.2.3. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 11.1.2.4. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 11.1.2.5. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 11.1.2.6. Once the above process is complete, notify the Waste Disposal Group (EM-7) to initiate waste disposal.

11.2. Liquid waste.

- 11.2.1. Liquid waste is generated from the process of liquid scintillation analysis. After the samples have been counted, return them to EM-9 at TA-59, and store with the routine tritium analysis sample vials.

11.3. Waste pickup.

- 11.3.1. Contact a radiation protection technician to monitor the surface exposure rate of the sealed box and record the information on the Radioactive Solid Waste Disposal (RSWD) Record form.
- 11.3.2. Request pickup by the Waste Management group of the full boxes of waste using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile form (WPRF) that describes the waste is referenced on both disposal request forms.
- 11.3.3. The Waste Management Group picks up the waste for disposal according to Laboratory policy.

12. Source Materials

- 12.1. Instruction manual for the IR-100 Moisture Analyzer, Denver Instrument Company, P.O. Box 39575, Denver, CO. 80239 (10/91).
- 12.2. G. Brooks, "Data Reduction Program for the Mobile Radiological Analysis Laboratory," in progress, Environmental Chemistry Group, Los Alamos National Laboratory, (1992).
- 12.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).
- 12.4. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Gross Moisture Analysis of silicates in a Mobile Radiological Laboratory

Method No.: MLR400

Revision No.: 0

Section Leader	<u>D. Knab</u>	Date:	<u>2-18-93</u>
Group Leader	<u>C. D. E.</u>	Date:	<u>2/18/93</u>
QA Concurrence	<u>Margaret A. Gautier</u>	Date:	<u>2-18-93</u>

TRITIUM

GROSS TRITIUM ANALYSIS OF SILICATES IN A MOBILE RADIOLOGICAL LABORATORY

Analyte: Tritium (^3H)

Method No.: MLR300

Matrix: Silicates

Minimum Detectable Activity: 1.0 pCi/g

Procedure: Liquid scintillation
analysis

Accuracy and Precision:
93 \pm 16%

Effective Date: 06/22/92

Author: George Brooks

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.4 and 13.5 for proper waste disposal practices

1. Principle of Method

- 1.1. A 15-g silicate sample is mixed with 15 mL of deionized water and shaken. A 5-mL aliquot of the sample extract is taken, immersed in liquid scintillation cocktail, and counted.
- 1.2. The silicate sample extracts are counted in a low-level liquid scintillation counting system for 5 min.

2. Sensitivity

- 2.1. The sensitivity will vary as a result of color quenching that may be taking place within the sample. This is a direct result of the inefficiency of the filter to exclude the media causing the quenching. The sensitivity may also be limited by the range of the counter background. In general, the detection limit for this system is approximately 1.0 pCi/g, based on a 15-g soil sample, a 2-min shakeout, spin-out in a centrifuge (until sample is clear), and immersion in 15 mL of Ultima Gold liquid scintillation cocktail.

3. Accuracy and Precision

- 3.1. This method is intended as a preliminary step in the analysis of silicates samples submitted to a field laboratory. It does not supersede fixed-base laboratory distillation methods.
- 3.2. The following accuracy and precision measurements were derived from soil overspikes using two NIST ^3H SRMs, No. 4361B-57 and No. 4926D-51.

Silicate samples: Tritium = $93.0 \pm 16.0\%$ (N = 12)

4. Interferences

- 4.1. Any sample that contains some form of chemical quenching agent that can be carried through filtration will experience count quench.
- 4.2. Other nuclides with low-energy beta emission similar to ^3H can cause false positive results.
- 4.3. It must be assumed that the sample contains ^3H in the form of HTO and that all the unbound fraction of ^3H has been extracted.

5. Collection and Storage of Samples

- 5.1. There are no special collection and storage requirements for these types of samples.

6. Apparatus

- 6.1. Low-level liquid scintillation counting system: Packard Instrument Corporation Model 2500 TR with refrigeration option.
- 6.2. Liquid scintillation vials: Wheaton model no. 66021-690, 25-mL capacity, plastic.
- 6.3. Centrifuge tube: 50-mL, clear polypropylene, Corning model no. 21008-74.
- 6.4. Syringe: 10-cc, model no. BD-1604.
- 6.5. Filter disk: 5- μm , Gelman Acrodisc model no. 28144-095.
- 6.6. Safety bottle: 4-L, plastic coated with 15-mL automatic pipette dispenser.
- 6.7. Automatic 15-mL pipette dispenser: to fit the liquid scintillation cocktail bottle.
- 6.8. Analytical balance: 300-g minimum capacity.
- 6.9. Pipette: 100- to 1000- μL Eppendorf micropipette.
- 6.10. Pipette: 5-mL adjustable macropipette.
- 6.11. Pipette tips: 100- to 1000- μL Eppendorf pipette tips, model no. 53511-880.
- 6.12. Pipette tips: 1- to 5-mL polypropylene, model no. 53503-826.

6.13. Spatula.

6.14. Permanent ink marker.

6.15. Funnel: polypropylene.

7. Reagents

7.1. Liquid scintillation cocktail: Ultima Gold (Packard Instrument Company Inc., Catalog No. 6013324, VWR Scientific) or similar commercial product. Evaluate each new lot number to assure reproducibility of results.

7.2. Low-background water: obtain from a water source free of radionuclide contamination (deep well water from well no. PM-1 can be obtained from EM-8).

8. Calibration and Standards

8.1. Quench curves.

8.1.1. In order to properly characterize and quantitate a sample, a quench curve must be established. This curve provides information (efficiency versus quench within the sample, expressed as some variable specific to the instrument; i.e., tSIE factor for Packard) to the instrument that can accurately correct for quench occurring in the samples due to chemical or color quench. This quench curve must represent as closely as possible the actual samples that are analyzed. This requires that each quench curve must be specific to the sample to be counted: (1) the sample-to-cocktail ratio (i.e., 5 mL of sample to 15 mL of cocktail), (2) the specific manufacturer of the cocktail, and (3) the specific matrix that is to be analyzed (soil, water, etc.).

8.1.1.1. Generate a set of quench standards. Place 15 mL of the Ultima Gold cocktail in each of 10 liquid scintillation vials. Mark the top of each vial with a permanent marker for identification. Record this information in the appropriate notebook.

8.1.1.2. Obtain a ^3H (NIST SRM 4926D) standard having a suitable activity level (100,000 dis/min per vial is adequate). Adding 700 μL to each vial provides an activity level close to 100,000 dis/min in each sample.

8.1.1.3. Make a solution that can provide adequate quench in the samples. Mix 5 mL of NaI in 40 mL of deionized water. Shake the solution until all the salt has dissolved.

- 8.1.1.4. The purpose is to provide a series of samples with the same amount of standard in each sample while varying the amount of quench agent. This requires 10 separate and varied additions of these quench standards. The following quench amounts are adequate with the above sample configurations: 0, 10, 50, 100, 250, 500, 800, 1000, 2000, and 3500 μL .
- 8.1.1.5. The samples must be normalized to the total 20-mL sample volume. This requires the addition of the following amounts of "clean" deionized water to each of the samples: 4300, 4290, 4250, 4200, 4050, 3800, 3500, 3300, 2300, and 800 μL .
- 8.1.1.6. After all additions to each sample are complete, vigorously shake each sample to mix. The sample will at first appear cloudy but should become clear.
- 8.1.1.7. Place the quench standards into the sample holder trays in the liquid scintillation analyzer. Allow the samples to cool for at least 20-30 min before counting.
- 8.1.1.8. Set up the protocol number that will be used to count the quench standards. The protocol number allows the user to define the count times, the name of the protocol, the exact range to be analyzed, etc. See chapter 7 in the operations manual for the Packard 2500 TR for more information on setting up the appropriate quench curve.
- 8.1.1.9. After the samples have been counted, the program processes the information and produces a quench curve. In some instances, the curve is not curvilinear because of irregularities in some of the quench standards. This requires that some of the standards (counts) be removed from the protocol information file (see chapter 7 in the 2500 TR operations manual). The program will replot the standards with the new data configuration. The data should provide a plot such as Fig. 1.
- 8.1.1.10. This file is addressed in other counting protocols as the quench curve to use for this particular sample configuration.
- 8.1.1.11. The quench curves should be regenerated every year to compensate for system degradation, new batches of liquid scintillation cocktail, or other conditions that could alter the counting process.

8.2. Quality control standards.

8.2.1. In order to provide high-quality data, run appropriate quality control (QC) materials with each sample set. This provides the analyst and the end user with a high degree of confidence in the data. Run two types of QC samples through the system, soil overspike QCs and system QCs.

8.2.1.1. Soil overspike QCs.

- 8.2.1.1.1.** Place 15 g of "clean" soil in the 50-mL centrifuge tube.
- 8.2.1.1.2.** Add a known amount of tracer to the sample matrix. Use either NIST SRM 4361B or 4926D as the QC material. Calculate the amount of activity that should be in the sample.
- 8.2.1.1.3.** Add 15 mL of "clean" water to the sample and overspike matrix. Cover the sample.
- 8.2.1.1.4.** Shake the sample for 2 min.
- 8.2.1.1.5.** Let the sample stand for 2-4 min to allow the water and soil to separate.
- 8.2.1.1.6.** Attach a 5- μ m filter to the end of a syringe. Immerse the end of the filter in the sample extract.
- 8.2.1.1.7.** Pull 5 mL of solution through the filter into the syringe.
- 8.2.1.1.8.** Remove the filter from the syringe and dispense the 5 mL of extract into 15 mL of liquid scintillation cocktail.
- 8.2.1.1.9.** Shake the sample until it is no longer cloudy. Mark the amount of spike added to the soil sample on the top of the sample container. Use this as a reference number for this QC.
- 8.2.1.1.10.** Count the QC sample with the other samples. Examine the data to determine the ratio of the measured activity to the actual activity levels in the QC sample.

- 8.2.1.1.11. If the ratio is 80-120%, accept the data as valid. If the ratio is outside that range, contact the Mobile Radiological Analysis Laboratory (MRAL) manager to correct the problem.

8.2.2.1. System QCs.

- 8.2.2.1.1. Prepare 10 samples for quality assurance standards. Place 15 mL of Ultima Gold cocktail in each sample vial.
- 8.2.2.1.2. Add varying but known amounts of ^3H standard to each sample. Normalize each sample to a total volume of 20 mL (this may require that "clean" water be used to normalize the volume). Use NIST SRMs 4361B or 4926D. Try to develop an activity range between 100 and 3000 dis/min per sample.
- 8.2.2.1.3. Mark each sample with a unique number and record the number and its calculated activity in the appropriate notebook. This series will be used for long-term quality assurance for the sample sets.
- 8.2.2.1.4. Place the system QCs in a sample cassette and place in the instrument. Keep the samples in the instrument to maintain a constant temperature. This allows rapid determination of the sample activity with any sample set.

8.3. Weekly calibrations.

- 8.3.1. In order to maintain accurate instrument performance assessment records, run known standards through the system each week. These standards consist of a ^{14}C unquenched standard, a ^3H unquenched standard, and an unquenched background sample. Load these samples into a special sample cassette marked for IPA ASSESSMENT in the order mentioned. Various statistical parameters are examined (chi-square, figure of merit, standard efficiency, and backgrounds) and plotted within the instrument's software programs. Examine this information each week to determine if any trends are occurring in the instrument. If further information is needed, refer to chapter 10 in the 2500TR operations manual. If other problems are found, contact the MRAL manager immediately.

9. Procedure

9.1 Silicates.

- 9.1.1. Obtain the sample aliquot from the cooler holding the samples. This cooler is the sample holder that the ER sampling team delivers each day to the MRAL van.
- 9.1.2. Determine the total number of samples to be analyzed for ^3H . Remove the appropriate number of liquid scintillation vials and centrifuge tubes.
- 9.1.3. Mark each scintillation vial and centrifuge tube with the correct sample number, using a permanent marker.
- 9.1.4. Place 15 mL of the Ultima Gold cocktail in each sample vial.
- 9.1.5. Weigh 15 g of each sample into the appropriately marked centrifuge tube.
- 9.1.6. Add 15 mL of "clean" water to each sample. Use the 4-L bottle with the automated pipettor for the "clean" water.
- 9.1.7. Shake each sample for 2 min to allow for the transfer of unbound ^3H from the soil to the water carrier.
- 9.1.8. Allow each sample to stand for approximately 2-4 min. This should allow the sediments to separate from the water extract and minimize the amount of possible quench agent pulled through to the sample. If this does not provide a clear sample, centrifuge the tubes until the solution is no longer cloudy (2-20 min).
- 9.1.9. Place a 5- μm filter on the end of a 10-mL syringe.
- 9.1.10. Place the end of the filter into the 15 mL of water extract in the centrifuge tube. Draw 5 mL of sample through the filter into the syringe. The sample should be fairly clean. If not, flush the sample back into the centrifuge tube, replace the filter, and draw another sample.
- 9.1.11. Remove the filter from the syringe and place it in the appropriate disposal container.
- 9.1.12. Introduce the sample from the syringe into the appropriately marked liquid scintillation vial. Replace the top and secure the lid.
- 9.1.13. Shake the vial to promote homogeneity within the sample. The sample should change from cloudy to clear within a few seconds. If it remains

cloudy, the sample condition is inappropriate for counting and may need to be redone.

10. Operation of the Instrument

10.1. Preparation of samples for counting.

10.1.1. Place the samples in the sample cassette holders. Place the protocol ID marker, number 2, on the front of the sample cassette holder. Make sure that the magnetic bar on the protocol ID marker is pushed to the left position. This cues the instrument that this sample set is ready to be counted.

10.1.2. Make sure that the necessary number of QC samples (both soil overspikes and system QCs) are in place with the sample set. A 1:10 ratio of QCs to samples is reasonable.

10.1.3. Keep the samples within the instrument for at least 15–20 min to allow photoluminescence in the sample to subside.

10.2. Sample counting.

10.2.1. When the samples are ready to count, depress the green button on the upper right-hand corner of the system keyboard. This causes the system to rotate the cassette holders within the instrument to the next sample set ready to count.

10.2.2. After the counting sequence is complete, a printout will be available with all the appropriate information. This will include the sequence number, count time, count per minute, disintegrations per minute, activity and the associated error (3σ), and the tSIE (transformed spectral index of the external standard).

10.2.3. In addition to this printout, an ASCII file should be generated. The creation of this file will allow the user to take the data from the MRAL to the laboratory and upload it into the EM-9 database for storage and archival purposes. For further information on the initial setup of the data file format, consult chapter 9, Data Output, in the 2500TR operation manual.

11. Calculations

11.1. The liquid scintillation analyzer internally performs the necessary calculations to derive the proper activity and standard error calculations for each sample and to generate a report (Fig. 2). The reporting algorithm in the instrument CPU provides for the correction that only 1/3 of the original sample was extracted.

It corrects to the original sample size of 15 g and reports the activity in pCi/g, $\pm 3 \sigma$.

- 11.2. The operator of the MRAL transcribes the data from the LSC report for inclusion in the MRAL report. This algorithm corrects for soil moisture as calculated from the soil moisture analyzer. The report is printed for final dissemination to the Sample Receiving section, the contract laboratory, the ER program office, and in-house users.
- 11.3. The report is a file generated in a WordPerfect (WP) file format. The typical naming convention for each file utilizes the day's date as the file name; i.e., 6_25_92.WP. The user can retrieve the file from the WP directory.
- 11.4. The computing system has the necessary hardware to allow archiving of all the systems' files. Maintain data integrity using the automated backup routine in place on the system.

12. Proper Waste Disposal Practices

12.1. Solid waste.

12.1.1. Sample-contaminated waste.

- 12.1.1.1. Sample-contaminated waste includes plastic weigh boats, spatulas, used planchets, Mylar, syringes, centrifuge tubes, filter disks, and gloves. Accumulate the waste in a plastic bag on a daily basis, seal the bag, and place it within a 1- x 2- x 2-ft cardboard box kept within the van.
- 12.1.1.2. Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
- 12.1.1.3. When the box is full, seal it with tape, remove it from the mobile lab, and return it to TA-59. Prepare a new box (tape the end of the box and line with a new plastic bag) and place it in the mobile lab.
- 12.1.1.4. Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 12.1.1.5. When the above process is completed, notify the Waste Disposal Group (EM-7) to initiate the waste disposal procedure.

12.1.2. Sample waste.

- 12.1.2.1.** The sample waste is identified as the sample after the counting process has been completed. This includes the 100-g sample from the NaI(Tl) counter, the 1-g sample from the gross alpha/beta instrument, the 15 g from the extraction for tritium analysis, and the 5-g sample for the soil moisture analysis.
- 12.1.2.2.** Accumulate the waste on a daily basis and place it within a smaller bag. Seal this bag and mark it with the date the waste was accumulated and the sample range within the bag (this is for later sample retrieval, if necessary).
- 12.1.2.3.** Label the box as compactible waste. Open the box only for the period of time necessary to add waste.
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- 12.1.2.5.** Store the box at TA-59 until the remainder of the analytical results characterizing the waste are obtained.
- 12.1.2.6.** Once the above process is complete, notify the Waste Disposal Group (EM-7) to initiate waste disposal.

12.2. Liquid waste.

- 12.2.1.** Liquid waste is generated from the process of liquid scintillation analysis. After the samples have been counted, return them to EM-9 at TA-59, and store with the routine tritium analysis sample vials.

12.3. Waste pickup.

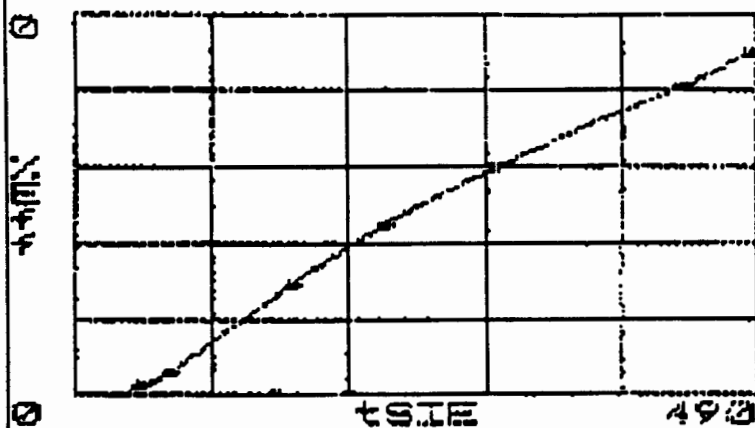
- 12.3.1.** Contact a radiation protection technician to monitor the surface exposure rate of the sealed box and record the information on the Radioactive Solid Waste Disposal (RSWD) Record form.
- 12.3.2.** Request pickup by the Waste Management group of the full boxes of waste using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile form (WPRF) that describes the waste is referenced on both disposal request forms.

12.3.3. The Waste Management Group picks up the waste for disposal according to Laboratory policy.

13. Source Materials

- 13.1. Operation Manual, Tri-Carb Liquid Scintillation Analyzer, Models 2500TR, 2550TR/LL, 2569TR/XL. Publication Number 169-4044, Rev. D. Packard Instrument Company, One State Street, Meriden, CT, 06450 (1990).
- 13.2. H. Ross, J. Noakes and J. D. Spaulding, Eds., *Liquid Scintillation Counting and Organic Scintillators*, Lewis Publishers, Inc., 121 South Main Street, Chelsea, MI, 48118 (1991).
- 13.3. Method No. R230, "Tritium (T_2O or TOH)-Direct Procedure," *Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance*, M. A. Gautier, Ed., Los Alamos National Laboratory Manual LA-10300-M, Vol. I (1989).
- 13.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).
- 13.5. "Chemical, Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Mode: DPM
 type: tSIE/AEC



tSIE	%E11
484.43	44.99
435.58	40.38
301.58	29.94
222.88	22.64
*194.92	7.50
155.79	14.72
*143.11	0.56
65.72	2.77
46.43	1.07

* indicates deleted point

Figure 1

Time: 5.00		Data Mode: DPM		Nuclide: TRAC-H3		Quench. Set: TRAC	
Background Subtracts: None							
	LL	UL	LLH	20%	OKC		
Region A:	0.0 - 10.0	0	0.0	0.00			
Region B:	2.0 - 10.0	0	0.0	0.00			
Region C:	0.0 - 0.0	0	0.0	0.00			
Quench Indicators: LSIE/REC							
Ext Std Terminator: Count							
Luminescence Correction: Off							
Color Quench Correction: On							
High Sensitivity Count Mode: On							
SN	TIME	CPHA	CPM1	LSI/A	3918 UNC	LSIE	FLAW
1	5.00	4.20	14.47	0.25	13415.00	530.50	C
2	5.00	19.20	38.79	1.18	-24082.00	535.42	E
3	5.00	15.00	36.29	1.09	-4133.00	473.02	
4	5.00	15.00	37.93	1.14	5785.00	477.79	
5	5.00	17.60	34.63	1.10	-26497.00	432.20	
6	5.00	0.00	0.00	0.00	0.00	487.51	E
7	5.00	1.20	2.39	0.07	-27473.00	543.25	E
8	5.00	20.20	40.15	1.21	32740.00	541.34	C
9	5.00	24.00	193.60	3.27	18143.00	477.30	
10	5.00	123.20	283.60	8.22	12434.00	479.08	
11	5.00	131.50	278.57	8.97	17104.00	479.02	
12	5.00	0.20	0.20	0.01	867.30	542.57	E
13	5.00	0.00	0.00	0.00	0.00	544.32	E
14	5.00	1143.60	2284.24	88.64	-10133.00	540.91	E
15	5.00	1586.20	3392.36	107.88	-13493.00	479.13	
16	5.00	2449.80	4747.19	204.12	-21005.00	478.54	
17	5.00	3044.20	7201.33	210.25	14584.00	478.54	
18	5.00	3150.20	7367.34	227.25	-14150.00	401.33	

Figure 2

EM-9 ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Gross Tritium Analysis of Silicates in a Mobile Radiological Laboratory

Method No.: MLR300

Revision No.: 0

Section Leader *D. Kneel* **Date:** *2-18-93*

Group Leader *C. J. R.* **Date:** *2/18/93*

QA Concurrence *Margaret A. Santuri* **Date:** *2-18-93*

G-SPEC

Quantitative Gamma Spectrometry

Method currently being adapted from fixed lab method to mobile lab equipment.

Estimated completion date May 15, 1993.