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FAX TRANSMISSION

DATE: 3-3-95 FROM: AAT (Ken Jones)

TO: Susan Hugo FAX NO. (510) 337-9335

COMPANY: Alameda Co. Health Care Services.

MESSAGE: Here is the information you requested, re: Tuneupmasters Shop #318 San Pablo Ave, Oakland, CA. I hope ~~you~~ this is the correct information. method State DOHS, extract in freon, then filtered thru sodium sulfate, then filtered thru silica gel, then analised on on Spectronixen this removes the heavey, ionic, and waxey oils. Then, gives results on everything not extracted.

TOTAL NUMBER OF PAGES, INCLUDING COVER SHEET: 24

SIGNED: Ken Jones

If you do not receive all the pages, or if you have a problem with receiving, please call (209) 661-2011.

(f) Analyze the standard and adjust instrument sensitivity to give minimum response of at least two times the background. Record and sum up all peak areas of the gasoline standard.

(g) Analyze the spike sample in the same manner. Record all peak areas.

(h) Analyze the undosed sample in (g) above.

(i) Small sample size should be used if the concentration is found to be outside the concentration range of the instrument.

g. Standard laboratory quality control practices should be used with this method.

Determination of Organolead -- DHS Method

1. Discussion

Organolead compounds constitute the largest single industrial application of organo-metallic chemistry. Estimates indicate that about 1,450 organolead compounds were known in 1968, and the number has increased with synthesis of about 130 new compounds each year. The widespread presence of toxic, volatile, lipophilic organolead compounds in the environment can lead to serious public health effects and damage to the aquatic biota. With the phasing out of leaded fuels, substantial amounts of lead compounds from petroleum sludges are being discharged into waste streams. There is also evidence to suggest that the more toxic organoleads such as tetramethyl-lead can be synthesized from lead salts and simple chemical reagents in aqueous solutions.

Caution: Some organolead compounds are volatile and toxic. Process the samples in a well-ventilated hood.

2. Scope

The method describes the determination of organolead compounds in various types of hazardous material samples. In this method, a rapid organic extraction technique is applied to separate the organo Pb from a matrix with xylene, followed by reaction with 1% Aliquat 336/MIBK on I_2 solution. The extract is then analyzed by a flame atomic absorption spectrophotometer. The detection limit for organolead is 0.05 ppm as lead.

3. Reagents

3.1 (MIBK) methyl-isobutyl ketone (4-methyl-2-pentanone).

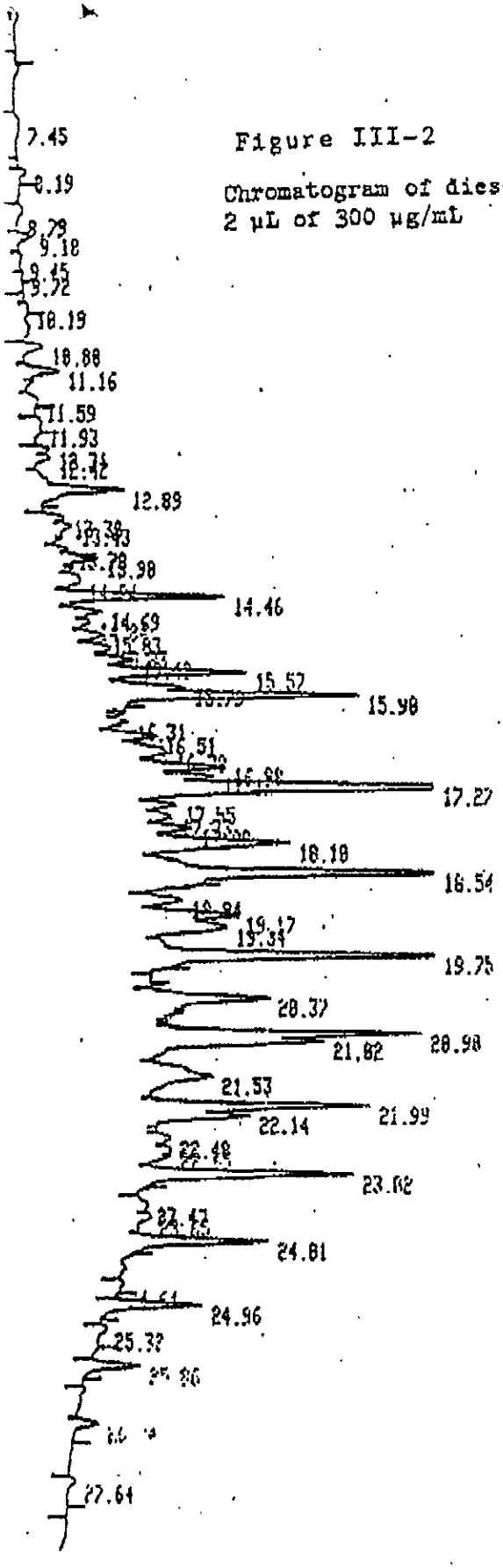

Figure III-2

Chromatogram of diesel.
2 µL of 300 µg/mL

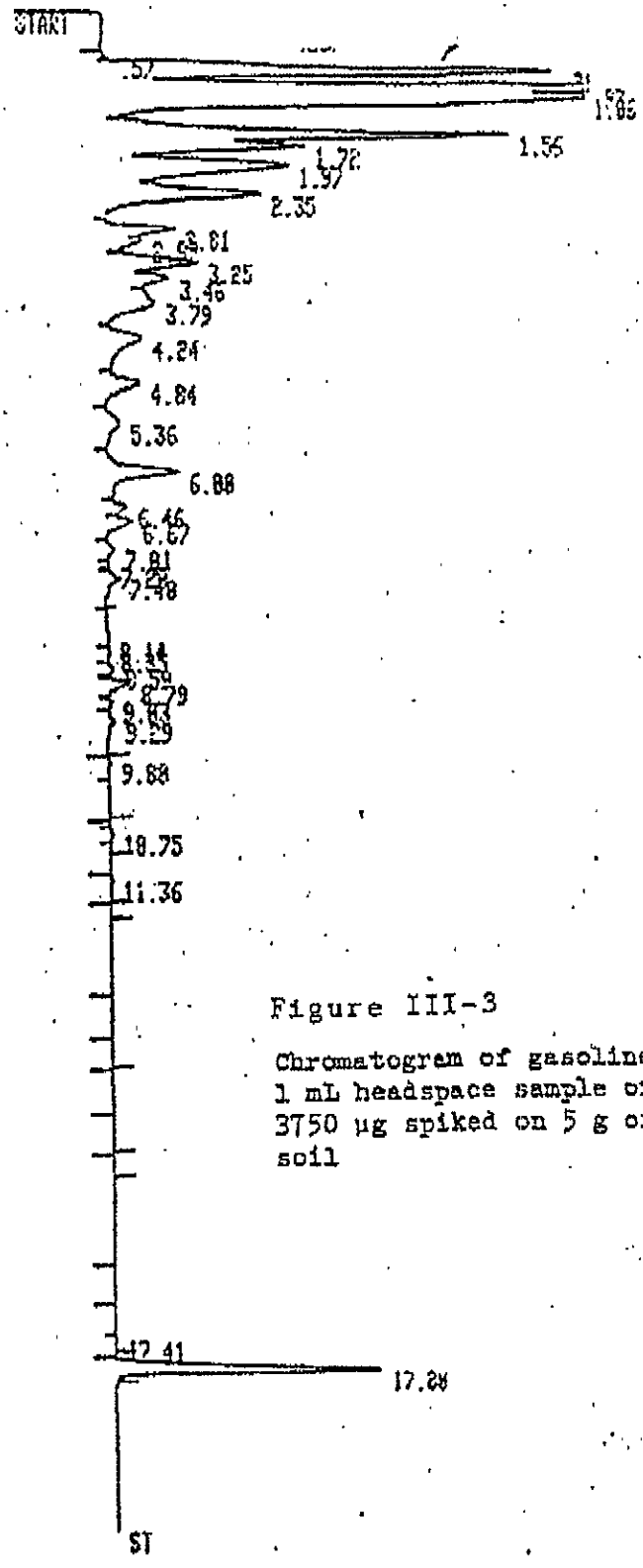

Figure III-3

Chromatogram of gasoline.
1 mL headspace sample of 3750 µg spiked on 5 g of soil

APPENDIX B

SAMPLE COLLECTION, TRANSPORT, AND LABORATORY ANALYSES

A. Sample Collection

1. Field Notebook

The field investigator should keep a field notebook (preferably bound with pages numbered) to record sample collection procedures, dates, laboratory identification, sample collection location, and the name of the sampler. This is important for later recall or legal challenge.

2. Soil Samples

a. Hydrocarbons: Soil samples collected from a backhoe or from the ground should be collected in a thin-walled stainless steel or brass cylinder at least three inches long by one inch in diameter that has been prepared by the laboratory doing the analysis or the project consultant. About one inch of soil should be removed from the immediate surface area where the sample is to be taken and the cylinder then pounded into the soil with a wooden mallet. No headspace should be present in the cylinder once the sample is collected. When the sample is collected, each end of the cylinder should be covered with aluminum foil and then capped with a polyethylene lid, taped, and labeled. The sample should then be immediately placed in an ice chest containing dry ice and kept frozen for delivery to the laboratory. Care should be taken throughout to avoid contamination of both the inside and outside of the cylinder and its contents (1).

Samples should be kept frozen at the laboratory until they are analyzed. Holding time should not exceed 14 days from the time of collection. Frozen soil cores should be removed from the cylinders by spot heating the cylinder and immediately extruding the sample (or a portion of it). A portion of the frozen sample should be removed and prepared for analysis according to approved EPA methods.

In situations where the above procedure is inappropriate, i.e. semi-solid samples, glass vials (properly prepared by contract laboratory or consultant) with Teflon seal and screw cap should be used, and maintained at 4°C until analysis.

b. Organolead: Tetraethyl/tetramethyl-lead are volatile; therefore, soil samples should be collected in cylinders and frozen as described for volatile hydrocarbons above.

TABLE 3-4

SUMMARY OF ANALYTICAL PROCEDURES

Substance to be Analyzed	Analytical Method	Reference
1. Gasoline:		
a. Benzene, toluene, xylene, ethylbenzene (aromatic volatile organics)	EPA 8020 (soil)	2
	EPA 602 (water)	3,5
b. Total Petroleum Hydrocarbons	DHS (recommended procedure)	See attached method
c. Halogenated volatile organics, including 1,2-dibromoethane (EDB) 1,2-dichloroethane (EDC)	EPA 8010 (soil)	2
	EPA 601 (water)	3,5
EDB	DHS extraction method 1/	6
2. Diesel:		
a. Total Petroleum Hydrocarbons	DHS (recommended procedure)	See attached method
b. Total Recoverable Petroleum Hydrocarbons (TRPH) 2/	EPA 418.1	4
3. Organolead:	DHS	See attached DHS method
4. Ignitability: Flash Point	EPA 1010, 1020	2

1/ This is a liquid/liquid extraction procedure for water samples. The method was developed by DHS and provides a means for detecting EDB at a lower concentration (parts per trillion) than does EPA method 8010 (parts per billion). The procedure was developed to detect EDB in ground water as part of the AB 1803 program.

2/ This is a relatively quick analytical procedure that measures recoverable petroleum hydrocarbons, including oil and grease. It is applicable for measuring light fuel fractions, but loses approximately half of any gasoline present (ref. 4). The method costs less than the recommended procedure and is useful primarily as a survey tool.

DRAFT

Draft Method*

for

Total Petroleum Hydrocarbons

and

Total Organic Lead

Hazardous Materials Laboratory
California Department of Health Services
2151 Berkeley Way
Berkeley, CA 94704
(415)540-3003

February, 1988

* The draft methods are reproduced from: LEAKING UNDERGROUND FUEL TANK (LUFT) FIELD MANUAL, California State Water Resources Control Board, Division of Water Quality, December 17, 1987. Complete copies of LUFT field manual are available from Ms. Diane Edwards at (916)324-9088. The draft methods for Total Petroleum Hydrocarbons and Total Organic Lead may be replaced by future revisions.

b. Nonvolatile hydrophobic organics (e.g., PCBs): Due to the hydrophobic character of these compounds, it is not practical to split an aqueous sample. Consequently, it is recommended that replicates be run on the extract only. That is, when the analytical procedure for a hydrophobic organic is followed, the extract should be carried through in replicate through the column chromatography and analytical determinations.

c. Other analyses: Samples are split into portions while the original sample container is agitated.

d. Metals, except chromium VI and dissolved metals: When splitting samples for metal analyses, the sample must be acidified with nitric acid to pH <2 before dividing the sample. Acidification is especially critical if the sample is basic, in order to prevent precipitation of metallic hydroxides.

REFERENCES

1. D. B. Cohen, D. Gilmore, C. Fischer, and G. W. Bowes. 1983. Water Quality and Pesticides: 1,2-Dichloropropane (1,2-D) and 1,2-Dichloropropene (1,3-D). Special Projects Report No. 83-8SP. California State Water Resources Control Board, Sacramento, CA.

2. U. S. EPA. 1982. Test Methods for Evaluating Solid Waste; Physical/Chemical Methods. SW-846, Second Edition. Office of Solid Waste and Emergency Response, U. S. EPA, Washington, D.C. (A third edition is available now, but because of extensive changes that were made, U. S. EPA has not incorporated the third edition into RCRA regulations at this time.)

3. U. S. EPA. 1982. Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. .EPA 600/4-82-057, U. S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH.

4. U. S. EPA. 1983. Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020, Revised March 1983. U. S. EPA Environmental Monitoring Laboratory, Cincinnati, OH.

5. U. S. EPA. 1984. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act. Federal Register: 40 CFR, Part 136, Friday, October 26, 1984. Washington, D.C.

6. Department of Health Services. 1985. Recommended Methods of Analysis for the Organic Components Required for AB 1803, Fourth Edition. California DHS Sanitation and Radiation Laboratory, Berkeley, CA.

7. Fischer, C. 1986. Quality Assurance Management Guidelines for Environmental Studies. Draft Report. California State Water Resources Control Board, Sacramento, CA.

8. National Research Council. 1981. Prudent Practices for Handling Hazardous Chemicals in Laboratories. National Academy Press, Washington, D.C.

TABLE 3-3

HOLDING TIME FOR SOIL SAMPLES 1/

Analyte	Holding Time for Soil
Benzene, toluene, xylenes	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as gasoline	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as diesel	Extract within 14 days, analyze within 40 days

1/ Results from samples not meeting the listed holding times should be considered minimum values. That is, the actual concentration is equal to or greater than the concentration determined after the holding time has expired.

C. Recommended Analytical Methods

Recommended analytical procedures are summarized in Table 3-4. The Department of Health Services may approve an alternate method which has at least equivalent detection limits, precision, and accuracy as the referenced methods. For example, a cyrogenic gas chromatography/mass spectrometry (GC/MS) system may be used instead of a gas chromatography (GC) system, provided the GC/MS system can produce data which are equal or better than data provided by the referenced GC system in terms of detection limits, precision, and accuracy for an identical sample matrix.

Total Petroleum Hydrocarbons (TPH) arising from gasoline or diesel and total organic lead can be analyzed by the attached Department of Health Services (DHS) methods. The investigator should alert the laboratories to the procedures given in Table 3-4 and supply the laboratories with copies of the TPH and total organic lead methods, if necessary.

B. Guidelines for Handling Samples (Presented in Tables 3-2 and 3-3)

TABLE 3-2

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR WATER SAMPLES 1/

Test	Container 2/	Preservation	Maximum Holding Time 3/
Purgeable aromatic hydrocarbons (BTX&E) Method 8020 or 602	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$ 4/ HCl to pH2 5/	Analyze as soon as possible (max. 14 days)
Total petroleum hydrocarbons as gasoline	G	Cool, 4°C 0.008% $Na_2S_2O_3$ 4/ HCl to pH2 5/	Analyze as soon as possible (max. 14 days)
Total petroleum hydrocarbons -- diesel fuel oil	G	Cool, 4°C	14 days; analyze extract within 40 days

1/ Modified from 40 Code of Federal Regulations (CFR), Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act.

2/ Glass (G).

3/ Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for a longer period only if the collector or laboratory has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table.

4/ Should only be used in the presence of residual chlorine.

5/ Sample receiving no pH adjustment must be analyzed within seven days of sampling.

E. Quality Assurance (QA) and Quality Control (QC)

1. Definition

Quality Assurance: Systematic procedures that are used to provide assurance to a producer or user of information that defined standards of quality were met. QA covers field and laboratory performance, i.e., the quality control procedures that have been followed.

Quality Control: The activities that are used to implement the quality assurance plan. Quality includes adequacy of the methods employed, reliability of the results, and cost effectiveness.

2. Chain of Custody

A Chain of Custody Record is the disposition of a sample from collection to laboratory delivery. A Chain of Custody Record should be made out after samples are collected and signed by individuals collecting, relinquishing, and receiving samples. See Figure III-4 for an example of a U. S. EPA Chain of Custody form.

3. Laboratory Certification

All soil and water samples should be analyzed by a DHS-certified laboratory. Two certification programs exist in California and both are administered by DHS. Additional information can be obtained from the addresses listed:

- Hazardous Materials Laboratory Certification Prbgram

  California Department of Health Services
  Hazardous Materials Laboratory
  2151 Berkeley Way, Room 234
  Berkeley, CA 94704
  (415) 540-3003

- Drinking Water Laboratory Certification

  California Department of Health Services
  Sanitation and Radiation Laboratory
  2151 Berkeley Way, Room 465
  Berkeley, CA 94704
  (415) 540-2201

Figure III-4

EPA

United States Environmental Protection Agency

Region 10
1200 Sixth Avenue
Seattle WA 98101

CHAIN OF CUSTODY RECORD

PROJECT				SAMPLERS: (Signature)							
LAB #	STATION	DATE	TIME	SAMPLE TYPE						NUMBER OF CONTAINERS	REMARKS
				WATER	SEDIMENT	TISSUE	AIR	OIL	OTHER		

RELINQUISHED BY: (Signature)	RECEIVED BY: (Signature)	DATE/TIME
RELINQUISHED BY: (Signature)	RECEIVED BY: (Signature)	DATE/TIME
RELINQUISHED BY: (Signature)	RECEIVED BY: (Signature)	DATE/TIME
RELINQUISHED BY: (Signature)	RECV'D BY MOBILE LAB FOR FIELD ANAL.: (Signature)	DATE/TIME
DISPATCHED BY: (Signature) DATE/TIME	RECEIVED FOR LAB BY: (Signature)	DATE/TIME
METHOD OF SHIPMENT:		

Distribution: Original—Accompany Shipment
One Copy—Survey Coordinator Field Files

U.S. EPA Chain of Custody Form

4. QA Project Plan: This is a plan that outlines objectives, operational procedures, and the means for assuring how data of known and acceptable quality can be obtained. Where major projects are involved in remedial action, a plan for a performance audit (field and laboratory operations) and corrective action may be needed.

5. Number of Samples to Collect: The number of samples required relates directly to project objectives and the level of data reliability desired. The following are minimal recommendations and do not ensure that representative or statistically valid sampling of a site has been achieved.

   - Soil -- Tank excavation hole: At least two samples collected immediately after the tank is removed. This number should be increased for more accurate representation in very large excavations.
   - Soil background: Average of three samples.
   - Soil: Where >10 samples are to be collected at the same site, five percent duplicates should be collected and analyzed.
   - Water: Volatile organic analysis (VOA): All VOA samples should be collected in duplicate and analyzed in duplicate.
   - Water: Non-VOA analysis (.5-1-liter volume): One sample.
   - QC for remedial action should be designed to meet clean-up/closure objectives for the particular site. The basic principles outlined should be applied.

   A general guide for field QC samples is presented in Table 3-7.

6. Special Split-Sample Collection Instructions (7)

   a. Purgeable organics or VOAs: Individual samples are taken rapidly in succession in the specified containers. The individual samples may then be analyzed in replicate. With the exception of samples collected in a bailer, VOA splits should not be collected by pouring from one container into another.

Table 3-7

A General Guide for Collection of Field QC Samples (7)

Sample	Description and Purpose	Number of QC Samples
Trip or Travel Blank (Mandatory for volatile organics)	A sample container filled in the laboratory with organic-free water and carried unopened during the sampling trip. It must be prepared by the laboratory supplying sample containers. It is used to identify contamination introduced from the originating Laboratory. The trip blank remains with the collected samples and is analyzed along with the field samples to check residual contamination. Trip blanks are mandatory for volatile hydrocarbon analysis in water.	1. One per sample set. 2. Greater than 20 samples per set 5 percent trip blank analysis should be done. Statistical need and cost effectiveness should be considered where large numbers of samples are involved.
Field Blank (optional)	A sample container filled with organic-free water that is taken on the field trip. It is opened and exposed at the sampling site to detect contamination from air exposure. The water sample may be poured into appropriate containers to simulate actual sampling conditions. Contamination from air exposure can vary considerable from site to site therefore, the need for this sample should be evaluated relative to the sampling situation. Reference material (i.e., chemically defined soil) can be used in lieu of organic-free water as dictated by the sampling needs.	1. One for each team per trip or 2. One for each relevant sample type or 3. One per day at a single site 4. The need for field blanks should be made relative to site specific conditions and sampling requirements.
Blind Sample (optional)	A sample whose composition or source is known to the submittee but not known by the person logging in samples or the analyst. It is submitted along with the regular field sample set. When both the anticipated sample composition and the blind status of the sample are not known to the analyst, the sample is called a a "double blind" sample. A blind sample is used to check analytical performance and proficiency.	1. One per sample set up to 10 samples. 2. 10-14 samples: 5 percent blind sample analysis. >40 samples: requirements should be based on the needs of the project.
Field Duplicate (optional except required for volatile analysis (VOA)	A second field sample collected identically to and immediately after the first sample. This provides a measure of analytical precision and second sample confirmation. It provides a means of determining random error when adequate numbers of duplicates are collected. Field duplicates may also be collected as splits. Duplicates can also serve as blind field samples.	1. The need to collect duplicates is determined by project objectives. 2. The number of sample duplicates required is determined by project objectives and QC requirements.
Split Sample 1/ (optional)	The goal in obtaining splits is to obtain subsamples that do not differ significantly from each other or from the original sample. These are used to compare performance between/among laboratories.	1. 10 percent 2. Need for these is determinec by project objectives.

1/ Split sample collection has critical limitations. See special instructions in the following section.

c. Shipping Samples: Where commercial shippers are involved, dry ice may present Department of Transportation (DOT) shipping problems and "blue ice" may have to be substituted.

3. Water Samples

a. Free floating product (from a well): Sampling of free floating product on the surface of ground water should not be performed until the well has been allowed to stabilize for at least 24 hours after development or other withdrawal procedure. A sample should be collected that is indicative of the thickness of floating product within the monitoring well. This may be accomplished by the use of a clear, acrylic bailer designed to collect a liquid sample where free product and ground water meet. A graduated scale on the bailer is helpful for determining the thickness of free product. Samples should be field-inspected for the presence of odor and/or sheen in addition to the above evaluation.

Electronic measuring devices also are available for determining the thickness of the hydrocarbon layer floating on ground water.

b. Dissolved product (from a well): If free product is detected, analysis of water for dissolved product should be conducted. Prior to collecting a water sample, a well should be purged until temperature, conductivity and pH stabilize. Often, this will require removal of four or more well volumes by bailing or pumping. Once well volumes are removed and well water is stabilized, a sample can be taken after the water level approaches 80 percent of its initial level. Where water level recovery is slow, the sample can be collected after stabilization is achieved.

Ground water samples should be collected in a manner which reduces or eliminates the possibility of loss of volatile constituents from the sample. For collecting samples, a gas-actuated positive displacement pump or a submersible pump is preferred. A Teflon or stainless steel bailer is acceptable. Peristaltic pumps or airlift pumps should not be used.

Cross-contamination from transferring pumps (or bailers) from well to well can occur and should be avoided by thorough cleaning between sampling episodes. Dedicated (i.e., permanent installation) well pumps, while expensive, are often cost effective in the long term and ensure data reliability relative to cross-contamination. If transfer of equipment is necessary, sampling should proceed from the least contaminated to the most contaminated well, if the latter information is available before sample collection.

Water samples should be collected in vials or containers specifically designed to prevent loss of volatile constituents from the sample. These vials should be provided by an analytical laboratory, and preferably, the laboratory conducting the analysis. No headspace should be present in the sample container once the container has been capped. This can be checked by inverting the bottle, once the sample is collected, and looking for bubbles. Sometimes it is not possible to collect a sample without air bubbles, particularly if water is aerated. In these cases, the investigator should record the problem and account for probable error. Cooling samples may also produce headspace (bubbles), but these will disappear once the sample is warmed for analysis.

Samples should be placed in an ice chest maintained at 4°C with blue ice (care should be taken to prevent freezing of the water and bursting of the glass vial). A thermometer with a protected bulb should be carried in each ice chest.

c. Surface water: Grab samples should be collected in appropriate glass containers supplied by the laboratory. The sample should be collected in such a manner that air bubbles are not entrapped. Semisolid samples should be collected the same way. The collected samples should be refrigerated (blue ice, 4°C) for transport and analyzed within 14 days of collection.

Detection Limits for LUFT Investigations

Minimum detection limits for key analytes are listed in Table 3-5. The detection limits for benzene, toluene, and xylene are consistent with the experience of several commercial laboratories under optimal conditions. The detection limits for benzene, toluene, and xylene in soil assume the direct purging of a soil-water mixture and subsequent gas chromatography -photoionization detection (GC-PID). Lower detection limits are achievable with available technology by using: modifications of reference methods, a larger sample or additional concentration techniques. Detection limits may be significantly higher in samples with interfering organics or matrix effects. The readily obtainable 0.3 ppm detection limit cited on page 20 takes into account potential sample interferences.

TABLE 3-5

DETECTION LIMITS FOR COMMONLY ANALYZED FUEL PRODUCTS

Analyte	Water µg/l	Soil µg/kg	Method
Benzene	0.3	5	EPA 602, 8020
Toluene	0.3	5	EPA 602, 8020
Xylenes, total	0.6	15	EPA 602, 8020
Total Petroleum Hydrocarbons	500.0	10,000	DHS: GC-FID

D. Recommended DHS Analytical Methods

Total Petroleum Hydrocarbons (TPH) Analysis -- Gasoline and Diesel

1. Scope and Application

   a. This method is for the determination of gasoline and diesel in contaminated ground water, sludges, and soil.

   b. This method is recommended for use by, or under the supervision of, analysts experienced in the operation of GC and in the interpratation of chromatograms.

2. Summary of Method

a. This method involves the determination of volatile hydrocarbons (gasoline) by the headspace method or the purge and trap method (EPA method 5030) (2) and the determination of semivolatile organics (diesel) by the extraction method. A sample, after headspace, purge and trap, or extraction treatment, is injected into a GC, and compounds in the GC effluent are detected by an FID. An aliquot of each sample will be spiked with standards to determine percent recovery and limits of detection for that sample.

b. The sensitivity of this method usually depends on the level of interference rather than on instrument limitations. Table 3-6 lists the limits of detection in the absence of interferences for water and soil samples.

TABLE 3-6

TPH METHOD DETECTION LIMITS

Parameter	Matrix	Extraction Method	Headspace Method
Gasoline	Aqueous	0.5 mg/l	5.0 mg/l
	Soil	10.0 mg/kg	5.0 mg/kg
Diesel	Aqueous	0.5 mg/l	
	Soil	10.0 mg/kg	

3. Interferences

a. Solvents, reagents, glassware, and other sample-processing hardware must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

b. Before processing any samples, the analyst should demonstrate daily, through the analysis of a solvent blank, that the entire system is interference-free.

4. Apparatus and Materials

a. Gas-tight syringe: One cubic centimeter (cc) with chromatographic needles.

b. Vial with cap: 40 milliliter (ml) capacity screw cap (Pierce number 13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C before use.

c. Septum: Teflon-faced silicone (Pierce number 12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C for 30 minutes before use.

d. Separatory funnel: 2-liter with Teflon stopcock.

e. Kuderna-Danish (K-D) apparatus.

f. Boiling chips: Solvent extracted approximately 10/40 mesh.

g. Water bath: Heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

h. GC: Analytical system completed with programmable GC suitable for on-column injection and all required accessories, including FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

i. GC column: 6 feet by 1/8 inch ID glass column packed with 5% SP-2100 on Supelcoport 60/80 mesh.

j. Detector: FID.

k. Microsyringes: 10 µl, 100 µl, 200 µl.

l. Erlenmeyer flask: Pyrex, 250 ml capacity with a screw cap.

m. Mechanical shaker.

Reagents

a. Stock diesel standard solutions: Prepare a commercial diesel standard in carbon disulfide. Place 9 ml of CS_2 into a 10 ml glass-stoppered volumetric flask. Allow to stand for a few minutes. Weigh the flask to the nearest 0.1 mg. Using a 100 µl syringe, immediately add an amount of diesel to the flask, then reweigh. Be sure that the liquid falls directly into the CS_2 without contacting the neck of the flask. Dilute to volume, stopper, mix by inverting the flask several times. Calculate the concentration in µg/ l from the net gain in weight. Secondary working standards can be prepared from the stock standards.

b. Stock gasoline standard solutions: Gasoline stock standards can be prepared as above using commercial gasoline as standard in dodecane.

c. Sodium sulfate, anhydrous, ACS, granular.

d. Carbon disulfide, glass distilled, high purity. Another solvent such as ethyl acetate or methylene chloride may be used provided that the solvent can extract the petroleum hydrocarbons and does not interfere with the resulting gas chromatogram of the TPH. This must be demonstrated by spike and recovery prior to the analysis of samples.

e. Dodecane, purified.

6. Procedures

a. Organic Liquid

Organic liquid can be analyzed by dissolving a known amount of sample into a certain volume of carbon disulfide in a volumetric flask.

b. Water

(1) Transfer one liter of sample to the two liter separatory funnel.

(2) Add 60 ml of solvent to the separatory funnel.

(3) Seal and shake the funnel for 60 seconds with periodic venting to release vapor pressure.

(4) Allow the phases to separate for minimum of 10 minutes. If emulsion occurs, the analyst must employ mechanical techniques to complete the phase separation.

(5) Collect the extract and repeat the extraction two more times using fresh portions of solvent.

(6) Combine three extracts and dry by passing through a column of anhydrous sodium sulfate.

(7) Collect the dried extract in a K-D evaporative concentrator equipped with a 10 ml collection ampule.

(8) Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml of solvent to the top. Place the K-D apparatus on a steam or hot-water bath. Adjust the water temperature as required to complete the concentration in 15 to 20 minutes. When the volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

(9) Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 5 ml with the solvent to be used in instrument analyses.

c. Soil and Sludges

(1) Weigh 20.0 gram (g) sample into a 250 ml screw cap Erlenmeyer flask. Add 80 ml of solvent.

(2) Cap the flask and shake on a mechanical shaker for at least four hours.

(3) After the extraction is completed, filter the extract and dry it by passing through a column of anhydrous sodium sulfate.

(4) Collect the dried extract in K-D flask, fitted with a 10 ml concentrator tube and a three-ball Snyder column. Wash the extractor flask and the sodium sulfate with a portion of carbon disulfide and collect it into the K-D flask.

(5) Add one or two clean boiling chips and concentrate the extract to 5 ml as discussed in steps (8) and (9) (page 63).

d. GC Conditions

The recommended GC column and operating conditions are:

Column: 6 feet by 1/8 inch ID glass column packed with 5% SP-2100 on Supelcoport, 60/80 mesh with nitrogen carrier gas at 20 ml/minute flow rate. Column temperature is set at 40°C at the time of injection, hold for 4 minutes, and programmed at 10°C/minute to a final temperature of 265°C for 10 minutes.

Calibration

(1) Establish GC operating parameters as specified in d. above. By injecting secondary standards, adjust the sensitivity of the analytical system for the analysis of gasoline and diesel in environmental samples. Detection limits for the extraction method and the headspace method are listed in Table 3-6 (page 61). Calibrate the chomatographic system with the external standard technique. At least three concentration levels should be used for the preparation of the calibration curve. One of the external standards should be at a concentration near, but above, the method detection limit. The other standard should

correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

(2) Using injections of 2 to 5 µl of each calibration standard, tabulate total peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for gasoline and diesel.

(3) The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response varies from the predicted response by more than + ten percent, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

f. Analysis of Samples

(1) Extract

(a) Inject 2 to 5 µl of the sample extract using the solvent flush technique. Record the volume injected to the nearest 0.05 µl, and the resulting total peak areas.

(b) If the total peak areas exceed the linear range of the system, dilute the extract and reanalyze.

(2) Headspace Method [Note: Purge and trap (EPA 5030) may be used instead of headspace.]

(a) Place 20 g (ml) each of the waste sample into three separate 40 ml septum seal vials.

(b) Inject into one sample vial through the septum 200 µl of the gasoline standard in dodecane (concentration 7,500 µg/ml). Label this "spike".

(c) Inject into a separate (empty) 40 ml septum seal vial 200 µl of the same standard. Label this "standard".

(d) Place the sample, spike, and standard vials into a 90°C water bath for one hour. Store the remaining sample vial at 4°C for possible future analysis.

(e) While maintaining the vials at 90°C, withdraw 1 ml of the headspace gas with a gas-tight syringe and analyze by injecting into a GC.

3.2 Iodine solution: Weigh 3.0 g of I_2 and dissolve and dilute to 100 ml with benzene. Store in brown bottle.

3.3 Aliquat 336 (tri-capryl methyl ammonium chloride), available from McKesson Company, Minneapolis, Minnesota.

10% V/V Aliquat 336/MIBK
1% V/V Aliquat 336/MIBK

3.4 Xylene.

3.5 $PbCl_2$ -- Lead chloride

1. Stock $PbCl_2$ solution. Dissolve 0.3356 g $PbCl_2$ previously dried at 105°C for 3 hours in 10% Aliquat 336 in MIBK solution and dilute to 250 ml. Store in brown bottle. This solution contains 1,000 µg/ml of Pb.

2. Preparation of intermediate Pb standard: Pipet 10 ml of the stock solution (1,000 µg/ml Pb) and dilute to 100 ml with xylene/MIBK solution (40% xylene).

3.6 Sodium sulfate (Na_2SO_4), anhydrous, crystals.

4. Apparatus

4.1 Erlenmeyer flask with ground glass stopper, 250 ml.

4.2 Mechanical shaker.

4.3 Filter funnel and paper (Whatman No. 40 or equivalent).

4.4 Flame atomic adsorption spectrophotometer and recorder or integrator.

4.5 Lead hollow cathode or electrodeless discharge lamp.

5. Procedure

5.1 Sludges, sediments, and soils: Weigh out to the nearest 0.1 g about 50 g of homogenized sample into an Erlenmeyer flask. Add 100 ml xylene. Stopper the flask and shake it for 1/2 hour on a mechanical shaker. Filter the extract through filter paper and anhydrous sodium sulfate.

5.2 Add 20 ml of MIBK to a 50 ml volumetric flask.

5.3 Pipet 20.0 ml of the xylene extract (Step 5.1) into the flask and mix.

5.4 Pipet 0.1 ml of I_2 solution into the flask and mix for about one minute.

5.5 Pipet 5 ml of 1% Aliquat 336 in MIBK and mix.

5.6 Dilute to volume with MIBK and mix.

6. Standard and Blank Preparation

Prepare appropriate working standards and blank from 100 g/ml Pb standard.

6.1 Add approximately 20 ml of xylene to 50 ml volumetric flask. Pipet the correct amount of the 100 µg/ml Pb standard into the flask to prepare the right standard.

6.2 Add immediately 0.1 ml of I_2 solution and mix well.

6.3 Add 5 ml of 1% Aliquat 336/MIBK and mix well.

6.4 Dilute to volume with MIBK and mix well.

6.5 Blank xylene/MIBK (40% xylene) should be treated as the working standard solutions.

7. Analysis

7.1 Set up the AA according to the manufacturer's instructions. Use background correction to decrease broad band absorption interference.

7.2 Aspirate H_2O into the flame and adjust the acetylene flow to 8.5 l/min and the air flow to 25 l/min.

7.3 Aspirate MIBK containing 40% xylene into the flame.

7.4 Reduce the acetylene flow to about 4.8 l/min and make fine adjustments in the acetylene flow to produce an even flame with no yellow luminescence to obtain optimum conditions.

7.5 Aspirate into the flame blank, working standards, and sample to measure the absorbencies. Estimate the concentrations of organolead in sample.

8. Calculations

Solids:

$$\frac{100\ ml}{50g} \quad \frac{50\ ml}{20\ ml} \quad \frac{\mu g/l}{1000\ ml/l} \times F = \mu g/g \text{ organolead calculated as Pb.}$$

where F = dilution factor.