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CLOSURE PLAN

GENERAL ELECTRIC COMPANY
INACTIVE DRY WELL
APPARATUS SERVICE SHOP
ALBUQUERQUE, NEW MEXICO

MARCH, 1985

As Modified By New Mexico Environmental Improvement Division

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1.0 FACILITY AND SITE DESCRIPTION

The General Electric Service Shop, 4420 McLeod Road, NE, Albuquerque, New Mexico, is located on a two acre site in a light industrial park. The facility is northeast of the metropolitan area of Albuquerque and approximately four miles east of the Rio Grande River (Figure 1). Site topography is generally level.

The facility consists of a 5,300 square foot building with a steel frame structure and exterior metal siding founded on a concrete slab at grade (Figure 2). The north wall of the building faces McLeod Road. A 1,200 square foot shed on a concrete slab is attached to the south building wall. A concrete pad extends south of the shed an additional 25 feet. A compacted gravel area extends approximately 40 feet south of the concrete pad. Asphalt concrete pavement extends approximately 80 feet from the north building wall to McLeod and approximately 40 feet from the east wall of the building to the east property line. Surface soils on the remainder of the site are generally silty coarse to fine sand, 2 to 4 feet thick, overlying slightly cemented silty fine sand.

The facility is in the vicinity of the Vol Andia well field with the closest well, No.1, approximately 800 feet southwest from the southwest corner of the site.

2.0 FACILITY OPERATIONS AND ENVIRONMENTAL HISTORY

The General Electric Service Shop was constructed in 1969 for the repair of industrial equipment, primarily electric motors. Solvents, paints, paint and varnish thinners, and steam cleaning detergents are used in the repair operations.

Review of the purchasing records at the Albuquerque Service Shop shows the following approximate usage quantities of solvents:

Material	Primary Application	Quantity
Xylene	Parts Cleaning and Varnish Thinning	1200 gals/yr
Kerosene	Fuel for Steam Cleaning Jenny	250 gals/yr
1,1,1-Trichloroethane	Parts Cleaning	<55 gals/yr
Methylene Chloride	Motor Stripping Dip Tank Process	<55 gals/yr
Methyl Ethyl Ketone	Parts Cleaning	<10 gals/yr
Toluene	Thinning	<10 gals/yr

Transformers filled with askarels and insulating oils containing PCB's (Polychlorinated biphenyls) were repaired at the Service Shop. The original construction of the facility included a two-chamber drainage sump located below floor level in the shed area near the west wall. Wash products from the steam cleaning of equipment being repaired are collected by the drainage sump. Prior to November 1983, the sump discharged into a dry well that is shown on the original construction drawings as being 5 feet in diameter

by 10 feet deep, located approximately 10 feet west of the shed's west wall.

An application was submitted to the City of Albuquerque for permission to discharge the cleaning effluent into the MOPTW. Connection to the MOPTW was completed in November 1983 and the discharge to the dry well terminated.

In 1980 a Notification of Hazardous Activity was submitted to the EPA to establish the site's status as a generator of hazardous waste and to obtain an EPA Identification Number, NMD047140256. An inspection by an EPA contractor was conducted in October 1981 for compliance with the Toxic Substances Control Act.

A RCRA inspection was conducted by EPA in September 1982. A compliance order was received from the EPA Region VI in February 1983. This matter has been resolved by a consent agreement.

In August 1984 an inspection of the facility was conducted by the New Mexico Environmental Improvement Division (NMEID). A Notice of Violation was sent to the Service Shop by NMEID in October 1984. A Pre-closure Plan was submitted to NMEID on January 7, 1985, which specified detailed soil sampling required to assess the extent of contamination and described general remedial activities.

The shallow soil sampling was conducted in December 1984 and a

report with analysis results was submitted to NMEID on February 7, 1985.

The NMEID responded on February 4, 1985 to the Pre-closure Plan by requiring the development and submittal of a total Closure Plan, in accordance with New Mexico Hazardous Waste Management Regulations, to include additional details on sampling and specific remedial activities.

A Closure Plan dated March 1985 was transmitted to NMEID on March 22, 1985. NMEID's review comments on the Closure Plan were stated in a letter dated May 10, 1985. GE and its consultant met with NMEID personnel on June 5, 1985 in Santa Fe to discuss the review comments and Closure Plan requirements. The Closure Plan was resubmitted in July 1985 and comments and required modifications were sent to GE by NMEID in their letter of October 9, 1985. This revised Closure Plan incorporated these modifications.

3.0 CLOSURE EXTENT

The General Electric Service Shop is still in operation and is presently generating small quantities of hazardous wastes. The facility intends to maintain its status as a generator of hazardous wastes with storage less than ninety days. The portion of the facility to be closed is the abandoned dry well which received the discharge from cleaning operations prior to November 1983. Discussions with shop personnel indicated the possible existence of another previously used dry well. Since the original site construction drawings show the location of the dry well in its present location, any previous dry well would have been either adjacent to or replaced by the existing dry well. Therefore, evaluation activities to define the lateral and vertical extent of contamination in the surrounding soil will encompass the effects of any previous dry well and will include exploration to verify the number of existing dry wells.

of 19,000 ppm. A second portion of the same sample was tested in the second round and had a reported PCB concentration of 5,500 ppm.

Samples were selected for analyses primarily on the basis of sample locations and depths so as to provide representative site coverage. As a further assistance in selecting samples for VOC testing, samples were screened with an HNU Model PI-101 Photoionization Analyzer. Readings were made with the analyzer probe in the headspace of the sample jar. The probe was placed in the headspace by punching through the aluminum foil cover that had been placed over the jar mouth, beneath the screw-on cap, at the time of sampling.

The HNU was calibrated as described in the manufacturer's instruction manual. The calibration gas supplied by the manufacturer is isobutylene.

Six samples were selected for laboratory VOC analysis. On three of these, HNU readings were used to decide which one of the two portions of sample would be tested for VOC's. The portion having the highest HNU reading was chosen. These HNU readings ranged from 30 to 90 ppm. On the preliminary data sampling, except at those boring where samples were selected for VOC testing, HNU readings were typically 0 - 4 ppm, which was at or below ambient air readings.

Of the six samples analyzed for VOC's, four samples from two locations in the vicinity of the abandoned dry well showed the presence of benzene, ethylbenzene, methylene chloride, tetrachloroethylene, toluene, and 1,1,1-trichloroethane. Of these, ethylbenzene had the highest concentration (43.6 ppm) and this occurred at a sample depth of 13.5 to 14 feet. The two remaining samples analyzed at other site locations resulted in detection of methylene chloride only, at concentrations less than 1 ppm.

Based on the results of analyses performed on the soil samples taken in December, 1984, further contamination evaluation will be localized in the vicinity of the abandoned dry well.

A report describing the hydrogeology of the site vicinity, based on a review of existing data, was prepared and submitted to NMEID on March 8, 1985. The available data indicates that the ground water beneath the site is at a depth of about 200 to 230 feet with the flow direction undetermined due to the influence of withdrawal from wells in the site vicinity.

4.1 **Phase I Evaluation**

NMEID will be informed as to the start (and any other stage requested by NMEID) of exploratory work. NMEID will have the option of splitting samples and observing any exploratory activities.

4.1.1 Soil Sampling and Analyses in Dry Well Vicinity

The dry well(s) will be located by probing with hand tools. In the vicinity of the dry well, 5 soil test borings will be made. The locations and depths of the Phase I borings have been selected on the basis of the present estimate of the maximum extent of contamination. One boring will be located to pass through the bottom of the dry well structure which is the source of effluent percolation into the soil. The other 4 borings will be positioned on 4 sides of the dry well vicinity on a radius of approximately 20 feet from the centrally located boring. The centrally located boring will be drilled first since it would most likely reveal the maximum depth of contamination. Field results of the first boring will be used to determine whether adjustments to planned depths, locations, or procedures of the other borings are indicated. If a second dry well is located, a sixth boring will be drilled through it.

Drilling through dry well(s) will be done by setting casing into the soil in the bottom of the dry well. Based upon a recent visual examination of the dry well, it is believed there are no free liquids in the dry well. In any case, no materials are planned to be removed from the dry well during exploration, other than those removed in advancing the boring.

During drilling, soil samples will be screened with an organic vapor analyzer (HNU) to assist in selecting samples for chemical

testing and to aid in determining depths of Phase I borings. The organic vapor readings will be taken by sampling headspace in the soil sample jars. The soil sample jars that are used for headspace sampling will not be the same as those submitted for laboratory analyses. Samples submitted to the laboratory will be taken from a part of the split spoon sample that is separate from that part used for headspace analysis. Selection of samples for tested will also consider sample location and depth. Borings will be drilled to a minimum depth of 30 feet. If elevated organic vapor readings (readings above ambient air readings) are obtained on the 30-foot samples, the boring will be extended until elevated readings are no longer obtained or ground water is reached, whichever comes first. The ultimate testing depths of any boring will be determined by laboratory analyses results rather than HNU readings (See Contingency 3, page 17).

After completion, boreholes will be closed by grouting to the surface. Grouting of the holes is preferred over backfilling the holes with cuttings to avoid introducing potentially contaminated materials into uncontaminated zones.

During drilling, cleaning of tools and equipment will follow a written protocol to avoid cross contamination between samples or borings. The protocol is included in the Appendix. Tools and equipment will be cleaned prior to starting work and after each boring. Samplers will be cleaned after each sample. The cleaning

process will consist of brushing to remove debris, washing (steaming) with laboratory grade cleaning solution (such as LiquiNox), tap water rinse (steam), acetone rinse, and distilled water rinse.

Cuttings from the borings and excess samples will be placed either in drums or contained on site between visqueen sheets.

Residue from cleaning and decontamination will be placed in drums. Disposition of these captured materials will decided after receipt of analyses data and will involve either approved landfill disposal, on-site aeration, or returning to the site surface.

The holes will be advanced using temporary casing or hollow stem augers to minimize the risk of contamination being carried down by the drilling process. Soil samples will be taken with the type of split spoon sampler and procedure described by ASTM Standard D1586. A copy of ASTM D1586 is in the Appendix.

In the upper 30 feet, a sample will be taken from each one-foot increment of depth. Between depths of 30 and 60 feet, the sampling interval will be 2.5 feet. Below the 60 foot depth, samples will be taken at 5 foot intervals. Soil specimens will be taken from the central portion of each recovered foot of sample and placed in new 8-ounce glass jars having aluminum foil cap liners. The jars will have been rinsed in deionized water and allowed to dry.

Boring records will be kept and jars will be labeled. A small portion of each soil sample will also be sealed in a 40 ml glass vial fitted with a screw-on teflon septum cap. The 40 ml vials are designed for the collection of samples containing volatile organic compounds (VOC's).

The test borings will be drilled by a local geotechnical firm working under the supervision of Law Engineering Testing Company (now Law Environmental) who will provide technical direction, classify soil samples, conduct organic vapor screening of samples, sample selection and shipment for laboratory analysis.

Selected samples will be shipped, via an express delivery service such as Federal Express or Purolator, to a qualified laboratory for chemical analyses. Chemical analyses will be performed in accordance with the following methods from SW846. Copies of the methods are in the Appendix.

On two samples from the bottom of the dry well (sediment, sludge and/or the uppermost soil), analytical screens will be performed in accordance with EPA Methods 8240 (volatiles) and 8270 (semi-volatiles). These samples will also be analyzed for cyanides, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver in accordance with the procedures tabulated below. All other selected soil samples will be analyzed in accordance with the following.

	Substance	EPA Method	
		Sample Preparation	Detection
1.	Volatiles	5030	8240
2.	Semi-Volatiles Identified in Initial Screens	3540	8270
3.	PCB's	3540	8080
4.	Cyanides	9010	9010
5.	Phenols	8040	8040
6.	Arsenic	3050	7060
7.	Barium	3050	7081
8.	Cadmium	3050	7131
9.	Chromium	3050	7191
10.	Lead	3050	7421
11.	Mercury	7471	7471
12.	Selenium	3050	7740
13.	Silver	3050	7761

Of the samples taken in the upper 30 feet at the 5 initial borings (30 samples planned to be taken in each boring), at least 30 of these will be selected for chemical analysis. This will average an analysis in each 5 feet of depth drilled. If the borings are extended deeper than 30 feet, the following minimum numbers of samples will be selected for chemical analysis:

Depth (feet) From	To	Minimum Number of Samples to be Analyzed Per Boring
30	60	3 samples; average of one analysis per each 10 feet of depth drilled
60	200	7 samples; average of one analysis per each 20 feet of depth drilled

Moisture contents and grain size distributions will be done on samples from the centrally-located boring. At least one sample will be selected from each 10 foot interval of depth. Test procedures will be according to ASTM D 421 and D 422 for the sieve analyses and ASTM D 2216 for the moisture contents. Copies of

these ASTM procedures are in the Appendix.

Chain of Custody documentation will be maintained on all shipments for laboratory analyses. A copy of the Chain of Custody Form is in the Appendix. The form will be initially filled in and signed as "Sampler" by the on-site person providing technical direction to the drilling operations. This person will verify that shipping containers are sealed and sign the form when the samples are relinquished to the shipper. The receiving laboratory will sign the form upon receipt of the samples.

A written report will be submitted to NMEID. The report will include descriptions of the sampling activities, results of borings and analyses and an assessment of the degree to which Phase I data bracket the contamination. The report will also specify details on Phase II evaluation activities.

4.1.2 Ground Water Monitoring

Ground water monitoring will be performed. Well installation, developing and sampling are described in the RCRA Facility Investigation (RFI) Work Plan (Task II). The RFI Work Plan describes the well locations and construction design.

Appendix IX analyses of the water samples from the wells will be in accordance with the RFI Work Plan, and will include the following constituents and analytical techniques:

1. Volatile Organics

   a. Benzene (EPA Method 8020 and 8240)
   b. ethylbenzene (EPA Method 8020 or 8240)
   c. methylene chloride (EPA Method 8010 or 8240)
   d. methyl ethyl ketone (EPA Method 8015 or 8240)
   e. tetrachloroethylene (EPA Method 8010 or 8240)
   f. toluene (EPA Method 8020 or 8240)
   g. 1,1,1-trichloroethane (EPA Method 8010 or 8240)
   h. xylene (EPA Method 8020 or 8240)
   i. GC/MS scan (EPA Method 8240)

2. Semivolatile organics: GS/MS scan (EPA Method 8250)

3. Metals

   a. arsenic (EPA Method 7060 or 7061)
   b. barium (EPA Method 7080 or 7081 or 6010)
   c. cadmium (EPA Method 7030 or 7031 or 6010)
   d. chromium (EPA Method 7090 or 7091 or 6010)
   e. lead (EPA Method 7420 or 7421 or 6010)
   f. mercury (EPA Method 7470)
   g. selenium (EPA Method 7740 or 7741)
   h. silver (EPA Method 7760 or 7761 or 6010).

Water level measurements will be taken before the wells are pumped. The wells will be surveyed so that the water level information may be expressed as feet above mean sea level.

The sampling and analysis will be as described in the RFI Work Plan, a copy of which will be furnished to NMEID prior to the sampling. NMEID will have the option to split samples with GE.

The wells will be installed and sampled during the RFI. Well logs, ground water sample results and water levels will be submitted in the RFI report.

Should the water levels indicate that the wells are not located

upgradient and downgradient from the dry well, the installation of more wells may be installed. Should the sample analyses show that wastes from the dry well have contaminated ground water beneath the facility, GE will develop a corrective action plan to assess the extent of contamination and to restore the aquifer quality.

4.2 Phase II Evaluation

Three contingencies are anticipated for the Phase II evaluation. Those contingencies and the planned response for each, contingent upon NMEID approval, are as follows:

Contingency 1: The centrally located Phase I test boring shows detectable levels (above laboratory analysis method detection limit) of contamination and the four surrounding borings do not show detectable levels of contamination.

Response: Additional test borings will be drilled at reduced radii from the centrally located test boring with the number, location, and depth of the test borings based on Phase I test boring analyses results.

Contingency 2: Some or all of the Phase I test borings surrounding the centrally located test boring show detectable levels of contamination.

Response: Additional test borings will be obtained at increased radii from the centrally located test boring with the number, location, and depth of the test borings based on Phase I test boring analyses results.

Contingency 3: Laboratory test analyses on samples taken in Phase I borings show detectable levels of contamination at the maximum drilled depths.

Response: Additional test borings will be obtained to greater depths with the number, location and depth of the test borings based on Phase I test boring analyses results.

5.0 WASTE INVENTORY

The waste inventory associated with the dry well(s) consists of the dry well structure(s), connected drain lines, dry well contents, and associated contaminated soils which exhibit hazardous waste characteristics (PCB concentrations 50 ppm or greater, and/or constituents which pose a health or environmental threat to the ground water). Soil sampling as specified in the Contamination Evaluation Section is required for definitive quantification of the contaminated soil associated with the dry well(s). The maximum waste inventory will vary based on the result of these evaluations. The present estimate of the volume of soils with significant contamination associated with the dry well(s) was estimated to be an area approximately one-half the distance from the dry well(s) to the Phase I Evaluation boring locations. Based on the information available at this time, it is estimated that the maximum quantity of wastes affected by closure is approximately 13,500 cubic feet. Table 1 presents estimated volumes for the various categories of waste.

TABLE 1

ESTIMATED VOLUME OF WASTE
GE ALBUQUERQUE

Waste Material	Estimated Volume
Dry well structure 5' x 10' x 0.7' thick	95 cu. ft.
Dry well contents 3.6 dia. x 3'	31 cu. ft.
Previous dry well structure (if existing)	95 cu. ft.
Previous dry well contents (if existing)	31 cu. ft.
Dry well(s) associated Contaminated soil 20' x 20' x 30' deep	12,000 cu. ft.
Site areas with exposed soil containing PCB concentrations greater than 50 ppm	1,200 cu. ft.
TOTAL	13,452 cu. ft.

6.0 REMEDIAL ACTIVITIES

Any free liquids and pumpable sludges contained within the dry well structure(s) will be removed to appropriate EPA permitted treatment or disposal based on their waste characteristics. The dry well structure(s), contained solidified material, and connected drain lines will be excavated and removed to appropriate qualified disposal based on their waste characteristics. Soils containing PCB concentrations equal to or greater than 50 ppm or exhibiting RCRA Hazardous Waste characteristics will be excavated and removed to appropriate qualified disposal. The waste characteristics will have been determined in the exploratory work, using sampling and analytical procedures described in the "Contamination Evaluation" section. Any disposal of contaminated materials, if required, will be based on results of these analyses. Any disposal required in remedial activities will be specified and submitted to NMEID for approval.

Remedial activities for soils containing analyzed constituents which pose a health or environmental threat to the ground water will be based on the depth and quantity of contamination. In determining the minimum concentrations of various compounds which pose a threat so as to require remediation, levels with supporting justification will be submitted for NMEID's approval prior to implementing remedial activities. Anticipated scenarios and corresponding remedial activities are as follows:

Scenario 1: Contamination results in soil volumes which are less than or approximately equal to those estimated in the Waste Inventory Section.

Remedial Activity: The soil will be excavated and either removed to appropriate qualified disposal or treated on site depending on the constituent analyses. The excavation will be backfilled with clean soil, compacted to minimize future settlement, and graded to promote runoff and prevent ponding.

If the contaminants are volatile organic compounds then the excavated soil will be spread on the site and cultivated to promote aeration and volatilization.

Scenario 2: Contamination of the soils results in substantially larger volumes than estimated in Waste Inventory Section.

Remedial Activity: Contamination containment alternatives will be evaluated with the associated ground-water monitoring and may be implemented in lieu of or combined with soil excavation activities. Containment would consists of an impervious cover (e.g., concrete pad) of sufficient area to prevent infiltration and percolation. If a cover is deemed appropriate, the cover will be designed to meet NMEID's approval.

Scenario 3: When contamination of the ground water and/or contamination of the soils is established in or near the saturated zone.

Remedial Activity: Upon establishment of ground water contamination resulting from a site source, ground-water remediation will be implemented based on the contaminant constituents.

7.0 CLOSURE CERTIFICATION

Upon completion of the remedial activities, a certification of closure will be prepared and submitted to NMEID. This certification by the General Electric Company and an independent registered professional engineer will state that the closure of the dry well has been completed in accordance with the specifications in the approved Closure Plan. Planning of the remedial measures will include specifying minimum inspection requirements associated with PE certification.

8.0 POST-CLOSURE MONITORING

In the event that the Contamination Evaluation results in substantially larger volumes than estimated or determines that the site is a source of ground-water contamination requiring remedial activities other than contaminant removal, then appropriate Post-Closure Care will be implemented in accordance with New Mexico Hazardous Waste Management Regulations, Part V - Standards for Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities which adopts 40 CFR Part 264.

9.0 SCHEDULE

Figure 4 indicates the sequence of events and time required for each of the closure activities.

Upon receipt of notice that NMEID has approved this plan, GE will, within 7 calendar days of such notification, implement the plan by issuing notice to Law Environmental and the drilling company to proceed on the Phase I Evaluation. Phase I drilling will commence within three weeks after notice to proceed.

If the five initial borings terminate at the 30 foot depths, the drilling and soil sampling will require approximately two weeks to complete. If the initial boring extend to 200 feet, the drilling and soil sampling would have a total duration of about five weeks as shown on Figure 4.

Laboratory testing is estimated to require five weeks to complete.

Data evaluation and preparation of the Phase I written report will require three weeks after all laboratory data are available. The Phase II exploration will be planned during the evaluation process and described in the report.

As with the Phase I borings, Phase II drilling will be implemented within three weeks of notification to GE to proceed. The duration of the Phase II drilling is dependent on the location, depths, and

type of borings required. If borings terminate at depths of 30 feet or less in five locations, then drilling and sampling will require two weeks. If the Phase II Evaluation requires soil borings in more than five locations or depths greater than 30 feet, five weeks for drilling and sampling as shown on Figure 4 will be necessary.

Remedial activities will be planned and designed after completion of the contamination evaluation. These activities will be described in the Phase II report. The schedule for remedial activities is based on the Scenario 1 of the Remedial Activities Section. If the Contamination Evaluation results in substantially larger volumes of soils than estimated, then alternative remediation would be evaluated and submitted for NMEID approval resulting in an extended closure schedule.

10.0 COST ESTIMATE

The estimate of costs for closure are based on estimated quantities and unit costs at the time of preparation of this Closure Plan. This estimate includes a range of costs for various evaluation contingencies as specified in Section 4, Contamination Evaluation. Remedial costs are based on Scenario 1 of Section 6, Remedial Activities.

The estimated closure costs as presented in Table II are $187,000 - $252,000.

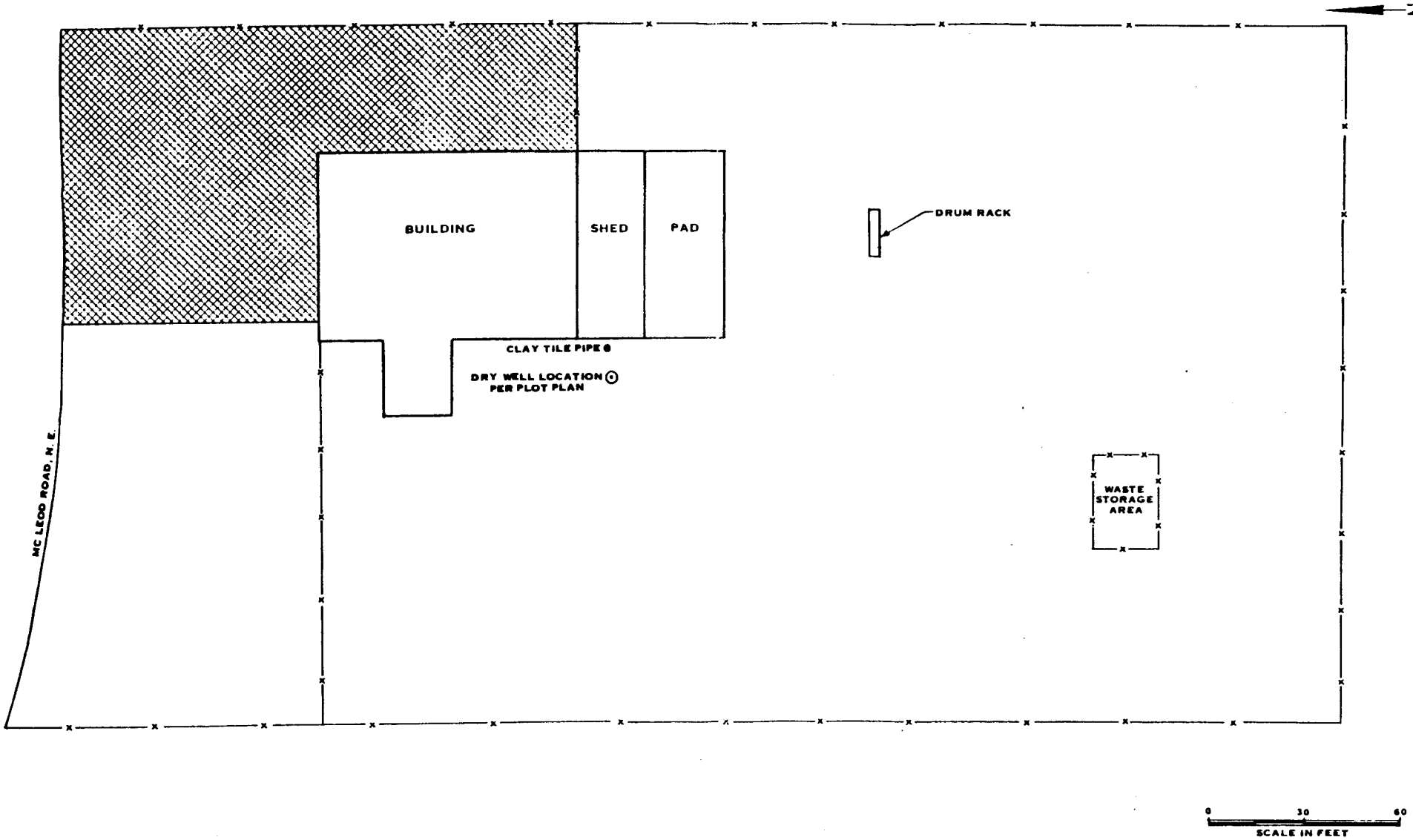
As evaluation progresses and additional data is obtained, the costs of closure will change and alternative remedial activities, approved by NMEID, may be implemented.

The estimate of costs for post-closure are based on the installation of an impervious cover to prevent infiltration and percolation in conjunction with four wells requiring monitoring for thirty years.

TABLE II
ESTIMATED CLOSURE COSTS
GE ALBUQUERQUE SERVICE SHOP

Professional Engineering and Testing Services		
Preliminary Data for Closure		$ 23,500
Regional Hydrogeology Study		5,500
Phase I Evaluation		
Soil Borings 30 to 200 feet	$ 33,000 - 86,000	
Phase II Evaluation		
Soil Borings 30 feet or Ground Water Monitoring Wells	$ 33,000 - 45,000	
	$ 95,000 -160,000	
Remedial Activities		
Removal of Surface Soils with PCB Concentrations of 50 ppm or greater Estimated Volume 1,200 cubic feet		$ 19,000
Removal of Dry Well Structure(s) and Contents Estimated Volume 250 cubic feet		11,000
Excavation of Dry Well(s) Associated Contaminated Soils Estimated Volume 12,000 cubic feet		38,000
Remedial Activity Supervision		16,000
		$ 84,000
Site Restoration		$ 5,000
Closure Certification		3,000
Estimated Closure Costs	$187,000 - 252,000	
Post Closure		
First Year Ground Water Monitoring		$ 20,000
29 Subsequent Years Monitoring		174,000
Containment Structure Inspection and Maintenance		30,000
Estimated Post Closure Costs		$224,000
Adjustments for Inflation 1985 through 1988		
Adjusted Closure Costs		$288,200
Adjusted Post Closure Costs		$256,200

AF 31527



LEGEND

—x— FENCE

PAVEMENT

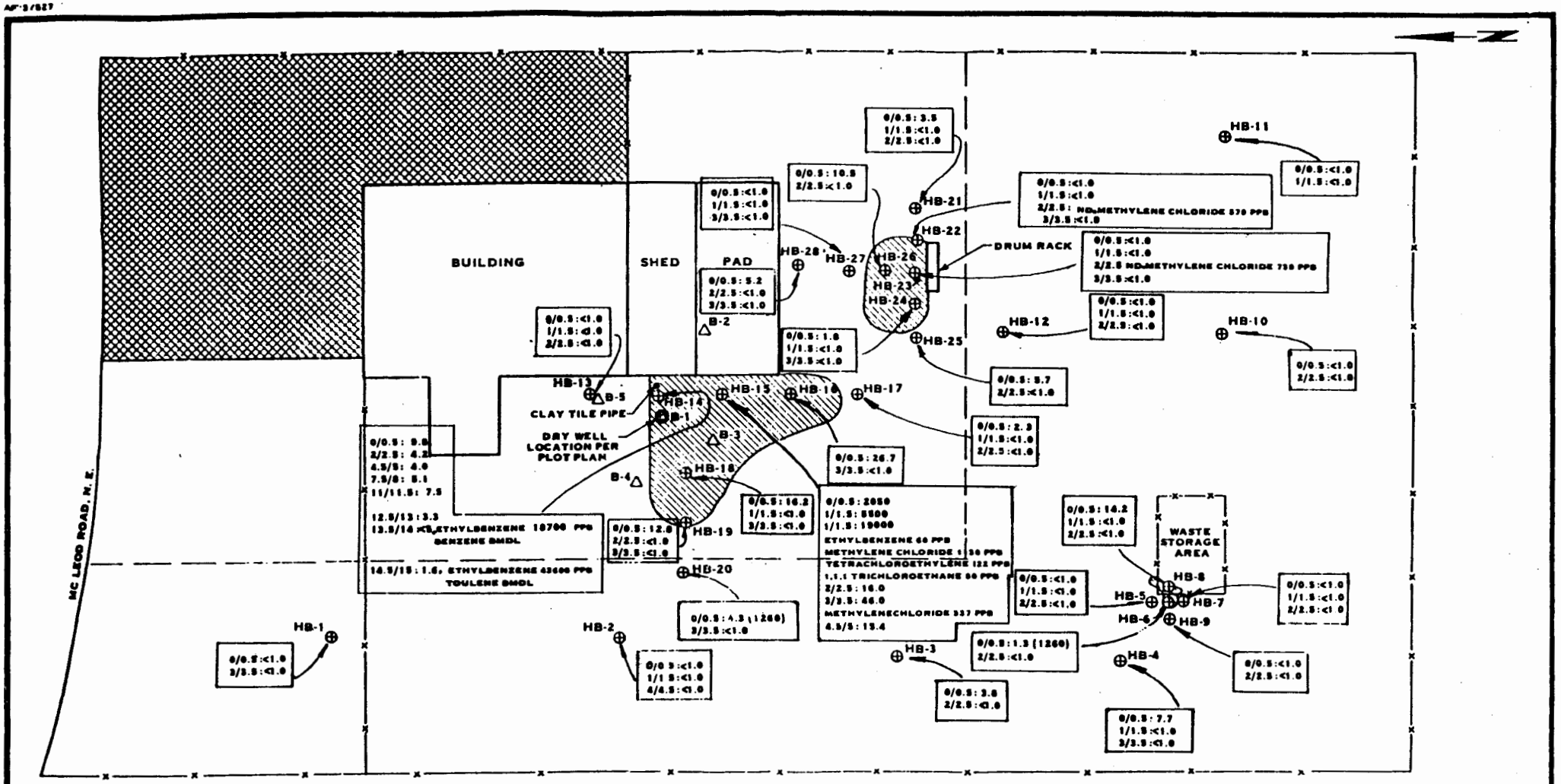
GENERAL ELECTRIC COMPANY
APPARATUS SERVICE SHOP
ALBUQUERQUE, NEW MEXICO

LAW ENGINEERING
TESTING COMPANY
MARIETTA, GEORGIA

SITE PLAN

JOB NO. ME4342

FIGURE 2



BORING NUMBER — HAND AUGER BORING LOCATION

HB-16 — 0/0.5:26.7 / 3/3.5:<1.0 — SAMPLE DEPTH, (FROM 0 FT. TO 0.5 FT.) — PCB CONCENTRATION, PPM AROCLOR 1254 UNLESS OTHERWISE NOTED

△ PROPOSED PHASE I SOIL BORING

—x— FENCE

— — — PREVIOUS PROPERTY BOUNDARY

GROUND SURFACE STAINING

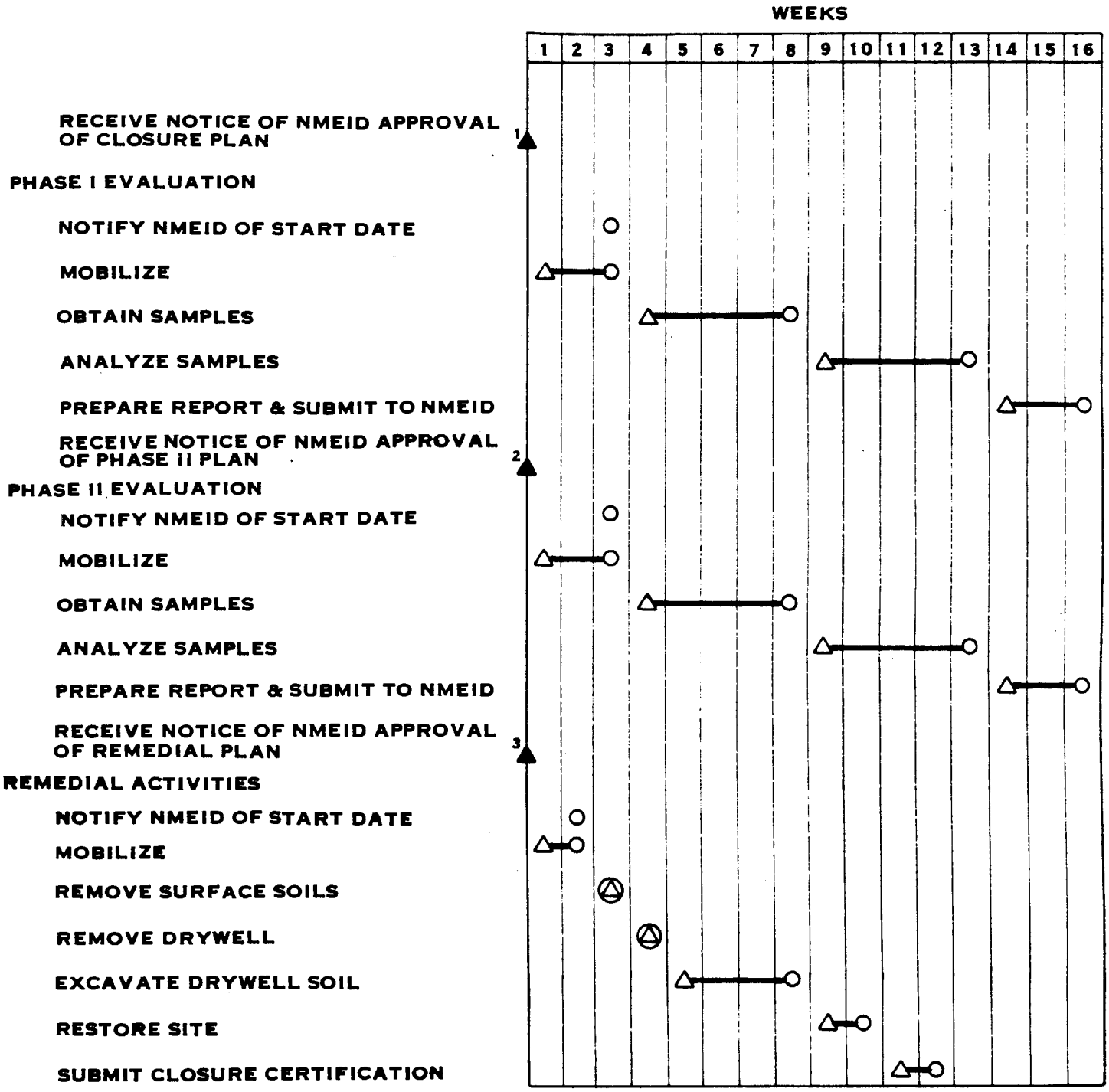
PAVEMENT

GENERAL ELECTRIC COMPANY
APPARATUS SERVICE SHOP
ALBUQUERQUE, NEW MEXICO

LAW ENGINEERING TESTING COMPANY
MARIETTA, GEORGIA

RESULTS OF CHEMICAL ANALYSES ON SOIL SAMPLES.
(REVISED JUNE 85)

GE ALBUQUERQUE SERVICE SHOP CLOSURE SCHEDULE



[1] ▲ CLOSURE PLAN WILL HAVE BEEN PREVIOUSLY SUBMITTED TO NMEID FOR APPROVAL

[2] ▲ PHASE I REPORT, INCLUDING PHASE II PLAN, WILL HAVE BEEN PREVIOUSLY SUBMITTED TO NMEID FOR APPROVAL

[3] ▲ PHASE II REPORT, INCLUDING REMEDIAL PLAN, WILL HAVE BEEN PREVIOUSLY SUBMITTED TO NMEID FOR APPROVAL

FIGURE 4

APPENDICES

CLEANING AND DECONTAMINATION PROTOCOL

DRY WELL EXPLORATION

GE SERVICE SHOP

ALBUQUERQUE, NEW MEXICO

Stage of Work	Item	Procedure
1. Before starting drilling and after completion of each boring	1. Drill Rig	1. Steam clean to remove soil and debris
2. Before starting drilling and after completion of each boring	2. Sampling and drilling tools and equipment	1. Brush to remove soil and debris. Includes running brushes throu drill rods and hollow stem augers 2. Steam with cleaning solution such as LiquiNox
3. After each sample is taken	3. Split Spoon Sampler	3. Steam with tap water 4. Rinse with acetone, hexane or methanol; sprayed or poured on 5. Rinse with distilled water, sprayed or poured on.

1. Cleaning residue to be retained and placed in drums.
2. Cleaned items are to be stored on visqueen until use.

CHAIN OF CUSTODY RECORD

SITE IDENTIFICATION

SITE NAME GE Apparatus Service Shop

ADDRESS 4420 McLeod Rd., N.E., Albuquerque, N.M.

EPA I.D. # NMD 047140256

RCRA PROGRAM FACILITY CODE

IDENTIFICATION OF SAMPLER

NAME (print) Wendell K. Rodgers

SIGNATURE Wendell K. Rodgers

COMPANY Law Environmental Services

ADDRESS 2749 Delk Road, S.E.

Marietta, Georgia 30067

SAMPLE IDENTIFICATION

QUARTER 1 2 3 (4) YEAR 1984

WELL NUMBER HB-2

SAMPLE NUMBER 1A, 1B, (2A) 2B, 3A, 3B, 4A, 4B, (5A) 5B

to S.W. Labs

SAMPLE MOVEMENT RECORD

DATE	RELINQUISHED BY (SIGNATURE)	RECEIVED (SIGNATURE)	NAME (PRINT) OR WAYBILL NUMBER	COMPANY OR CARRIER NAME AND ADDRESS	COMMENTS
12/12		WKR			Sampled
12/18/84	WKR			Federal Express	2A, 5A for PCB
1/4/85	MR Neel			Federal Express	1A for PCB at S.W. Labs.

Designation: D 421 – 58 (Reapproved 1978)[1]

Standard Method for DRY PREPARATION OF SOIL SAMPLES FOR PARTICLE-SIZE ANALYSIS AND DETERMINATION OF SOIL CONSTANTS[1]

This standard is issued under the fixed designation D 421; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[1] NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the dry preparation of soil samples as received from the field for particle-size analysis and the determination of the soil constants.

2. Applicable Document

2.1 *ASTM Standard:*

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[2]

3. Apparatus

3.1 *Balance*—A balance sensitive to 0.1 g.

3.2 *Mortar*—A mortar and rubber-covered pestle suitable for breaking up the aggregations of soil particles.

3.3 *Sieves*—A series of sieves, of square mesh woven wire cloth, conforming to Specification E 11. The sieves required are as follows:

No. 4 (4.75-mm)
No. 10 (2.00-mm)
No. 40 (425-μm)

3.4 *Sampler*—A riffle sampler or sample splitter, for quartering the samples.

4. Sampling

4.1 Expose the soil sample as received from the field to the air at room temperature until dried thoroughly. Break up the aggregations thoroughly in the mortar with a rubber-covered pestle. Select a representative sample of the amount required to perform the desired tests by the method of quartering or by the use of a sampler. The amounts of material required to perform the individual tests are as follows:

4.1.1 *Particle-Size Analysis*—For the particle-size analysis, material passing a No. 10 (2.00-mm) sieve is required in amounts equal to 115 g of sandy soils and 65 g of either silt or clay soils.

4.1.2 *Tests for Soil Constants*—For the tests for soil constants, material passing the No. 40 (425-μm) sieve is required in total amount of 220 g, allocated as follows:

Test	Grams
Liquid limit	100
Plastic limit	15
Centrifuge moisture equivalent	10
Volumetric shrinkage	30
Check tests	65

5. Preparation of Test Sample

5.1 Select that portion of the air-dried sample selected for purpose of tests and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture. Separate the test sample by sieving with a No. 10 (2.00-mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with a rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Then separate the ground soil into two fractions by sieving with a No. 10 sieve.

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Sept. 22, 1958. Originally issued 1935. Replaces D 421 – 38.

[2] *Annual Book of ASTM Standards*, Vol 14.02.

5.2 Wash that fraction retained after the second sieving free of all fine material, dry, and weigh. Record this mass as the mass of coarse material. Sieve the coarse material after being washed and dried, on the No. 4 (4.75-mm) sieve and record the mass retained on the No. 4 sieve.

6. Test Sample for Particle-Size Analysis

6.1 Mix the fractions passing the No. 10 (2.00-mm) sieve in both sieving operations thoroughly together, and by the method of quartering or the use of a sampler, select a portion weighing approximately 115 g for sandy soils and approximately 65 g for silt and clay soil for particle-size analysis.

7. Test Sample for Soil Constants

7.1 Separate the remaining portion of the material passing the No. 10 (2.00-mm) sieve into two parts by means of a No. 40 (425-µm) sieve. Discard the fraction retained on the No. 40 sieve. Use the fraction passing the No. 40 sieve for the determination of the soil constants.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Designation: D 422 – 63 (Reapproved 1972)[ε1]

Standard Method for PARTICLE-SIZE ANALYSIS OF SOILS[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Method for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft^3/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

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[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-μm)
1½-in. (37.5-mm)	No. 40 (425-μm)
1-in. (25.0-mm)	No. 60 (250-μm)
¾-in. (19.0-mm)	No. 140 (106-μm)
⅜-in. (9.5-mm)	No. 200 (75-μm)
No. 4 (4.75-mm)	

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-μm)
¾-in. (19.0-mm)	No. 50 (300-μm)
⅜-in. (9.5-mm)	No. 100 (150-μm)
No. 4 (4.75-mm)	No. 200 (75-μm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Method D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Method D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Method D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cyclinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hy-

drometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/l). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. Accord-

ing to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)] \times L/T}$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(*1*) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
(*2*) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  (*a*) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  (*b*) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  (*c*) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
(*3*) Silt size, 0.074 to 0.005 mm ..... %
(*4*) Clay size, smaller than 0.005 mm ..... %
  Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	.....
2-in.	.....
1½-in.	.....
1-in.	.....
¾-in.	.....
⅜-in.	.....
No. 4 (4.75-mm)	.....
No. 10 (2.00-mm)	.....
No. 40 (425-μm)	.....
No. 200 (75-μm)	.....
HYDROMETER ANALYSIS	
0.074 mm	.....
0.005 mm	.....
0.001 mm	.....

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

TABLE 1 Values of Correction Factor, a, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5

TABLE 2 Continued

Hydrometer 151H		Hydrometer 152 H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation:

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_B/A)]$$

where:

L = effective depth, cm,
L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,
L_2 = overall length of the hydrometer bulb, cm,
V_B = volume of hydrometer bulb, cm^3, and
A = cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

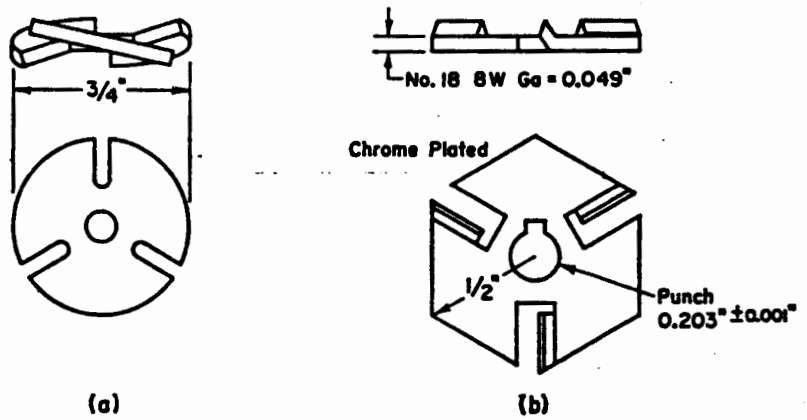
For both hydrometers, 151H and 152H:
L_2 = 14.0 cm
V_B = 67.0 cm^3
A = 27.8 cm^2

For hydrometer 151H:
L_1 = 10.5 cm for a reading of 1.000
= 2.3 cm for a reading of 1.031

For hydrometer 152H:
L_1 = 10.5 cm for a reading of 0 g/litre
= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

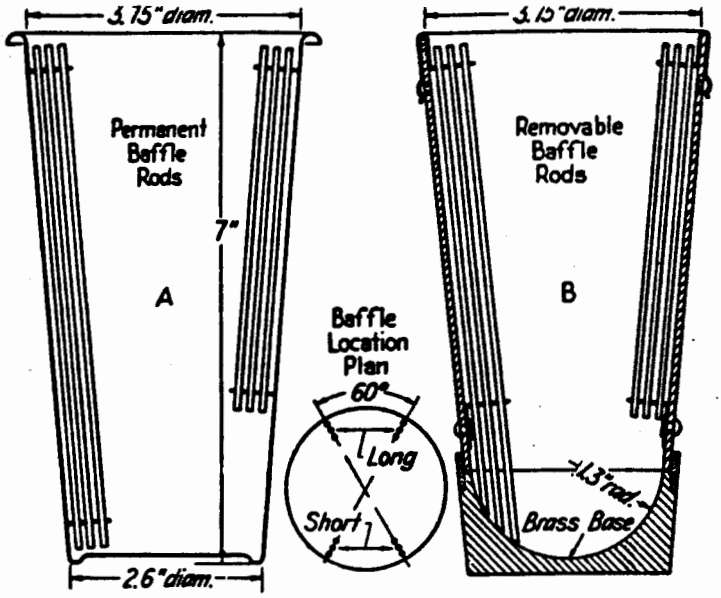
Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149



Metric Equivalents

in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



Metric Equivalents

in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

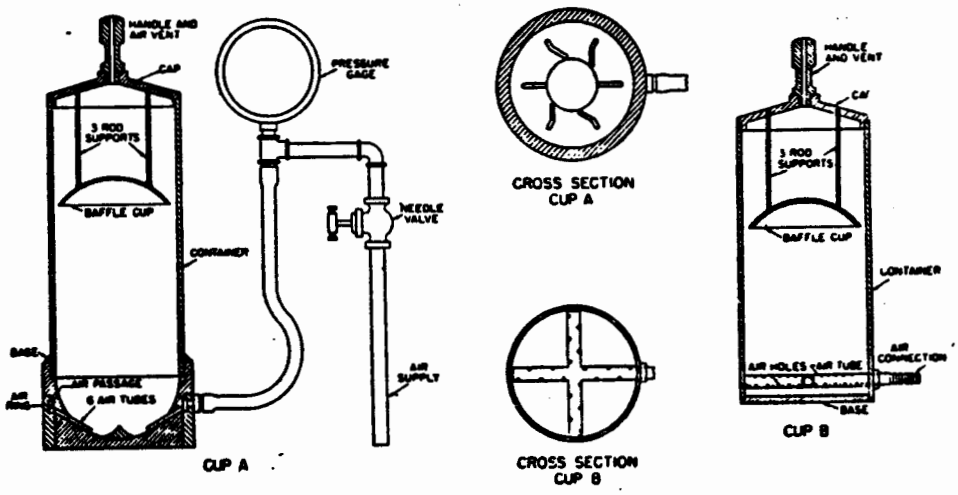
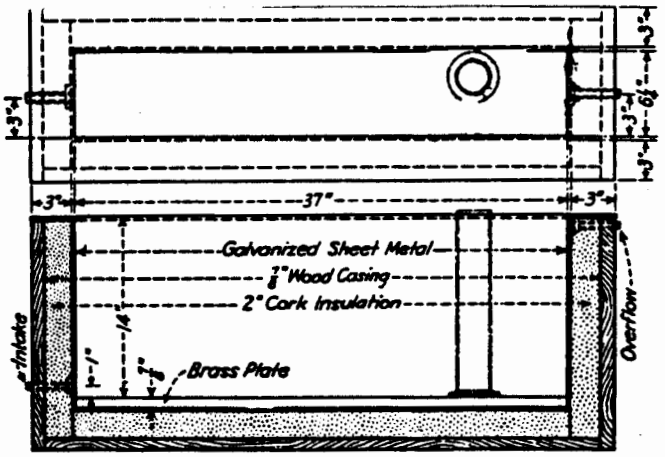


FIG. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents

in.	⅞	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

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6. Drilling Procedure

6.1 The boring shall be advanced incrementally to permit intermittent or continuous sampling. Test intervals and locations are normally stipulated by the project engineer or geologist. Typically, the intervals selected are 5 ft (1.5 mm) or less in homogeneous strata with test and sampling locations at every change of strata.

6.2 Any drilling procedure that provides a suitably clean and stable hole before insertion of the sampler and assures that the penetration test is performed on essentially undisturbed soil shall be acceptable. Each of the following procedures have proven to be acceptable for some subsurface conditions. The subsurface conditions anticipated should be considered when selecting the drilling method to be used.

6.2.1 Open-hole rotary drilling method.

6.2.2 Continuous flight hollow-stem auger method.

6.2.3 Wash boring method.

6.2.4 Continuous flight solid auger method.

6.3 Several drilling methods produce unacceptable borings. The process of jetting through an open tube sampler and then sampling when the desired depth is reached shall not be permitted. The continuous flight solid auger method shall not be used for advancing the boring below a water table or below the upper confining bed of a confined non-cohesive stratum that is under artesian pressure. Casing may not be advanced below the sampling elevation prior to sampling. Advancing a boring with bottom discharge bits is not permissible. It is not permissible to advance the boring for subsequent insertion of the sampler solely by means of previous sampling with the SPT sampler.

6.4 The drilling fluid level within the boring or hollow-stem augers shall be maintained at or above the in situ groundwater level at all times during drilling, removal of drill rods, and sampling.

7. Sampling and Testing Procedure

7.1 After the boring has been advanced to the desired sampling elevation and excessive cuttings have been removed, prepare for the test with the following sequence of operations.

7.1.1 Attach the split-barrel sampler to the sampling rods and lower into the borehole. Do not allow the sampler to drop onto the soil to be sampled.

7.1.2 Position the hammer above and attach the anvil to the top of the sampling rods. This may be done before the sampling rods and sampler are lowered into the borehole.

7.1.3 Rest the dead weight of the sampler, rods, anvil, and drive weight on the bottom of the boring and apply a seating blow. If excessive cuttings are encountered at the bottom of the boring, remove the sampler and sampling rods from the boring and remove the cuttings.

7.1.4 Mark the drill rods in three successive 6-in. (0.15-m) increments so that the advance of the sampler under the impact of the hammer can be easily observed for each 6-in. (0.15-m) increment.

7.2 Drive the sampler with blows from the 140-lb (63.5-kg) hammer and count the number of blows applied in each 6-in. (0.15-m) increment until one of the following occurs:

7.2.1 A total of 50 blows have been applied during any one of the three 6-in. (0.15-m) increments described in 7.1.4.

7.2.2 A total of 100 blows have been applied.

7.2.3 There is no observed advance of the sampler during the application of 10 successive blows of the hammer.

7.2.4 The sampler is advanced the complete 18 in. (0.45 m) without the limiting blow counts occurring as described in 7.2.1, 7.2.2, or 7.2.3.

7.3 Record the number of blows required to effect each 6 in. (0.15 m) of penetration or fraction thereof. The first 6 in. is considered to be a seating drive. The sum of the number of blows required for the second and third 6 in. of penetration is termed the "standard penetration resistance", or the "*N*-value". If the sampler is driven less than 18 in. (0.45 m), as permitted in 7.2.1, 7.2.2, or 7.2.3, the number of blows per each complete 6-in. (0.15-m) increment and per each partial increment shall be recorded on the boring log. For partial increments, the depth of penetration shall be reported to the nearest 1 in. (25 mm), in addition to the number of blows. If the sampler advances below the bottom of the boring under the static weight of the drill rods or the weight of the drill rods plus the static weight of the hammer, this information should be noted on the boring log.

7.4 The raising and dropping of the 140-lb

(63.5-kg) hammer shall be accomplished using either of the following two methods:

7.4.1 By using a trip, automatic, or semi-automatic hammer drop system which lifts the 140-lb (63.5-kg) hammer and allows it to drop 30 ± 1.0 in. (0.76 m ± 25 mm) unimpeded.

7.4.2 By using a cathead to pull a rope attached to the hammer. When the cathead and rope method is used the system and operation shall conform to the following:

7.4.2.1 The cathead shall be essentially free of rust, oil, or grease and have a diameter in the range of 6 to 10 in. (150 to 250 mm).

7.4.2.2 The cathead should be operated at a minimum speed of rotation of 100 RPM, or the approximate speed of rotation shall be reported on the boring log.

7.4.2.3 No more than 2¼ rope turns on the cathead may be used during the performance of the penetration test, as shown in Fig. 1.

NOTE 4—The operator should generally use either 1¾ or 2¼ rope turns, depending upon whether or not the rope comes off the top (1¾ turns) or the bottom (2¼ turns) of the cathead. It is generally known and accepted that 2¾ or more rope turns considerably impedes the fall of the hammer and should not be used to perform the test. The cathead rope should be maintained in a relatively dry, clean, and unfrayed condition.

7.4.2.4 For each hammer blow, a 30-in. (0.76-m) lift and drop shall be employed by the operator. The operation of pulling and throwing the rope shall be performed rhythmically without holding the rope at the top of the stroke.

7.5 Bring the sampler to the surface and open. Record the percent recovery or the length of sample recovered. Describe the soil samples recovered as to composition, color, stratification, and condition, then place one or more representative portions of the sample into sealable moisture-proof containers (jars) without ramming or distorting any apparent stratification. Seal each container to prevent evaporation of soil moisture. Affix labels to the containers bearing job designation, boring number, sample depth, and the blow count per 6-in. (0.15-m) increment. Protect the samples against extreme temperature changes. If there is a soil change within the sampler, make a jar for each stratum and note its location in the sampler barrel.

8. Report

8.1 Drilling information shall be recorded in the field and shall include the following:

8.1.1 Name and location of job,

8.1.2 Names of crew,

8.1.3 Type and make of drilling machine,

8.1.4 Weather conditions,

8.1.5 Date and time of start and finish of boring,

8.1.6 Boring number and location (station and coordinates, if available and applicable),

8.1.7 Surface elevation, if available,

8.1.8 Method of advancing and cleaning the boring,

8.1.9 Method of keeping boring open,

8.1.10 Depth of water surface and drilling depth at the time of a noted loss of drilling fluid, and time and date when reading or notation was made,

8.1.11 Location of strata changes,

8.1.12 Size of casing, depth of cased portion of boring,

8.1.13 Equipment and method of driving sampler,

8.1.14 Type sampler and length and inside diameter of barrel (note use of liners),

8.1.15 Size, type, and section length of the sampling rods, and

8.1.16 Remarks.

8.2 Data obtained for each sample shall be recorded in the field and shall include the following:

8.2.1 Sample depth and, if utilized, the sample number,

8.2.2 Description of soil,

8.2.3 Strata changes within sample,

8.2.4 Sampler penetration and recovery lengths, and

8.2.5 Number of blows per 6-in. (0.15-m) or partial increment.

9. Precision and Bias

9.1 Variations in *N*-values of 100 % or more have been observed when using different standard penetration test apparatus and drillers for adjacent borings in the same soil formation. Current opinion, based on field experience, indicates that when using the same apparatus and driller, *N*-values in the same soil can be reproduced with a coefficient of variation of about 10 %.

9.2 The use of faulty equipment, such as an extremely massive or damaged anvil, a rusty cathead, a low speed cathead, an old, oily rope, or massive or poorly lubricated rope sheaves can significantly contribute to differences in *N*-values

10. Precision and Accuracy

10.1 Requirements for the precision and accuracy of this test method have not yet been developed.

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METHOD 5030

PURGE-AND-TRAP METHOD

1.0 Scope and Application

1.1 Method 5030 is used to determine the concentration of volatile organic compounds in a variety of liquid and solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, groundwater, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method also depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

1.4 Method 5030 is based upon a purge-and-trap, gas chromatographic procedure.

1.5 This method is recommended for use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs and skilled in the interpretation of chromatograms.

2.0 Summary of Method

2.1 A portion of solid waste is dispersed in polyethylene glycol (PEG) or distilled-in-glass methanol to dissolve the volatile organic constituents. A portion of the PEG or methanol solution is combined with water in a specially designed purging chamber. For liquid and some semiliquid samples, PEG or methanolic extraction will not be necessary. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. (SPECIAL NOTE: For Methods 8020 and 8030, drying of the trap for 4 min under helium flow is required. See Figure 5 for configuration.) The gas chromatographic column is heated to elute the components which are detected by the appropriate detector (Methods 8010, 8020, 8030).

3.0 Interferences

3.1 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.3.

3.2 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water (PEG or methanol solution) to check for cross contamination. After each use, the purging chamber is cleaned as described in Section 7.12. The trap and other parts of the system are also subject to contamination; therefore, frequent additional bakeout and purging or the entire system may be required.

4.0 Apparatus and Materials

4.1 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are commercially available.

4.1.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.1.2 The sorbent trap consists of a 1/8-in. O.D. (0.105-in. I.D.) x 25-cm-long stainless steel tube packed with the appropriate absorbents as described in Table 1 (see Figures 2 and 3).

4.1.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec.

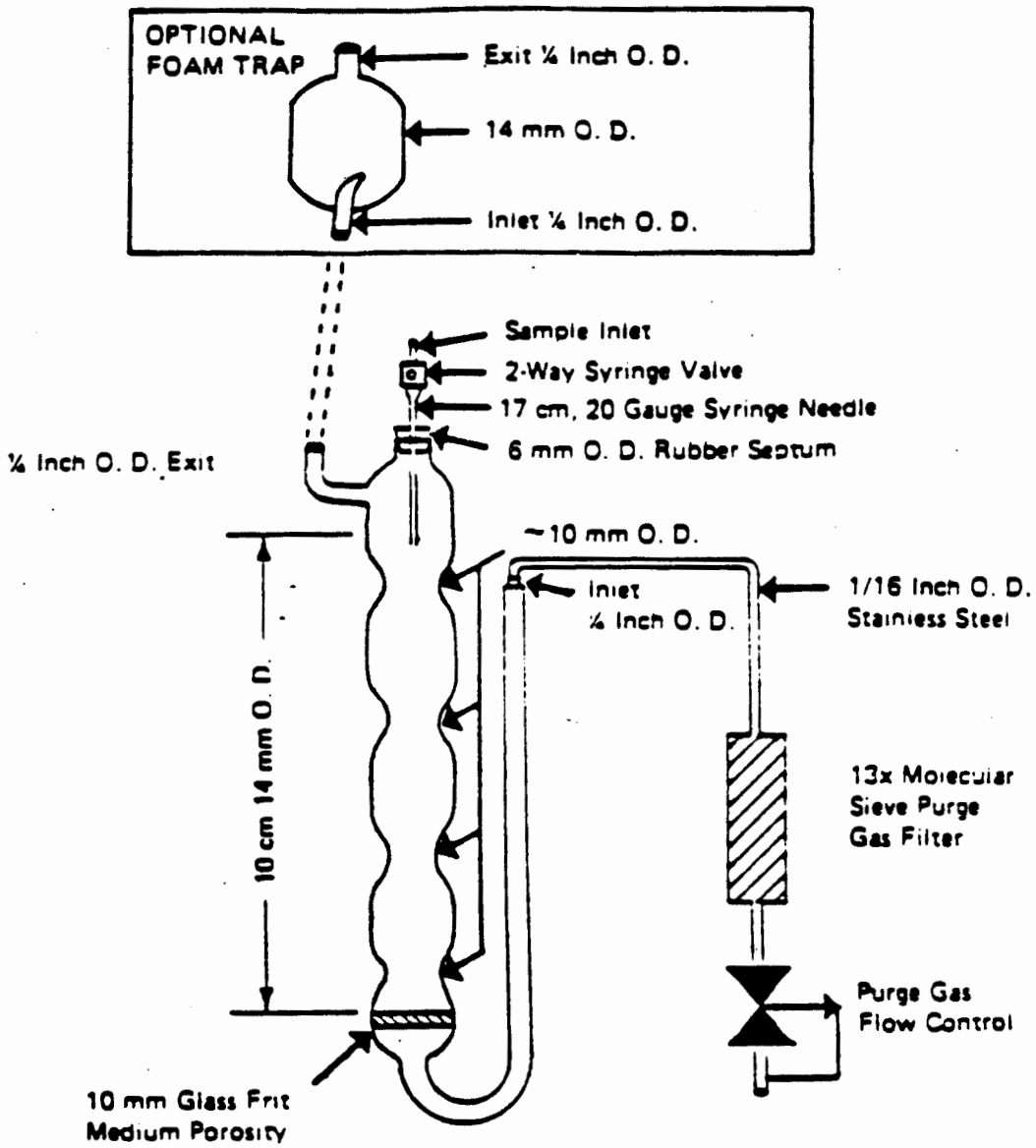

Figure 1. Purging chamber.

TABLE 1. PURGE-AND-TRAP PARAMETERS

	Analysis method[a]			
	8010	8015	8020	8030
Purge Gas	Nitrogen or Helium	Helium	Nitrogen or Helium	Helium
Purge Gas Flow Rate (ml/min)	40	40	40	20 ± 1
Purge Time (min)	11.0	12.0	12.0	30.0
Purge Temperature	Ambient	Ambient	Ambient	85° C
Desorb Temperature (°C)	180°	180°	180°	100°
Sorbents to be used in packing tube	A	B	B	B

[a]Measurement method to be employed for identification and quantification.

KEY: A = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

Silica gel, 35/60 mesh Davison grade-15 or equivalent.

Coconut charcoal, 6/10 mesh, Barnaby Chaney C.A. - 580-26 lot #M-2649 or equivalent.

Refer to Figure 2 for column packing.

B = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

Refer to Figure 3 for column packing.

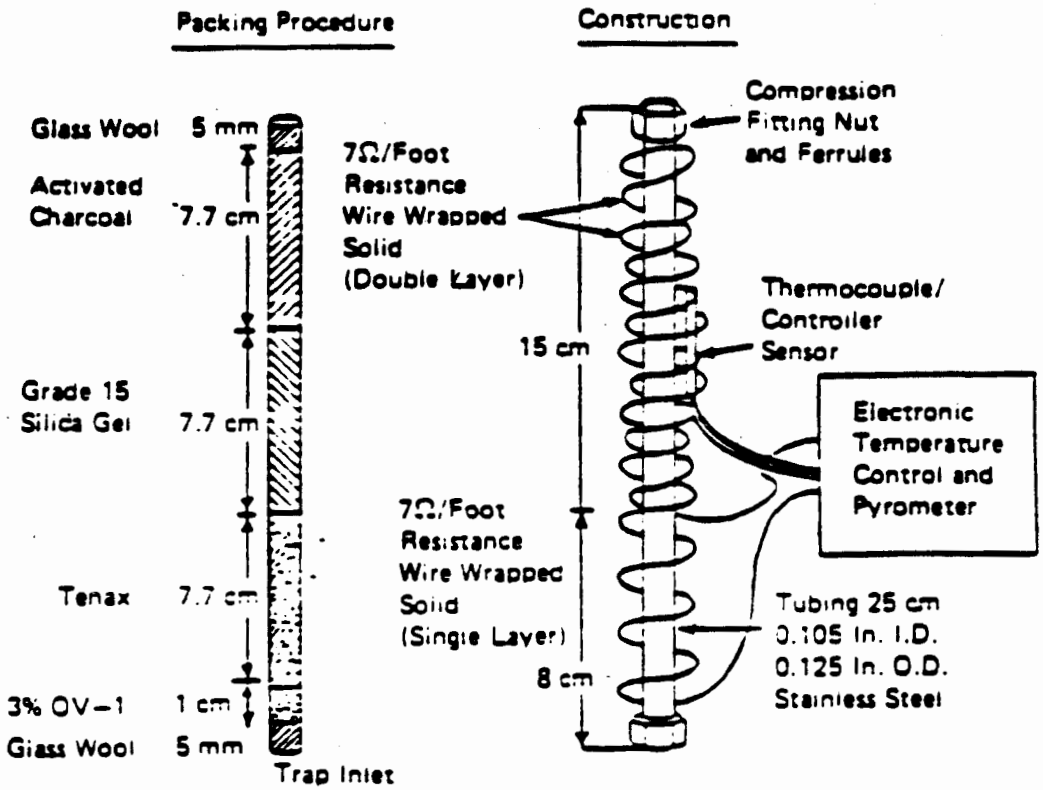

Figure 2. Trap packings and construction for Method 8010.

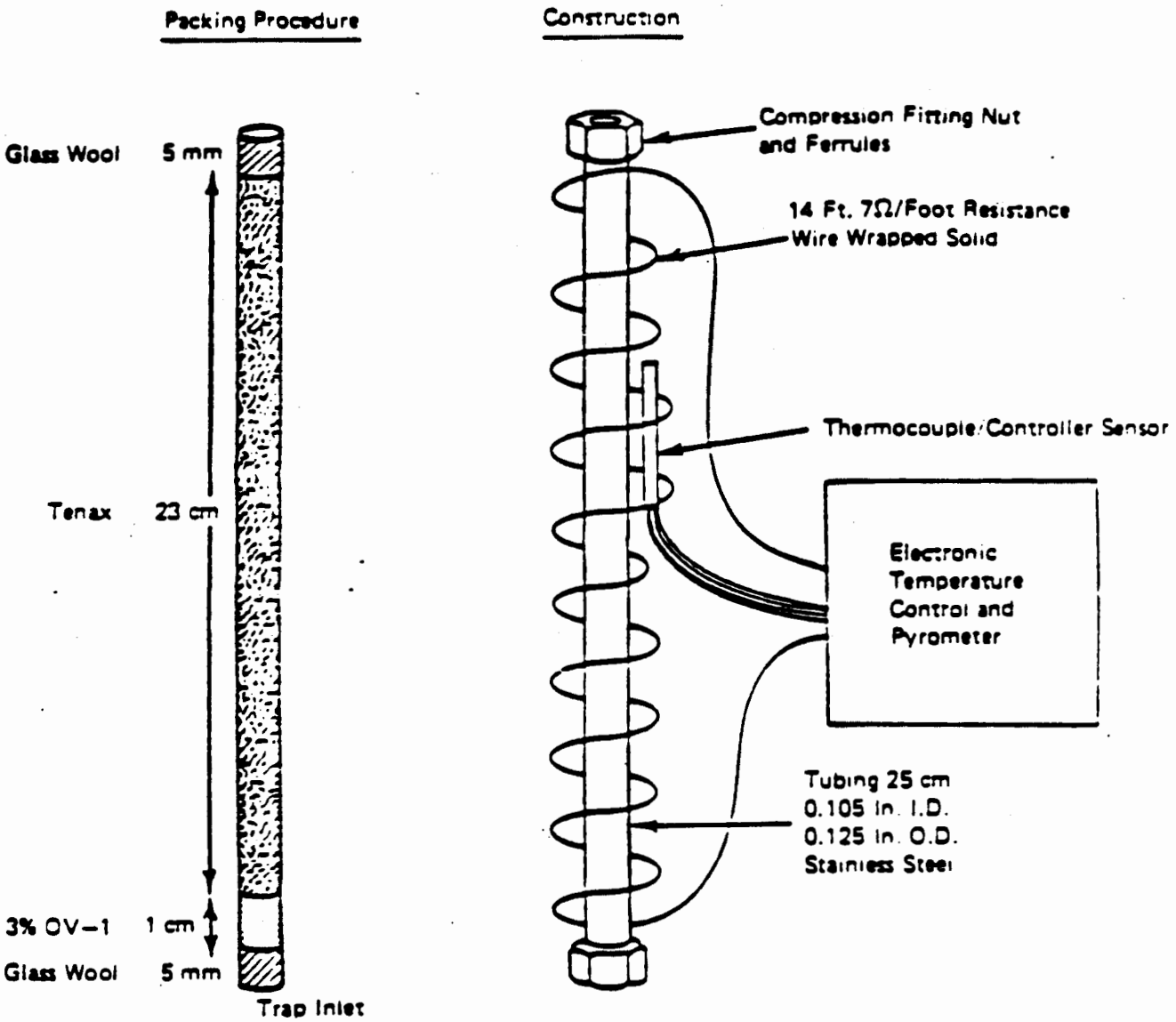

Figure 3. Trap packing and construction for Methods 8020 and 8030.

4.1.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 4 through 6.

4.2 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.3 Micro syringes: 10 µl, 25 µl, 100 µl, 250 µl, 500 µl, and 1,000 µl. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.4 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation (Kimble #45212 or equivalent).

4.5 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.6 Syringe valve: 2-way, with Luer ends (2 each; Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting or equivalent).

4.7 Syringe: 5-ml, gas-tight with shutoff valve.

4.8 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.9 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.10 Rotary evaporator: Equipped with Teflon-coated seals (Buchi Rotavapor R-110 or equivalent).

4.11 Vacuum pump: Mechanical, two-stage.

5.0 Reagents

5.1 Trap materials (see Table 1 and Figures 2 and 3 for configuration).

5.1.1 2,6-Diphenylene oxide polymer: 60/80 mesh Tenax, chromatographic grade or equivalent.

5.1.2 Methyl silicone packing: 3% OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.1.3 Silica gel, Davison Chemical (35/60 mesh), grade 15 or equivalent.

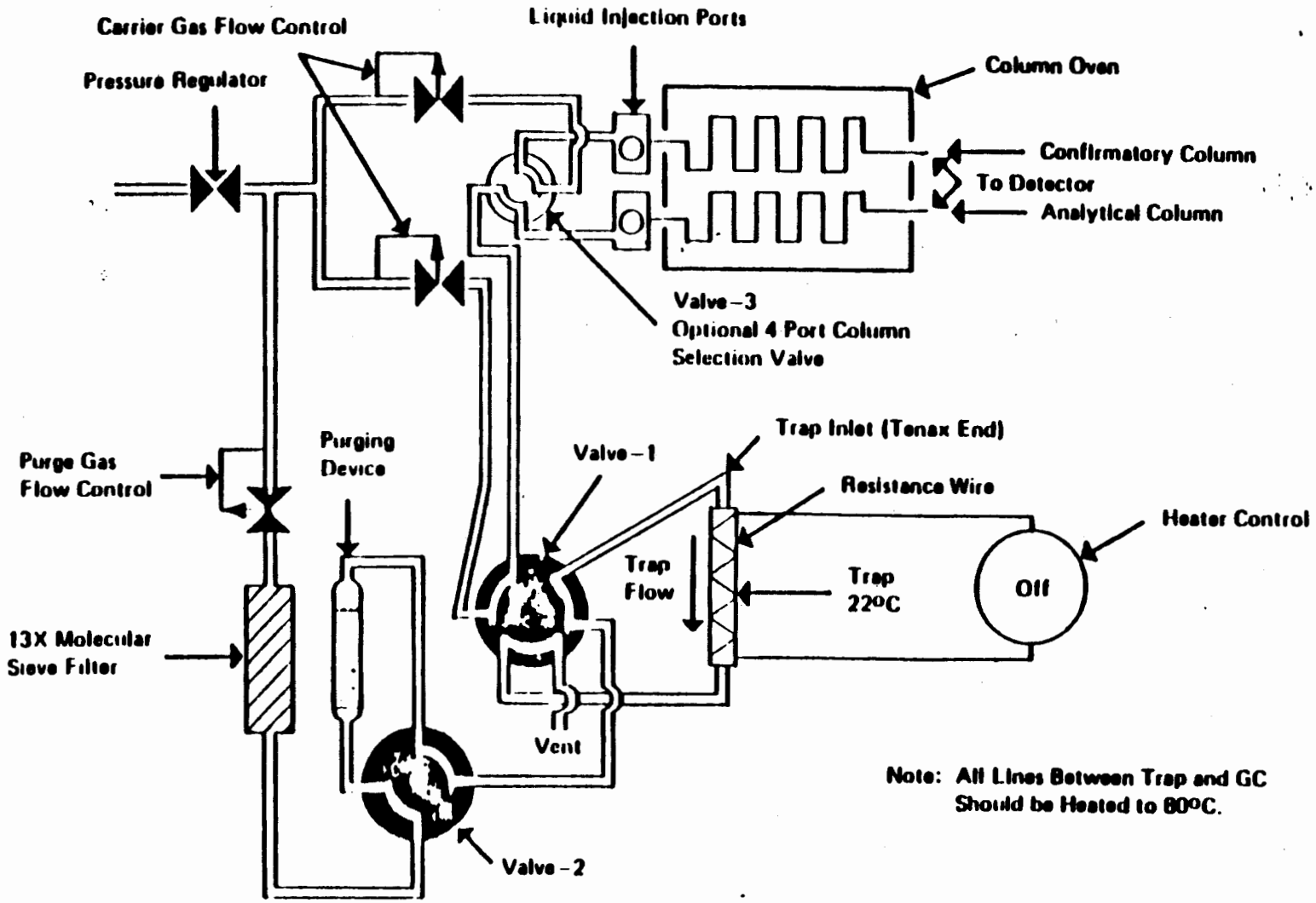

Figure 4. Purge and trap system, purge sorb mode, for methods 8010, 8020 and 8030.

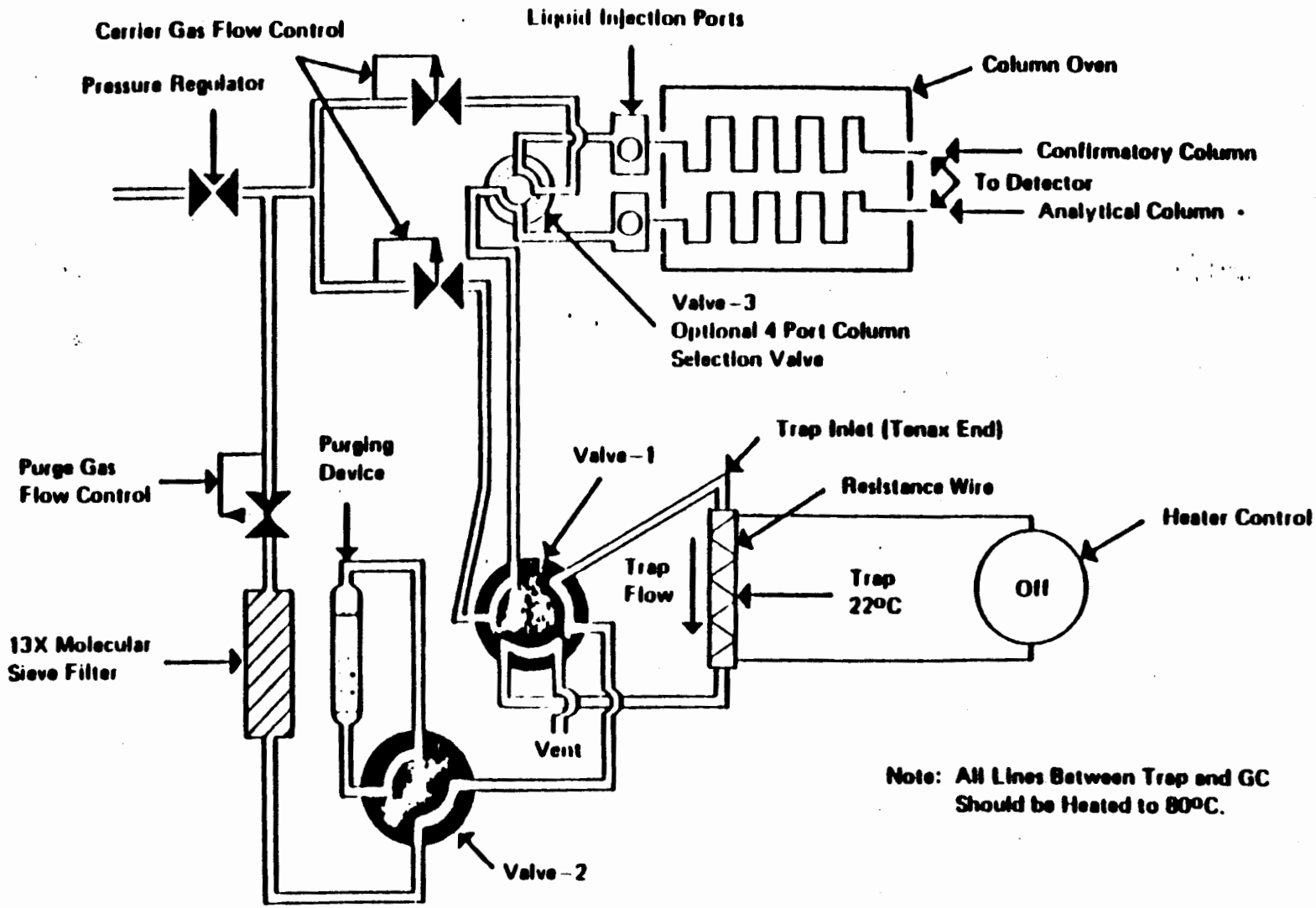

Figure 5. Purge and trap system, trap dry mode, for Methods 8020 and 8030.

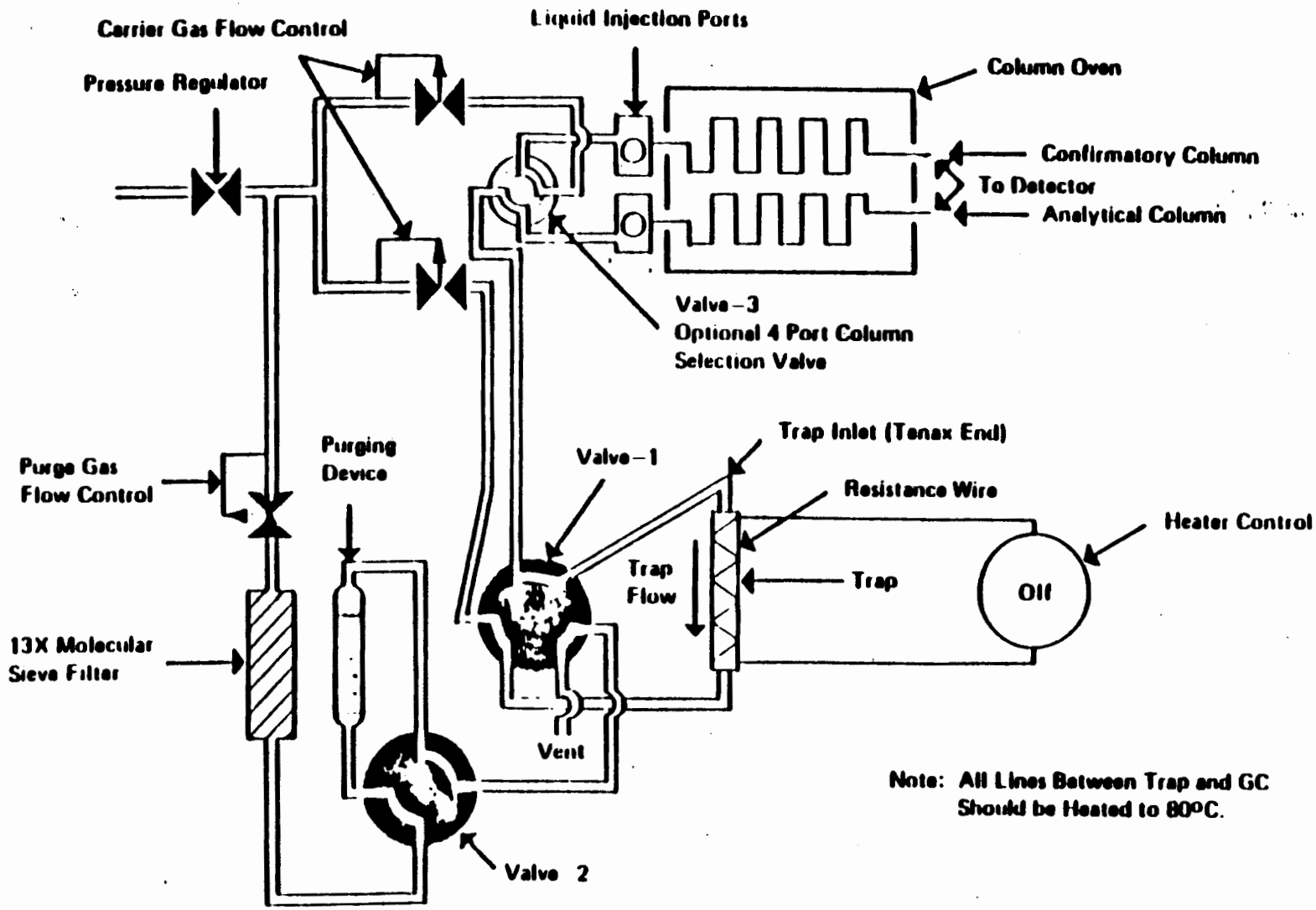

Figure 6. Purge and trap system, desorb mode, for Methods 8010, 8020 and 8030.

5.2 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.2.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.3 Reagent PEG (polyethylene glycol; for solid samples): Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest. Methanol which has been distilled in glass can be used as a substitute for PEG.

5.3.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.3.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Method 8010, 8020, or 8030 for pertinent information.

7.0 Procedures

7.1 Assemble the purge-and-trap device (see Figures 4 through 6). Purge parameters to be used depend on the compounds being analyzed for; see Table 1. Pack the trap as shown in Figure 2 or 3 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the trap for 10 min by backflushing at 180° C.

7.2 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20-25° C.

7.3 Adjust the purge gas (nitrogen or helium) flow rate according to Table 1.

7.4 Operate the gas chromatograph using the conditions described in the appropriate method, 8010, 8020, or 8030.

7.5 Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

7.6 Remove the plunger from a 5-ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. (NOTE: For pastes it may be necessary to dilute the sample by adding a nonvolatile solvent to the sample. In such cases diluting can be performed in the purging device.)

7.7 PEG extraction procedure for solids (methanol which has been distilled in glass can be used as a substitute for PEG). Sample aliquots for extraction should be transferred as quickly as possible to minimize loss of volatiles from the sample.

7.7.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent PEG. Weigh the capped centrifuge tube and PEG on an analytical balance.

7.7.2 Using an appropriate implement, transfer approximately 2 g of sample to the PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the PEG as quickly as possible. Take care not to touch the sample-transfer implement to the PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.7.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.7.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.7.5 Add an aliquot of the sample extract to 5 ml reagent water.

7.8 Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the liquid samples for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.

7.9 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber. Close both valves and purge the sample for the time specified in Table 1. If Method 8020 will be used for analysis of the sample, dry the trap by maintaining a flow rate of 40 ml/min dry purge for 4 min.

7.10 Attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to the backflush temperature indicated in Table 1, while backflushing the trap with an inert carrier gas at 20 to 60 ml/min for 4 min. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30° C (or subambient, if problems persist) instead of the initial program temperature of 45° or 50° C.

7.11 Return the purge trap device to the purge mode.

7.12 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105° C.

7.13 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.14 The analysis of blanks is most important in the purge-and-trap technique since the purging device and the trap can become contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water. Blanks should be sealed, stored at 4° C, and analyzed with each group of samples.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.

2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.

3. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

4. Ligon, W.V. and H. Grade. 1981. Poly(ethylene glycol) as a diluent for preparation of standards for volatile organics in water. Anal. Chem. 53:920-921.

METHOD 3540

SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

METHOD 3050

ACID DIGESTION OF SLUDGES

1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

Antimony	Lead
Arsenic	Nickel
Barium	Selenium
Beryllium	Silver
Cadmium	Thallium
Chromium	Zinc
Copper	

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Tl.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers.

4.2 Watch glasses.

4.3 Drying ovens that can be maintained at 30° C.

4.4 Thermometer that covers range of 0° to 200° C.

4.5 Whatman No. 42 filter paper or equivalent.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Weigh and transfer to a 125-ml conical Phillips' beaker a 1.0-g portion of sample which has been dried at 60° C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample at 95° C and reflux for 10 min. Allow the sample to cool, add 5 ml of conc. HNO_3, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2.)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 0.5% (v/v) HNO_3 and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume, add any required reagent or matrix modifier, and analyze by method of standard additions.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

METHOD 8240

GC/MS METHOD FOR VOLATILE ORGANICS

1.0 Scope and Application

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 The detection limit of Method 8240 for an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples containing more than 1 mg/g of total volatile material, the detection limit is proportionately higher.

1.3 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 Summary of Method

2.1 The volatile compounds are introduced to the gas chromatograph by direct injection, the Headspace Method (Method 5020), or the Purge-and-Trap Method (Method 5030). Method 5030 should be used for groundwater analysis. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample can be dispersed in methanol or polyethylene glycol (PEG) to dissolve the volatile organic constituents. A portion of the methanolic or PEG solution is combined with water in a specially designed purging chamber. An inert gas is then bubbled through the solution at ambient temperature and the volatile comnponents are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

2.3 An aliquot of each sample must be spiked with an appropriate standard to determine percent recovery and detection limits for that sample.

2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1[a]	Method detection limit (µg/l)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

[a]Column conditions: Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

3.0 Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the particular waste or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences under the conditions of the analysis by running method blanks. Method blanks are run by analyzing organic-free water in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce cross contamination, the purging device and sample syringe should be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.2.

4.0 Apparatus and Materials

4.1 Sampling equipment

4.1.1 Vial: 25-ml capacity or larger, equipped with a screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for 1 hr at 105° C before use.

4.1.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105° C for 1 hr before use.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

4.2.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

4.3 Gas chromatograph/mass spectrometer system

4.3.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carbopack B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

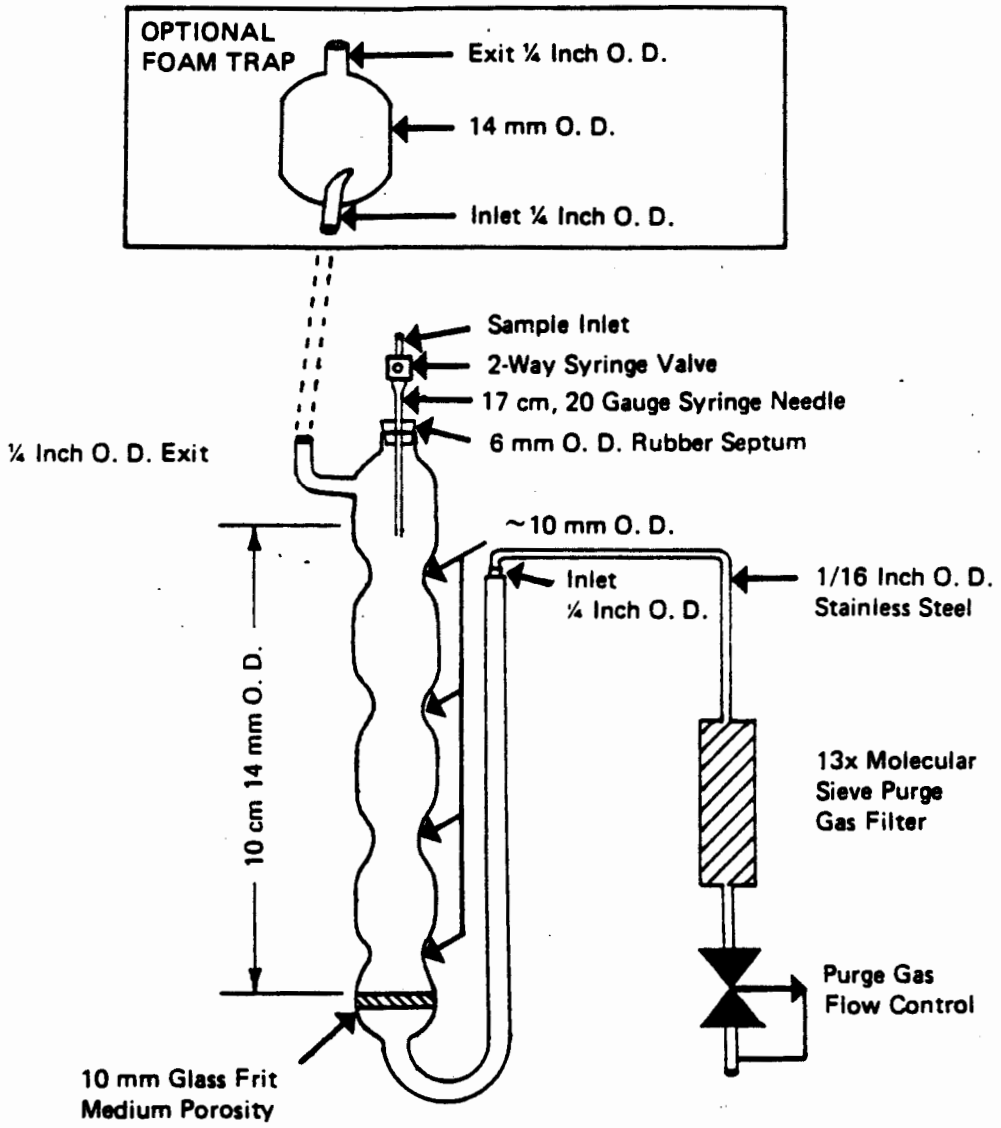

Figure 1. Purging chamber.

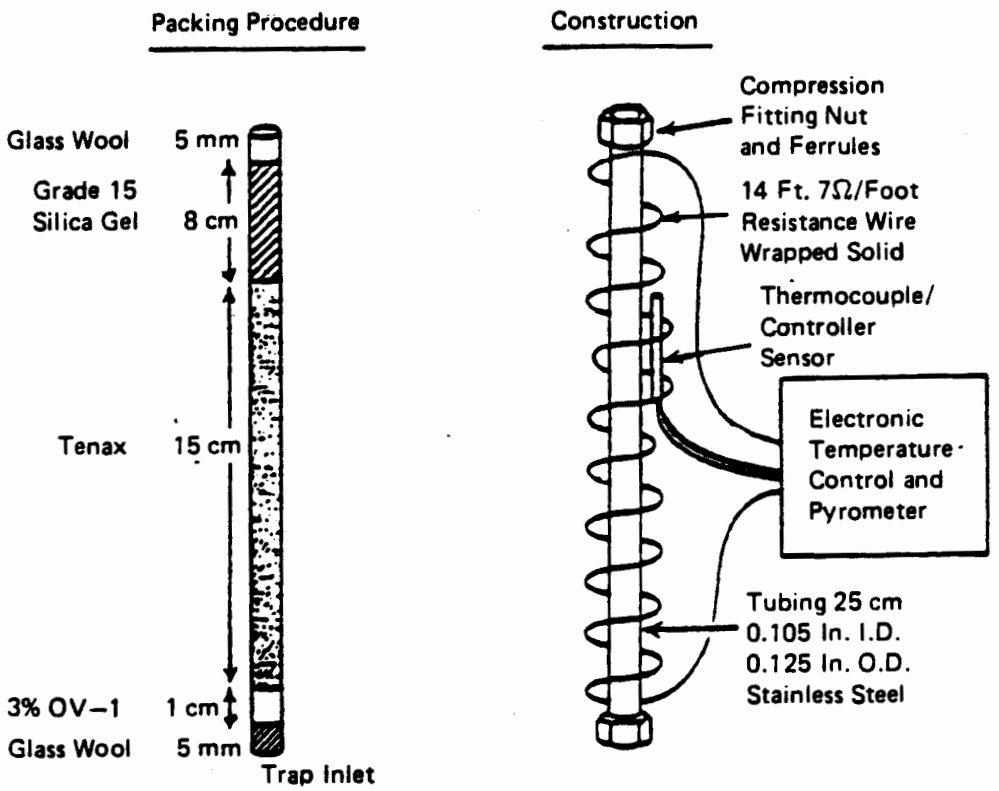

Figure 2. Trap packings and construction to include desorb capability.

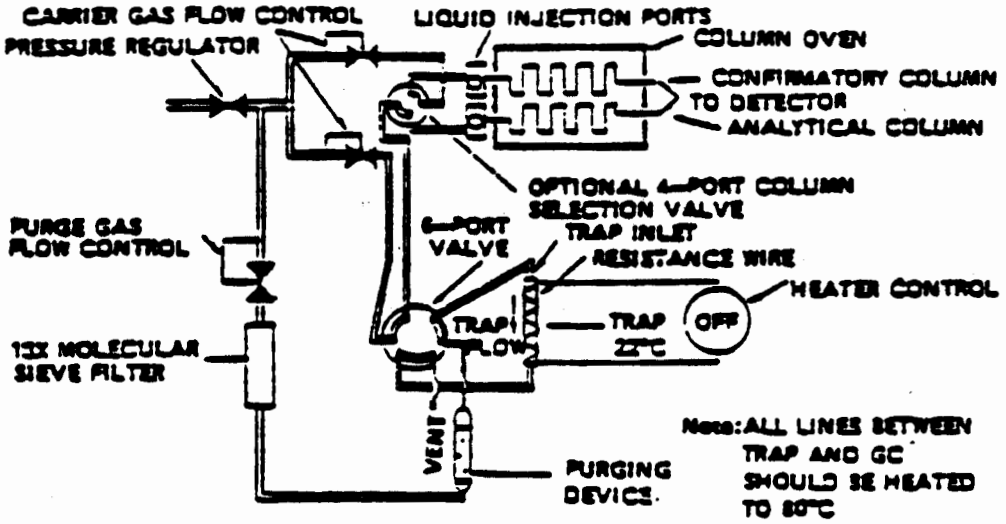

FIGURE 3. Schematic of purge and trap device — purge mode

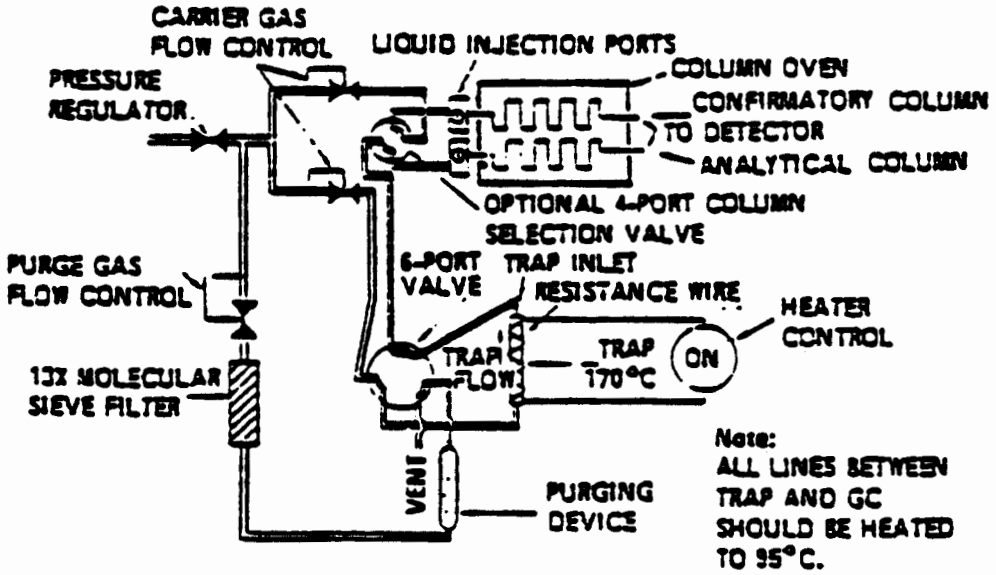

Figure 4. Schematic of purge and trap device - desorb mode

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific 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 abundance in any EICP between specified time or scan number limits. Hardware and software must be available to transform the data into a compatible format. These generally consist of a 9-inch, 800-bpi tape drive and the associated software.

4.4 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Samples should be introduced into the syringe by (1) removing the plunger from the syringe, (2) pouring the sample into the barrel, and (3) replacing the barrel and inverting the syringe to remove any air trapped in the syringe. Do not draw the sample up into the syringe. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syringe.

TABLE 2. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
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	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 100% of mass 174
177	5 to 9% of mass 176

4.5 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.6 Micro syringes: 10-µl, 25-µl, 100-µl, 250-µl, and 1000-µl. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.7 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation.

4.8 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.9 Syringe valve: 2-way, with Luer ends (2 each) (Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting, or equivalent).

4.10 Syringe: 5-ml, gas-tight with shut-off valve.

4.11 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.12 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.13 Rotary evaporator: equipped with Teflon-coated seals (Buchi Rotavapor R-110, or equivalent).

4.14 Vacuum pump: mechanical, two-stage.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn by analysts when handling high concentrations of these materials.

5.5.1 Place about 9.8 ml of methanol in a 10-ml ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material as described below.

5.5.2.1 Liquids: Using a 100-µl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30° C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-ml valved gas-tight syringe with a reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol.

5.5.3 Reweigh, dilute to volume, stopper, then mix by gently inverting the flask several times. Calculate the concentration in µg/µl per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20° C and protect from light.

5.5.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards; secondary dilution solutions: Using stock solutions described in Section 5.5, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the methanol or aqueous PEG calibration solutions prepared as described in Section 6.3.2 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards from them.

5.7 Surrogate standards: Surrogate standards may be added to samples and calibration solutions to assess the effect of the sample matrix on recovery efficiency. The compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride. Prepare methanolic solutions of the surrogate standards using the procedures described in Sections 5.5 and 5.6. The

concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D_4-1,2-dichloroethane, D_6-benzene, and D_5-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

7.0 Procedure

7.1 Calibration

7.1.1 Assemble a purge-and-trap device that meets the specifications in Section 4.2 and connect the device to a GC/MS system. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, condition the trap daily for 10 min while backflushing at 180° C.

7.1.2 Operate the gas chromatograph using the conditions described in Section 7.3.5 and operate the mass spectrometer using the conditions described in Section 7.3.2.

7.1.3 Calibration procedure

7.1.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be at a concentration near but above the method detection limit. The remaining two concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3.2 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. To the purging device, add 5.0 ml of reagent water or reagent water/PEG solution. This solution is prepared by taking 4.0 ml of reagent water or reagent PEG and diluting to 100 ml with reagent water. The reagent water/PEG solution is added to the purging device using a 5-ml glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of a 20-gauge needle. Next, using a 10-µl or 25-µl micro-syringe equipped with a long needle (see Section 4.6), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 5.6). Add the aliquot of calibration solution directly to the reagent water or reagent water/PEG solution in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe be sure that the end of the syringe needle is well beneath the surface of the reagent water or water/PEG solution. Similarly, add 20 µl of the internal standard solution (see Section 5.10). Close the 2-way syringe valve at the sample inlet.

7.1.3.3 Carry out the purge and analysis procedure as described in Section 7.3.4. Tabulate the area response of the primary characteristic ion against concentration for each compound

including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/A_{is} C_s)$$

where:

A_s = Area of the primary characteristic ion for the compound to be measured

A_{is} = Area of the primary characteristic ion of the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ±20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy:	70 volts (nominal)
Mass Range:	40 to 250 amu
Scan Time:	to give approximately 6 scans per peak but not to exceed 3 sec per scan.

7.2.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1. A solution containing 20 ng of BFB may be injected onto the gas chromatographic column in order to check the key ion criteria.

7.2.4 The peak intensity of D_6-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D_6-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D_6-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D_6-benzene observed during calibration was 355,000 area counts, then each subsequent sample or blank must give a D_6-benzene peak intensity of between 250,000 and 500,000 area counts. If the D_6-benzene peak intensity is outside the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

7.3 Sample extraction and analysis

7.3.1 The analytical procedure involves extracting the non-aqueous sample with methanol or polyethylene glycol (PEG) and analyzing a portion of the extract by a purge-and-trap GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated total volatile content (TVC) of the sample. The TVC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract by gas chromatography.

7.3.2 The estimated TVC is based on the total area response relative to that of n-nonane for all components eluting prior to the retention time of n-dodecane. The response factor for n-nonane and the retention time of n-dodecane are determined by analyzing a 2-µl aliquot of an n-hexadecane solution containing 0.20 mg/ml of n-nonane and n-dodecane.

7.3.2.1 The GC analyses are conducted using a flame ionization detector and a 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100-200 mesh Chromosorb W-HP. The column temperature is programmed from 80° C to 280° C at 8°/min and held at 280° for 10 min.

7.3.2.2 Determine the area response for n-nonane and divide by 0.2 to obtain the area response factor. Record the retention time of n-dodecane.

7.3.2.3 Add 1.0 g of sample to 20 ml of n-hexadecane and 2 ml of 2.0 M Na_2HPO_4 contained in a 50-ml glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse

during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2-µl aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$TVC = \frac{TAR_{sample} - TAR_{blank}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR_{sample} = total area response obtained for the sample

TAR_{blank} = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.3.3.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.3.4 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is connected to the purge-and-trap device and that has been flushed with helium during a 7-min trap reconditioning step (see Section 7.3.4.4). The additions are made using an appropriately sized syringe equipped with a 15-cm 20-gauge needle. Open the syringe valve of the sample inlet (shown in Figure 1) and insert the needle through the valve.

7.3.4.1 Add 5.0 ml of reagent water or aqueous sample to which 20.0 µl of the internal standard solution has been added (see Section 5.10) to the purging chamber. Insert the needle of the syringe well below the surface of the water for the addition of the internal standard solution. If the sample is aqueous go to Section 7.3.5.

7.3.4.2 Add an aliquot of the sample extract from Section 7.3.3.4. The total quantity of volatile components injected should not exceed approximately 10 µg. If the total volatile content (TVC) of the sample as determined in Section 7.3.1.4 is 1.0 mg/g or less, use a 200-µl aliquot of the sample extract. If the TVC is greater than 1.0 mg/g, use an aliquot of the sample extract that contains approximately 10 µg of total volatile components; the volume (in µl) of the aliquot to be taken can be calculated by dividing 200 by the TVC. If the TVC is greater than 20 mg/g, take a 500-µl aliquot of the sample extract and dilute to 10 ml with PEG. In this case calculate the aliquot volume (in µl) of the undiluted extract to be taken by dividing 4,000 by the TVC. If the TVC is less than 1.0 mg/g and greater sensitivity is desired, use a large purging chamber containing 25 ml of reagent water and use a 1.0-ml aliquot of the sample extract.

7.3.4.3 Close the 2-way syringe valve at the sample inlet.

7.3.5 The sample in the purging chamber is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

7.3.5.1 Adjust the gas (helium) flow rate to 40 ± 3 ml/min. Set the purging device to purge, and purge the sample for 11.0 ± 0.1 min at ambient temperature.

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

7.4.1.2 The retention time must fall within ±30 sec of the retention time of the authentic compound.

7.4.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within ±20% of the relative intensities of these ions in a reference mass spectrum. Reference spectra may be generated from the standards analyzed by the analyst or from a reference library. All reference spectra generated from standards must be obtained from an appropriately tuned mass spectrometer.

7.5 Quantitative determination

7.5.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used. Generally, the base peak of the mass spectrum is used.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of the data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1.3 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l.

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compunds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2-µm Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100-µl (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control (±2° C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ±0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot 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 abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 mm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D_{10}-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D_3-phenol, D_8-naphthalene, D_{10}-phenanthrene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{12}-perylene may be used in place of D_{12}-benzo(a)pyrene.

5.9 Column performance standards: D_3-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D_3-phenol, D_8-naphthalene, D_{10}-phenanthrene, D_{12}-chrysene and D_{12}-benzo(a)pyrene. D_{12}-perylene may be substituted for D_{12}benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D_3-phenol, D_8-naphthalene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{12}-perylene may be substituted for D_{12}-benzo(a)pyrene. D_{10}-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar netural compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D_5-phenol or D_3-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standards.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the compound to be measured in µg/l.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ±20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 µg/ml of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in questino is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2Cl_2 and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weight 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 $\pm$ 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4, the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2-μm Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \qquad \text{(Eq. 1)}$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \qquad \text{(Eq. 2)}$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as decribed in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c\ (7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 3)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 4)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{GPC\ (7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 5)}$$

where:

V_s = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{c(7.3.8)}$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_{F\ (7.3.7)}$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within ±15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within ±20% of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu g/g = \frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{RF} \qquad \text{(Eq. 6)}$$

where:

$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}}$ = internal standard concentration factor calculated in Section 7.3.8.

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in µg/g without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery (s/R x 100) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D_{10}-phenanthrene.

8.3 High Performance Liquid Chromatographic Methods (8300's)

Methods appropriate for organic analysis by HPLC methods are included on the following pages.

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCB'S

1.0 Scope and Application

1.1 Method 8080 is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls (PCB's) in groundwater, liquid, and solid sample matrices. Specifically, Method 8080 may be used to detect the following substances:

Aldrin	Endrin aldehyde
a-BHC	Heptachlor
ß-BHC	Heptachlor epoxide
w-BHC	Kepone
q-BHC (Lindane)	Methoxychlor
Chlordane	Toxaphene
4,4'-DDD	PCB-1016
4,4'-DDE	PCB-1221
4,4'-DDT	PCB-1232
Dieldrin	PCB-1242
Endosulfan I	PCB-1248
Endosulfan II	PCB-1254
Endosulfan sulfate	PCB-1260
Endrin	

1.2 Method 8080 is recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 Method 8080 provides cleanup and chromatographic conditions for the detection of ppb levels of organochlorine pesticides and PCB's. Prior to the use of this method, appropriate sample extraction techniques must be used. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5-µl sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or another halogen-specific detector. An aliquot of each sample will be spiked with standards to determine the spike recovery and the limits of detection for that particular sample. It is recommended that the analyst carefully select the compounds used in sample spiking to avoid coelution under the GC conditions given in Table 1. Aroclor 1221 will give minimal interference with the single component pesticides listed in Table 1. Chlordane and toxaphene may require individual spiked sample analysis to yield valid recovery data.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCB's[a]

Parameter	Retention time (min)		Detection limit[b] (µg/l)
	Column 1[c]	Column 2[d]	
Aldrin	2.40	4.10	0.004
a-BHC	1.35	1.82	0.004
β-BHC	1.90	1.97	0.006
w-BHC	2.15	2.20	0.009
q-BHC (Lindane)	0.70	2.13	0.004
Chlordane	e	e	0.014
4,4'-DDD	7.83	9.08	0.012
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.004
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
PCB-1016	e	e	ND
PCB-1221	e	e	ND
PCB-1232	e	e	ND
PCB-1242	e	e	0.065
PCB-1248	e	e	ND
PCB-1254	e	e	ND
PCB-1260	e	e	ND

ND = not determined.

[a]Taken from reference 6.

[b]Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10-ml final volume of a 1-liter liquid extract, and assuming a GC injection of 5 µl.

[c]Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

[d]Column 2 conditions: Supelcoport 100/200 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

[e]Multiple peak response.

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample may be significantly higher.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must therefore be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone, and finally pesticide-quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400° C for 15 to 30 min. Some high boiling materials, such as PCB's, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should

be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated. Calibration must be checked at 1.0- and 10.0-ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Boiling chips: Extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron-capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatographic column: Pyrex, 400 mm x 25 mm O.D., with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5.0 Reagents

5.1 Preservatives

5.1.1 Sodium hydroxide: (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1): (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride: Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Mercury: Triple distilled.

5.6 Hexane: Pesticide residue analysis grade.

5.7 Isooctane (2,2,4-trimethyl pentane): Pesticide residue analysis grade.

5.8 Acetone: Pesticide residue analysis grade.

5.9 Diethyl ether: Nanograde, redistilled in glass if necessary.

5.9.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523).

5.9.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.10 Florisil: PR grade (60/100 mesh); purchase activated at 1250° F; store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hr at 130° C in a foil-covered glass container.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in appropriately cleaned glass containers and the sampling bottle must not be prewashed with the sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedures

7.1 Sample preparation

7.1.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (3520). Extract solid samples with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication procedures (Method 3550). Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked to determine the % recovery and the limit of detection for that sample.

7.1.2 Florisil column cleanup

7.1.2.1: Add a weight of Florisil (nominally 21 g), predetermined by calibration (Section 7.3) to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1-2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Packing the Florisil in a hexane slurry is an alternative method which has proven effective. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate. Adjust the sample extract volume to 10 ml and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 ml hexane, adding each rinse to the column.

7.1.2.2 Place a 500-ml K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in hexane (Fraction 2), into a second K-D flask. Perform the third elution using 200 ml of 50% ethyl ether in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 2.

7.1.2.3 Concentrate the eluates by standard K-D techniques, as described in the referenced extraction procedures, substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

TABLE 2. DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCB's USING FLORISIL COLUMN CHROMATOGRAPHY[a]

Parameter	Percent recovery by fraction[b]		
	1(6%)	2(15%)	3(50%)
Aldrin	100		
a-BHC	100		
ß-BHC	97		
w-BHC	98		
g-BHC (Lindane)	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Methoxychlor	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Taken from reference 1.

[b]Eluting solvent composition given in Section 7.1.2.2.

7.2 Gas chromatography conditions. The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/ 1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Florisil standardization. The cleanup procedure described in Section 7.1.2 utilizes Florisil chromatography. Florisil from

different batches or sources may vary in absorption capacity. To determine the amount of Florisil to be used, the absorption capacity of each separate batch of Florisil is measured using lauric acid values (2). The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

7.4 Gas chromatographic analysis

7.4.1 Inject 2-5 µl of the sample extract using the solvent flush technique. Smaller (1.0 µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.4.2 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4.4 Examples of chromatograms for organochlorine pesticides are shown in Figures 1-5.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of the sample preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

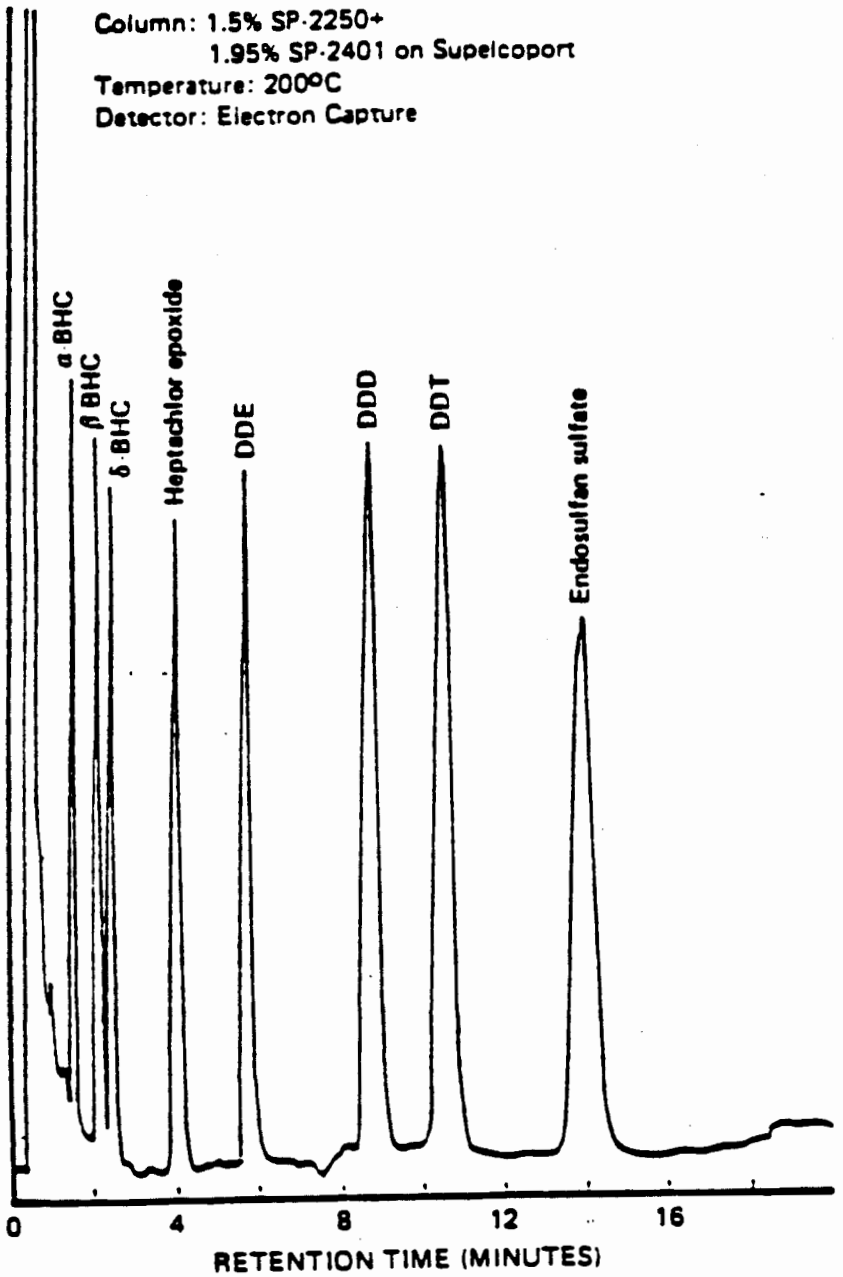

Figure 1. Gas chromatogram of pesticides.

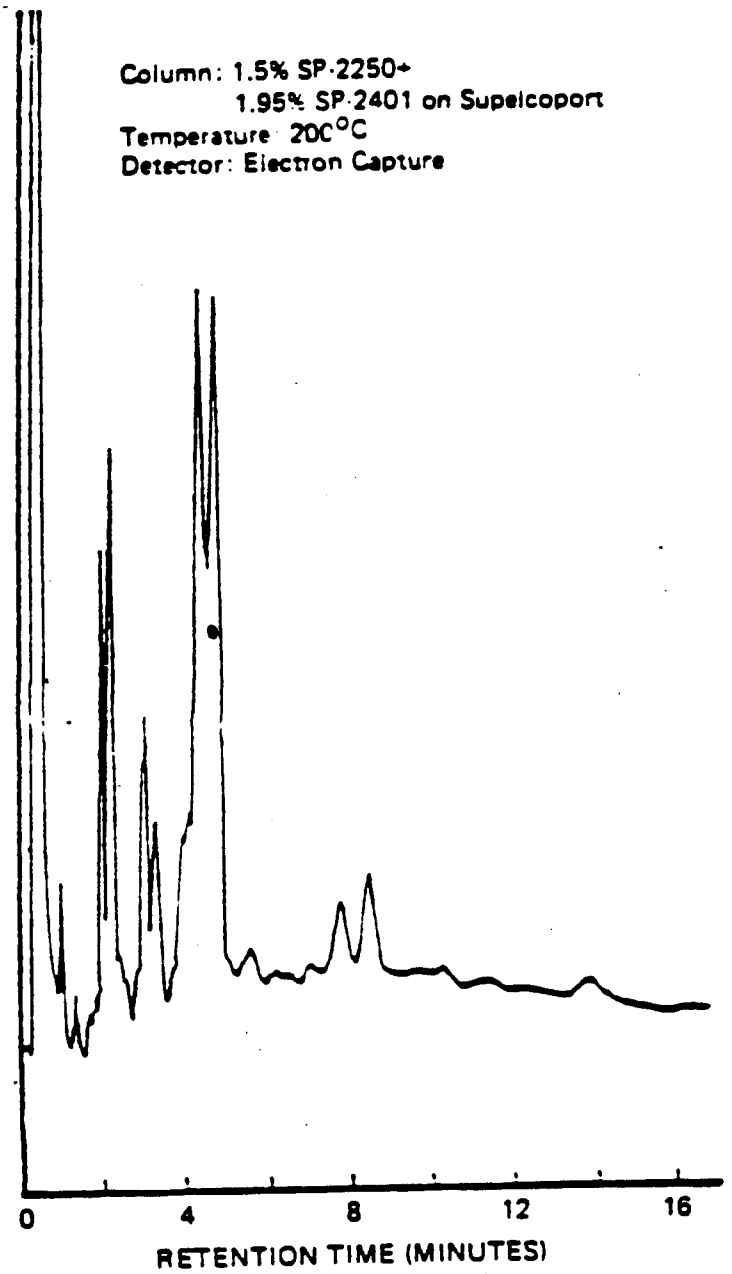

Figure 2. Gas chromatogram of chlordane.

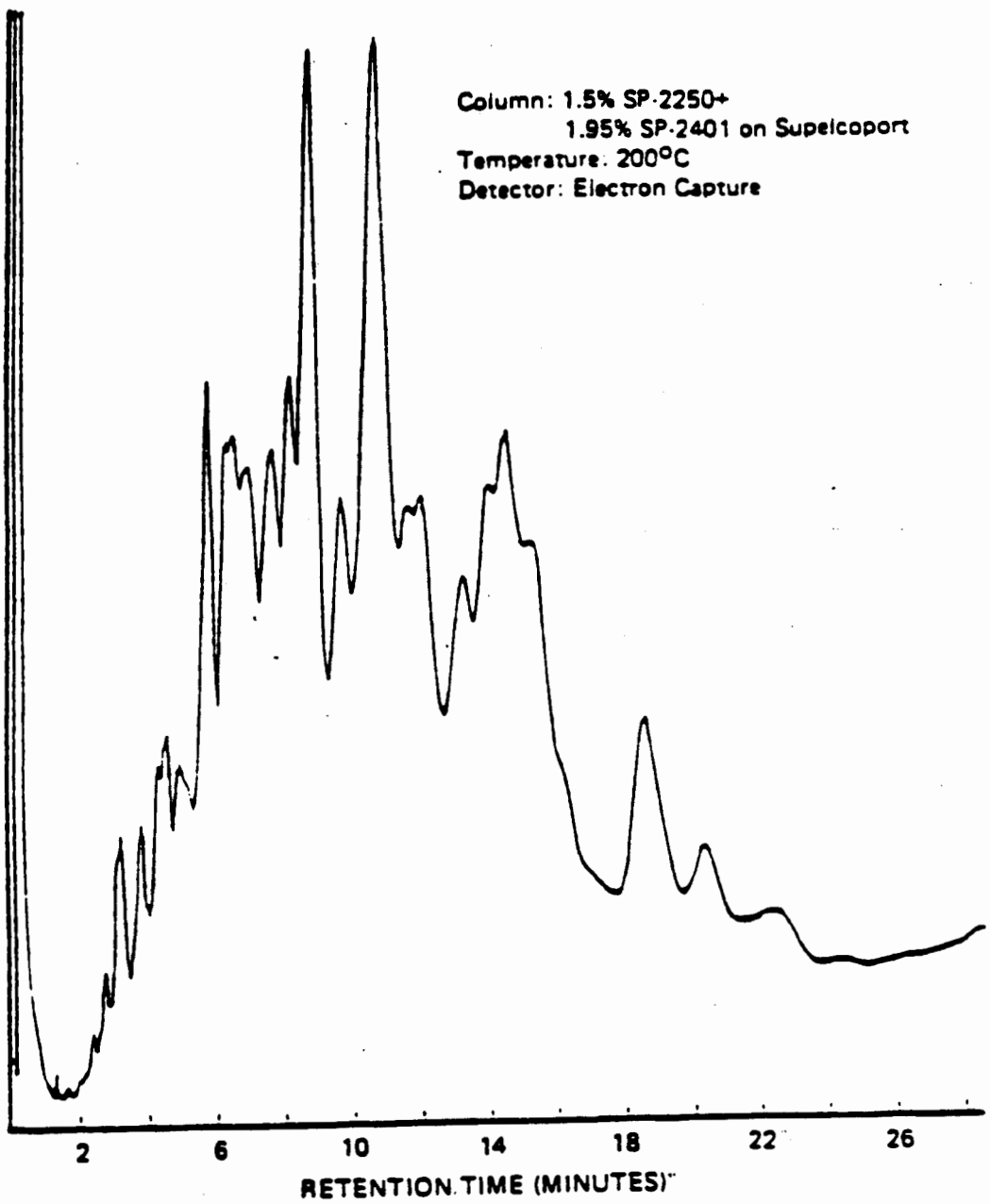

Figure 3. Gas chromatogram of toxaphene.

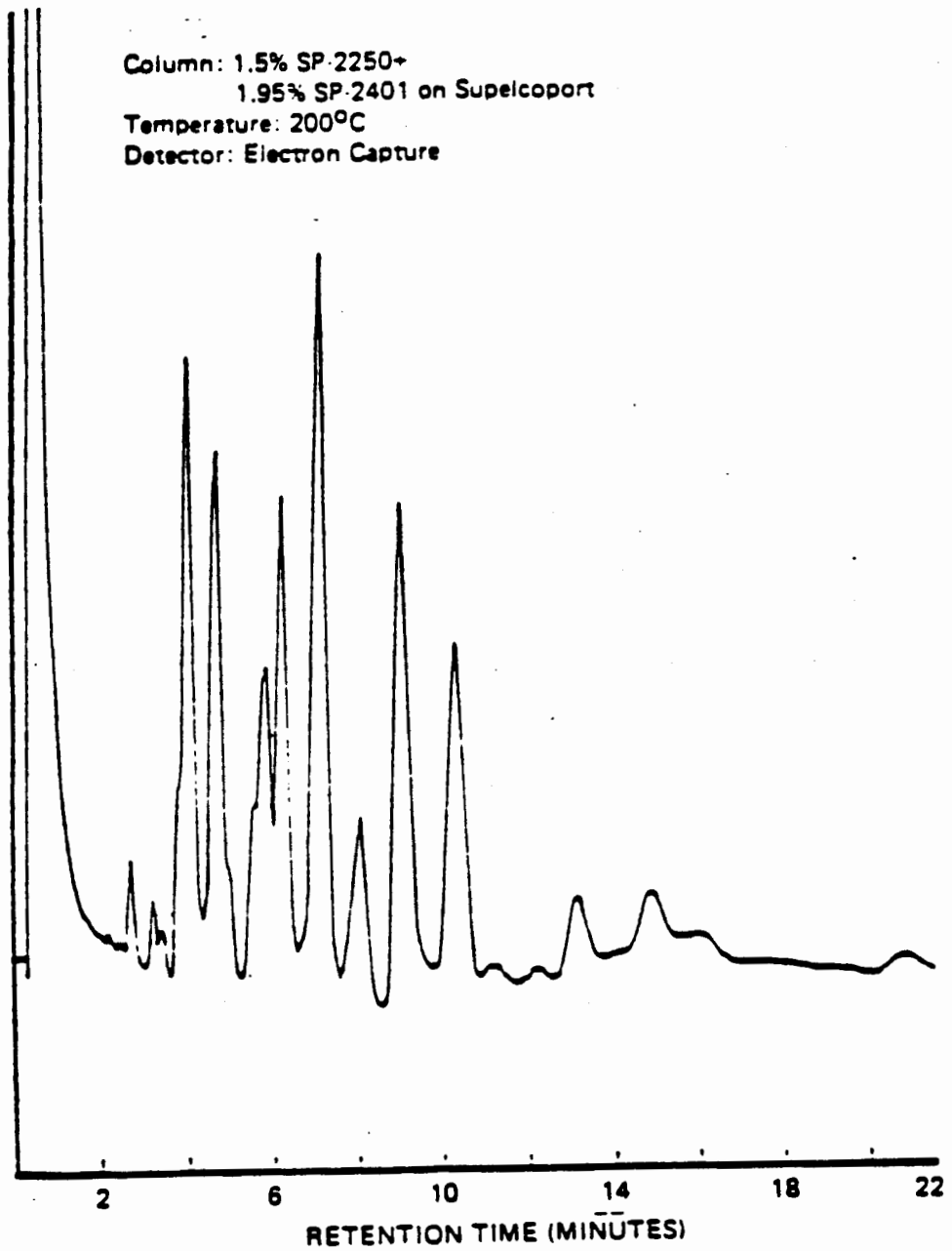

Figure 4. Gas chromatogram of PCB-1254.

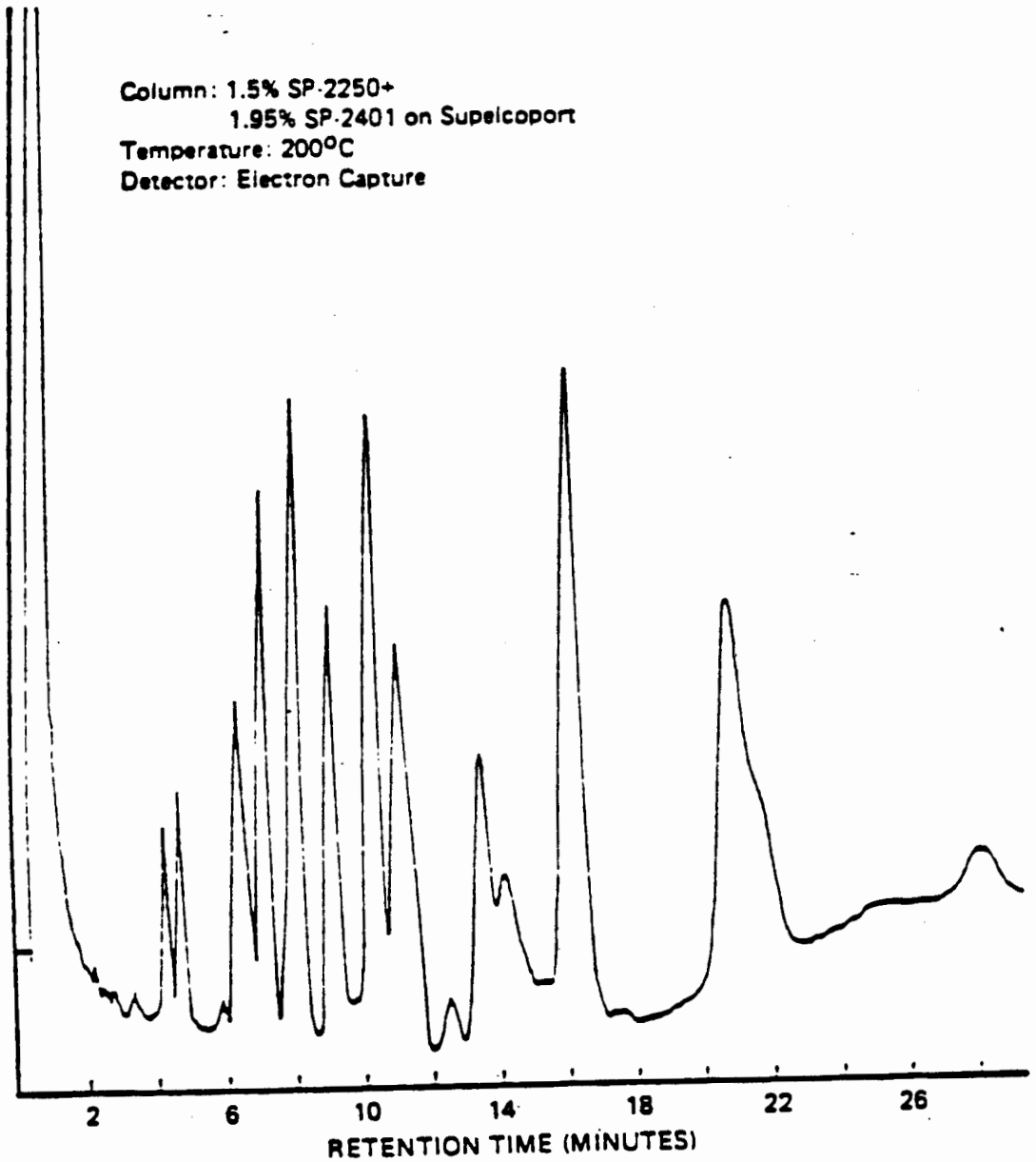

Figure 5. Gas chromatogram of PCB-1260.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Aldrin	89	2.5	2.0	15	3
a-BHC	89	2.0	1.0	15	3
B-BHC	88	1.3	2.0	15	3
w-BHC	86	3.4	2.0	15	3
q-BHC (Lindane)	97	3.3	1.0	15	3
Chlordane	93	4.1	20	21	4
4,4'-DDD	92	1.9	6.0	15	3
4,4'-DDE	89	2.2	3.0	15	3
4,4'-DDT	92	3.2	8.0	15	3
Dieldrin	95	2.8	3.0	15	2
Endosulfan I	96	2.9	3.0	12	2
Endosulfan II	97	2.4	5.0	14	3
Endosulfan sulfate	99	4.1	15	15	3
Endrin	95	2.1	5.0	12	2
Endrin aldehyde	87	2.1	12	11	2
Heptachlor	88	3.3	1.0	12	2
Heptachlor epoxide	93	1.4	2.0	15	3
Toxaphene	95	3.8	200	18	3
PCB-1016	94	1.8	25	12	2
PCB-1221	96	4.2	55-100	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	92	2.0	28-56	12	2
PCB-1248	90	1.6	40	12	2
PCB-1254	92	3.3	40	18	3
PCB-1260	91	5.5	80	18	3

9.0 References

1. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 10 - Pesticides and PCB's. Report for EPA Contract 68-03-2606.

2. Mills, P.A. 1968. Variation of florisil activity: simple method for measuring absorbent capacity and its use in standardizing florisil columns. J. Assoc. Official Anal. Chem. 51 (29).

3. U.S. EPA. 1980. Interim methods for the sampling and analysis of priority pollutants in sediments and fish tissue. October 1980. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

4. Bellar, T., J. Lichtenburg, and S. Lonnesman. 1980. Recovery of organic compounds from environmentally contaminated bottom materials. In Contaminants and sediments, Volume 2, ed. R. Baker, Ann Arbor Science Publ., Inc., Ann Arbor, Michigan.

5. Rodriguez, C., W. McMahon, and K. Thomas. 1980. Method development for determination of polychlorinated hydrocarbons in municipal sludge. EPA Report-600/2-80-029.

6. U.S. EPA. Method 617. Organochlorine pesticides and PCB's. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

METHOD 9010

TOTAL AND AMENABLE CYANIDE

1.0 Scope and Application

1.1 Method 9010 is used to determine the concentration of inorganic cyanide in a waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9010 does not determine the "reactive" cyanide content of wastes containing iron-cyanide complexes.

2.0 Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm for pyridine-barbituric acid reagent. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3.0 Interferences

3.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 7.2.3, 7.2.4, and 7.2.5.

3.2 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in procedure 7.2.3.

3.3. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These comounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

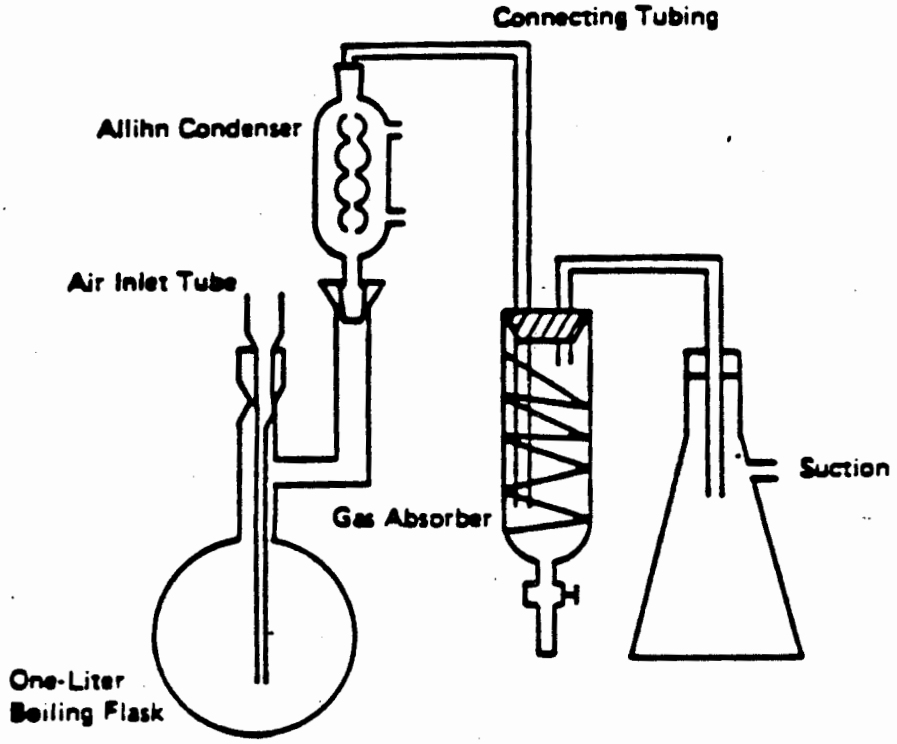

Figure 1. Apparatus for cyanide distillation.

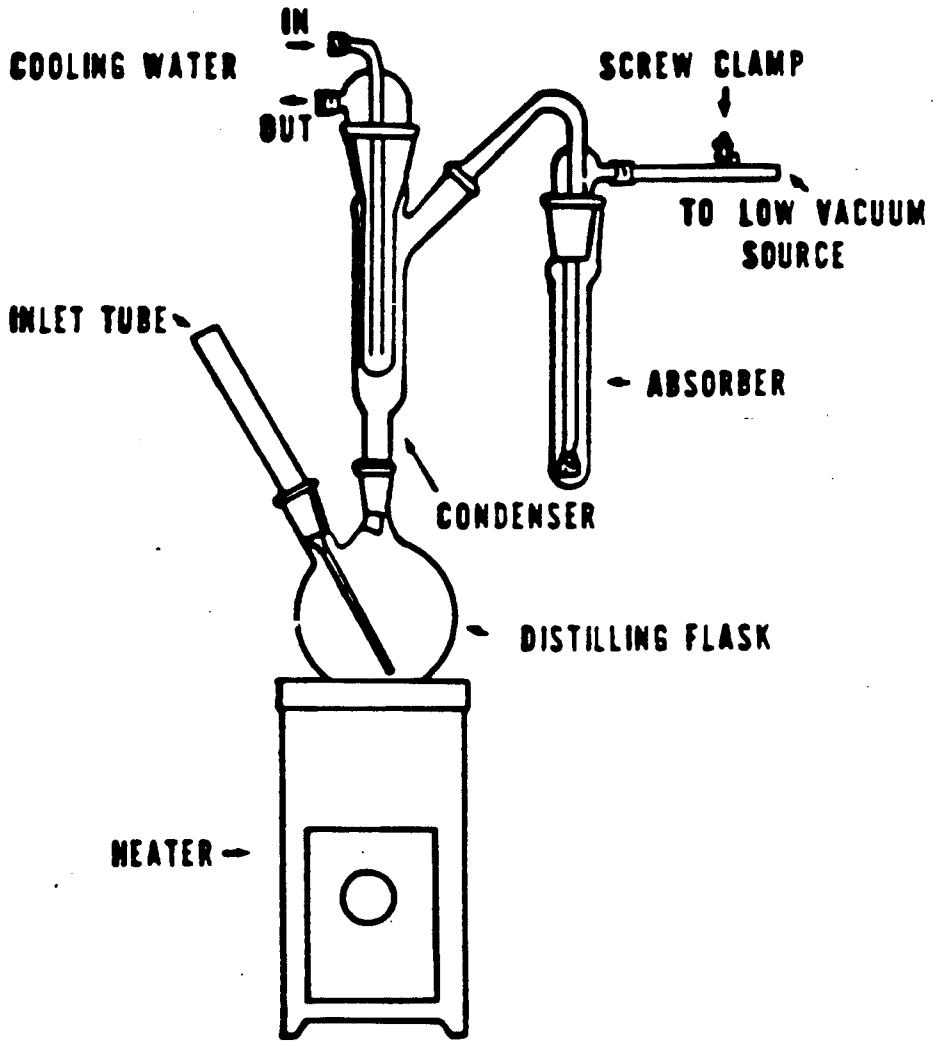

Figure 2. Cyanide distillation apparatus.

4.0 Apparatus

4.1 Reflux distillation apparatus such as shown in Figure 1 or 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

4.2 Spectrophotometer suitable for measurements t 570 nm with a 1.0 cm cell or larger.

4.3 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

4.4 Technicon Auto-Analyzer

4.4.1 Sampler

4.4.2 Cyanide manifold. (See Figure 3.)

4.4.3 Proportioning pump.

4.4.4 Colorimeter equipped with a 15 mm flowcell and 570 nm filter.

4.4.5 Recorder.

5.0 Reagents

5.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

5.2 Bismuth nitrate solution: Dissolve 30.0 grams of $Bi(NO_3)_3$ in 100 mls of distilled water. While stirring, add 250 mls of acetic acid. Stir until dissolved. Dilute to 1 liter with distilled water.

5.3 Sulfuric acid; 18N: Slowly add 500 ml of concentrated H_2SO_4 to 500 ml of distilled water.

5.4 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

5.5 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

5.6 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100 g).

5.7 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.

5.8 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

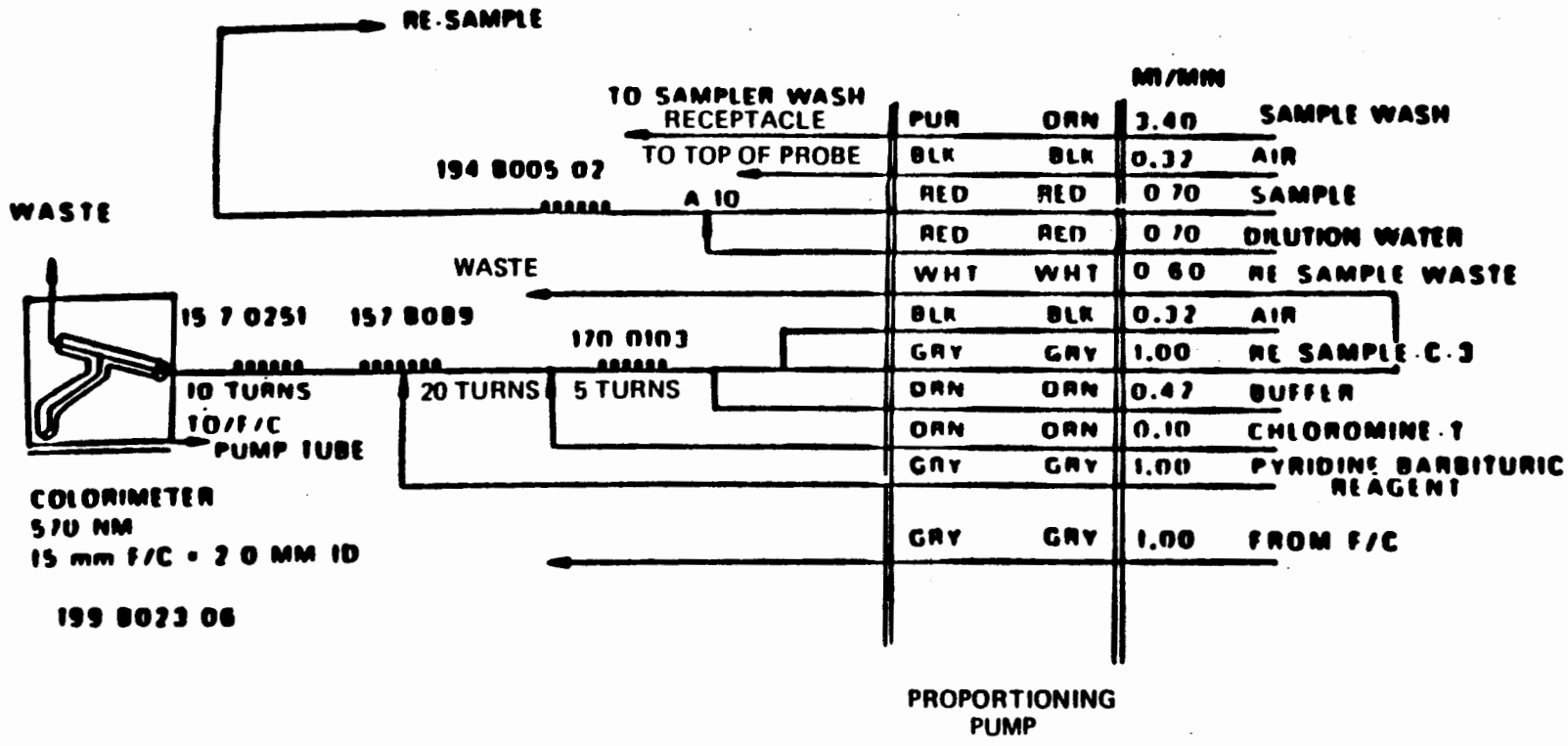

Figure 3. Cyanide manifold AA11.

5.9 Sulfamic acid solution: Dissolve 40 g of sulfamic acid in distilled water. Dilute to 1 liter.

5.10 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.

5.11 Potassium Iodide-starch test paper.

5.12 Reagents for manual colorimetric determination:

5.12.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix and cool to room temperature. Dilute to 250 ml with distilled water and mix., This reagent is stable for approximately six months if stored in a cool, dark place.

5.12.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 ml of distilled water and refrigerate until ready to use.

5.13 Reagents for automated colorimetric determination:

5.13.1 Distillation agent: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water, mix, and dilute to one liter with distilled water.

5.13.2 Sodium dihydrogenphosphate, 1M (phosphate buffer): Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

5.13.3 Chloramine-T: Dissolve 3.0 g of chloramine-T in 500 ml of distilled water.

5.13.4 Pyradine barbituric acid reagent: Refer to (5.12.1).

5.13.5 Sodium hydroxide, 1 N: Dissolve 40 g of NaOH in 500 ml of distilled water.

5.13.6 Stock cyanide solution: Refer to 5.5.

5.13.7 All working standards should contain 2 ml of 1 N NaOH (5.13.5) per 100 ml.

5.13.8 Dilution water and recepticle wash water (NaOH, 0.25 N): Dissolve 10.0 g NaOH in 500 mls of distilled water. Dilute to 1 liter.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples should be collected in plastic or glass bottles of 1-liter size or larger. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of water.

6.4 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH is greater than or equal to 12) at the time of collection.

6.5 Samples should be refrigerated at 4°C when possible and analyzed as soon as possible.

7.0 Procedure

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (5.10) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (5.1).

Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker be means of a magnetic stirring device.

7.1.2 Test for residual chlorine with KI-starch paper (5.11) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necesssary, add additional hypochlorite solution.

7.1.3 After one hour, add 0.5 g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

7.1.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorionation.)

7.2 Distillation Procedure

7.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (5.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube.

7.2.3 If samples contain sulfide, add 50 ml of bismuth nitrate solution (5.2) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

7.2.4 If samples contain NO_3 and/or NO_2, add 50 ml of sulfamic acid solution (5.9) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

7.2.5 Slowly add 50 ml 18 N sulfuric acid (5.3) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride (5.8) into the air inlet and wash down with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

7.2.7 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

7.3 Manual spectophotometric determination:

7.3.1 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (5.13.8). Add 15.0 ml of sodium phosphate solution (5.4) and mix.

7.3.2 Add 2 ml of chloramine-T (5.12.2) and mix. See note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (5.12.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development and then read absorbance at 570 nm in a 1-cm cell within 15 minutes.

7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipeting suitable volumes of standard solution (5.7) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Working Standard Solution (1 ml = 10 g CN)	Conc. g CN per 250 ml
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

7.4.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

7.4.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (5.6) or the working standard (5.7) to 500 ml of sample in insure a level of 20 µg/l. Proceed with the analysis as in Procedure (7.2.1)

7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

7.5.2 Prepare a standard curve by plotting absorbance of standards vs. cyanide concentrations.

7.6 Calculation: If the colormetric procedure is used, calculate the cyanide, in µg/l, in the original sample as follows:

$$\text{CN, } \mu g/l = \frac{A \times 1{,}000}{B} \times \frac{50}{C}$$

where:

A = µg CN read from standard curve
B = ml of original sample for distillation
C = ml taken for colorimetric analysis

7.7 Automated colorimetric determination

7.7.1 Set up the manifold as shown in Figure 3 in a hood or a well ventilated area.

7.7.2 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

7.7.3 Place appropriate standards in the sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples.

7.7.4 When the baseline becomes steady, begin the analyses.

7.8 Calculation: Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentrations of samples by comparing sample peak heights with standards.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occuring.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard referencee materials shall be periodically employed to ensure that correct prcedures are being followed and that all equipment is operating properly.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

METHOD 8040

PHENOLS

1.0 Scope and Application

1.1 Method 8040 is used to determine the concentration of various phenolic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8040 may be used to detect the following substances:

Phenol	4-Chloro-3-methylphenol
2-Chlorophenol	2,4-Dimethylphenol
2,4-Dichlorophenol	2-Nitrophenol
2,6-Dichlorophenol	4-Nitrophenol
Trichlorophenols	2,4-Dinitrophenol
Tetrachlorophenols	2-sec-Butyl-4,6-dinitrophenol (DNBP)
Pentachlorophenol	2-Cyclohexyl-4,6-dinitrophenol
Cresol (methyl phenols)	2-Methyl-4,6-dinitrophenol
4,6-Dinitro-o-cresol	

1.2 Method 8040 is recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 Method 8040 provides chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques. Water and groundwater samples are extracted at a pH of less than or equal to 2 with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a pH of less than or equal to 2 with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5-µl sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID). An aliquot of each sample must be spiked with standards to determine the spike recovery and the limits of detection for that particular sample.

2.2 Method 8040 also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives with additional cleanup procedures for electron capture gas chromatography to aid the analyst in the elimination of interferences.

2.3 The sensitivity of Method 8040 usually depends on the level of interferences rather than on instrumental limitations. The detection limits listed in Table 1 for some phenols represent sensitivities that can be achieved in wastewaters in the absence of interferences. However, in typical waste samples, detection limits would be higher. The use of derivatization cleanup, if necessary, will also increase detection limits.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from samples will vary considerably from source to source depending upon the waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis.

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS[a]

Compound	Retention time	Detection limit (μg/l)[b]
2-Chlorophenol	1.70	0.31
2-Nitrophenol	2.00	0.45
Phenol	3.01	0.14
2,4-Dimethylphenol	4.03	0.32
2,4-Dichlorophenol	4.30	0.39
2,4,6-Trichlorophenol	6.05	0.64
4-Chloro-3-methylphenol	7.50	0.36
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
Pentachlorophenol	12.42	7.4
4-Nitrophenol	24.25	2.8

[a]Taken from Reference 1.

[b]Detection limit is calculated from the minimum detectable GC response being equal to 5 times the GC background noise, assuming a 10-ml final extract volume of the 1-liter sample extract, assuming a GC injection of 5 ml.

Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 when analyzing groundwater samples.

4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. Pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs (Kontes K-662750-0012).

4.2.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories including flame ionization and electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatographic column: 10-mm I.D. by 100-mm length, with Teflon stopcock.

4.6 Reaction vial: 20-ml, with Teflon-lined cap.

5.0 Reagents

5.1 Preservatives

5.1.1 Sodium hydroxide: (ACS) 10 N in distilled or distilled, deionized water.

5.1.2 Sulfuric acid: (1:1) Mix equal volumes of conc. H_2SO_4 (ACS) with distilled or distilled, deionized water.

5.1.3 Sodium thiosulfate: (ACS) Granular.

5.2 Methylene chloride, acetone, 2-propanol, hexane, toluene: Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards.

5.5 Sulfuric acid: (ACS) 1 N in distilled water.

5.6 Potassium carbonate: (ACS) powdered.

5.7 Pentafluorobenzyl bromide (a-Bromopentafluorotoluene): 97% minimum purity.

5.8 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6): 98% minimum purity.

5.9 Derivatization reagent: Add 1 ml pentafluorobenzyl bromide and 1 g 18-crown-6 to a 50-ml volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly.

5.10 Silica gel: (ACS) 100/200 mesh, grade 923; activated at 130° C and stored in a desiccator.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg of sodium thiosulfate per ppm free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid solution or 10 N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedures

7.1 Sample preparation

7.1.1 Extraction

Extract water samples at a pH of less than or equal to 2 with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted at a pH of less than or equal to 2 with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. An aliquot of each sample must be spiked with standards to determine the percent recovery and the limits of detection for that sample.

7.1.2 Derivatization

If interferences prevent measurement of the peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.1.2.1 Pipet a 1.0-ml aliquot of the 2-propanol solution of standard or sample extract into a glass reaction vial. Add 1.0 ml derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/ml.

7.1.2.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

7.1.2.3 Cap the mixture and heat it for 4 hr at 80° C in a hot water bath.

7.1.2.4 Remove the solution from the hot water bath and allow it to cool.

7.1.2.5 Add 10 ml hexane to the reaction vial and shake vigorously for 1 min. Add 3.0 ml distilled, deionized water to the reaction vial and shake for 2 min.

7.1.2.6 Decant organic layer into a concentrator tube and cap with a glass stopper.

7.1.2.7 Pack a 10-mm I.D. chromatographic column with 4.0 g of activated silica gel. After settling the silica gel by tapping the column, add about 2 g of anhydrous sodium sulfate to the top.

7.1.2.8 Pre-elute the column with 6 ml hexane. Discard the eluate and just prior to exposure of the sulfate layer to air, pipet onto the column 2.0 ml of the hexane solution that contains the derivatized sample of standard. Elute the column with 10.0 ml of hexane (Fraction 1) and discard this fraction. Elute the column, in order, with: 10.0 ml 15% toluene in hexane (Fraction 2); 10.0 ml 40% toluene in hexane (Fraction 3); 10.0 ml 75% toluene in hexane (Fraction 4); and 10.0 ml 15% 2-propanol in toluene (Fraction 5). Elution patterns for some phenolic derivatives are shown in Table 2. Fractions may be combined as desired, depending upon the specific phenols of interest or level of interferences.

7.2 The recommended gas chromatographic columns and operating conditions for the instruments are:

Column 1 conditions: Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 6-ft long x 2-mm I.D. glass column with nitrogen carrier gas at 30 ml/min flow rate. Column temperature is 80° C at injection, and then programmed immediately at 8° C/min to a 150° C final temperature.

Column 2 conditions: Chromosorb W-AW-DMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8-m long x 2.0-mm I.D. glass column with 5% methane/95% argon carrier gas at 30 ml/min flow rate. Column temperature is 200° C.

TABLE 2. ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES[a]

Parent compound	Method detection limit (µg/l)	Retention time (min)[b]	Percent recovery by fraction				
			1	2	3	4	5
2-Chlorophenol	0.58	3.3			90	over 1	90
2-Nitrophenol	0.77	9.1				9	
Phenol	2.2	1.8			90	10	
2,4-Dimethylphenol	0.63	2.9			95	7	
2,4-Dichlorophenol	0.68	5.8			95	over 1	
2,4,6-Trichlorophenol	0.58	7.0		50	50		
4-Chloro-2-methylphenol	1.8	4.8			84	14	
Pentachlorophenol	0.59	28.8		75	20		
4-Nitrophenol	0.70	14.0				over 1	90
(2,4-Dinitrophenol)		46.9					
(2-Methyl-4,6-dinitrophenol)		36.6					

[a]Taken from Reference 1.

[b]Retention times included for qualitative information only. The lack of accuracy and precision of the derivatization reaction precludes the use of this approach for quantitative purposes.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.2. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Gas chromatographic analysis

7.4.1 Phenols are to be analyzed on a gas chromatograph equipped with a flame ionization detector according to column 1 conditions (Section 7.2). Table 1 summarizes estimated retention times and sensitivities that should be achieved by this method for clean water samples. Detection limits for a typical waste sample would be significantly higher. If peak detection is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to column 2 conditions (Section 7.2). Table 2 summarizes estimated retention times as well as percent recoveries for the fractionation procedure.

7.4.2 Inject 2 to 5 µl of the sample extract using the solvent flush technique. Smaller (1.0 µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.4.3 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and

reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of sample preparation and measurement. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

9.0 References

1. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 3 - Chlorinated Hydrocarbons and Category 8 - Phenols. Report for EPA Contract 68-03-2625. (In preparation.)

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
4-Chloro-3-methylphenol	82	15.0	0.70-3.5	21	3
2-Chlorophenol	67	14.8	0.74-3.7	21	3
2,4-Dichlorophenol	74	11.4	1.03-5.2	21	3
2,4-Dimethylphenol	51	14.0	0.82-4.1	21	3
2,4-Dinitrophenol	74	16.5	28.7	14	2
2-Methyl-4,6-dinitrophenol	86	12.4	34.6	21	3
2-Nitrophenol	67	12.9	0.80-4.0	21	3
4-Nitrophenol	45	7.9	15.9	21	3
Pentachlorophenol	79	8.8	21.0	21	3
Phenol	41	8.4	0.76-3.8	21	3
2,4,6-Trichlorophenol	71	14.5	1.20-6.0	21	3

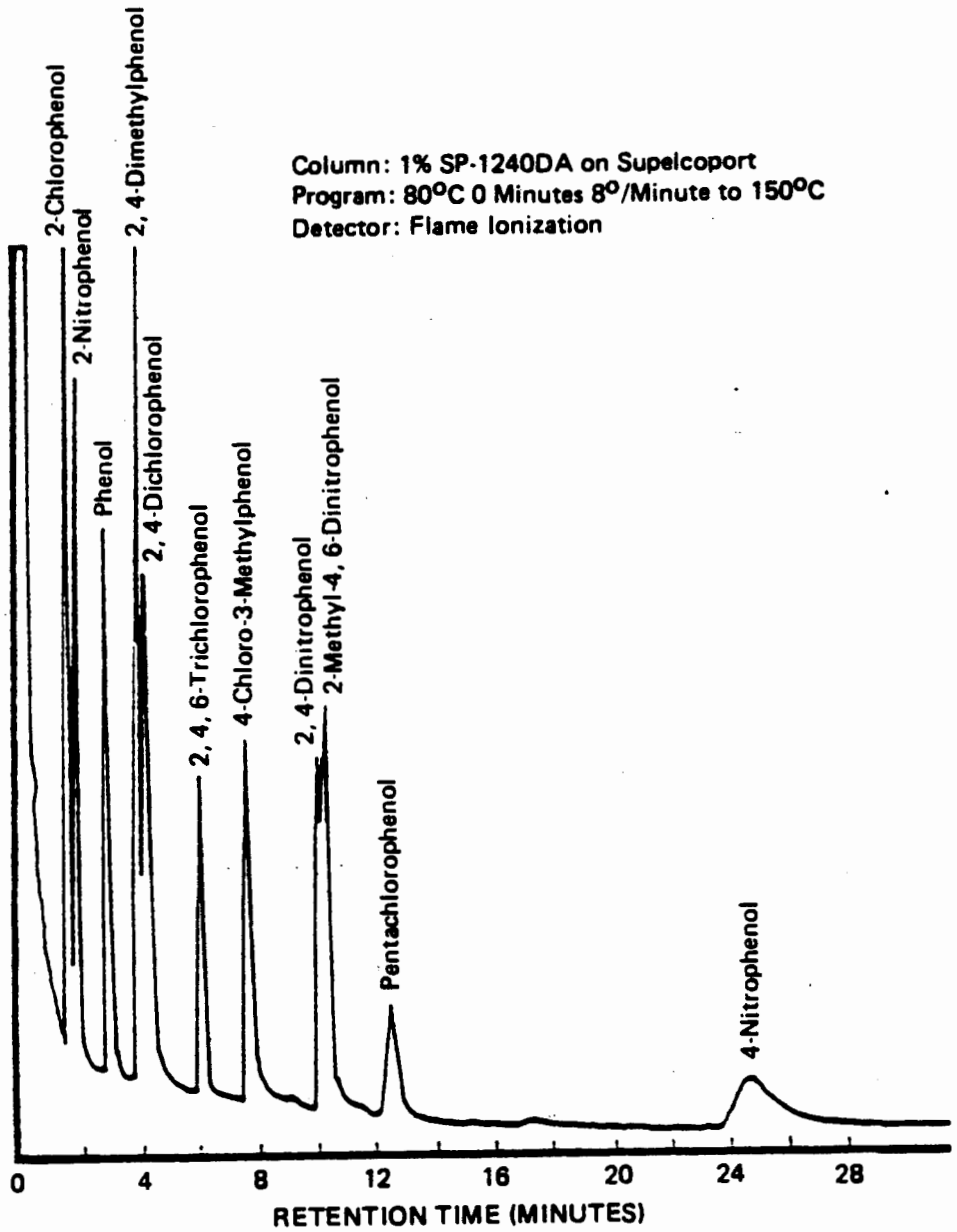

Figure 1. Gas chromatogram of phenols.

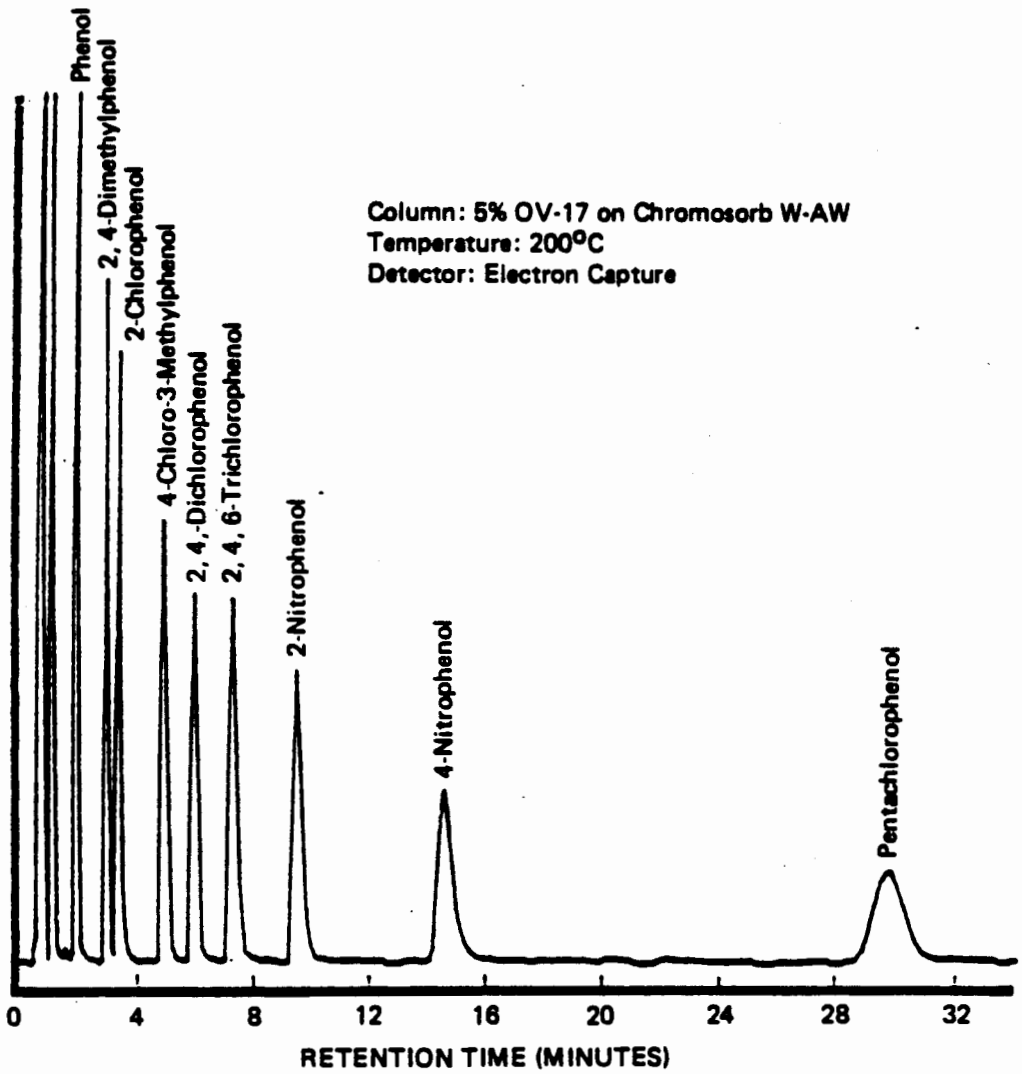

Figure 2. Gas chromatogram of PFB derivatives of phenols.

METHOD 7060

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 Scope and Application

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 Elemental arsenic and many of its compounds are volatile and therefore samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Arsenic hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000 µl as required.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Arsenic standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve

1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 ml of Type II water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2, and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7081

BARIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7081 is an atomic absorption procedure approved for determining the concentration of barium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7081, samples must be prepared in order to convert organic forms of barium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the barium concentration.

2.3 The typical detection limit for this method is 2 µg/l.

3.0 Inferences

3.1 Barium is known to form a barium carbide in the graphite furnace. This less volatile carbide can cause losses of sensitivity and memory effects.

3.2 The long residence time and the high concentration of the analyte in the optical path of the graphite furnace can lead to severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

3.4 Halide acids should not be used.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

4.2 Barium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.5 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000 µl as required.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Barium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in Type II water and dilute to 1 liter.

5.4 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

5.5 Barium working standards: Prepare dilution of the stock barium solution to be used as calibration standards. To each 100 ml of standard and sample add 2.0 ml potassium chloride solution.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 553.6-nm line is the analytical wavelength to be used for barium analysis.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of barium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7131

CADMIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7131 is an atomic absorption procedure approved for determining the concentration of cadmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7131, samples must be prepared in order to convert organic forms of cadmium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the cadmium concentration.

2.3 The typical detection limit for this method is 0.1 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Cadmium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade), in Type II water and dilute to 100 ml.

5.4 Cadmium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.282 g of cadmium sulfate (3 $CdSO_4 \cdot 8H_2O$), analytical reagent grade), in Type II water and dilute to 1 liter.

5.5 Cadmium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 228.8-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 For certain sample types the addition of 2 ml of an ammonium phosphate solution to 100 ml of standards and samples will elevate charring (ashing) temperatures which may eliminate matrix interferences. Ammonium sulfate, $(NH_4)_2SO_4$, has been reported to have a similar effect on these samples.

7.7 Either (1) run a series of cadmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7191

CHROMIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7191 is an atomic absorption procedure approved for determining the concentration of chromium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7191, samples must be prepared in order to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the chromium concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Low concentrations of calcium may cause interferences; at concentrations above 200 mg/l, calcium's effect is constant. Calcium nitrate (see Section 5.4) is therefore added to ensure a known constant effect.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Chromium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%).

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter.

5.5 Chromium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water and dilute to 1 liter.

5.6 Chromium working standards: These standards should be prepared to contain 0.5% (v/v) HNO_3; 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution may be added to lessen interferences.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 357.9-nm wavelength line shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7421

LEAD (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7421 is an atomic absorption procedure approved for determining the concentration of lead in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7421, samples must be prepared in order to convert organic forms of lead to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the lead concentration.

2.3 The typical detection limit for this method is 1 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, lead analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Sulfate can suppress lead absorbance. This interference can be eliminated or lessened by adding a lanthanum releasing agent (10 ml lanthanum solution per 100 ml of solution).

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Lead hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lanthanum nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml concentrated HNO_3 and dilute to 1000 ml with Type II water.

5.4 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.599 g lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in Type II water and acidify with 10 ml redistilled HNO_3. Dilute to 1 liter.

5.5 Lead working standards: These standards should be prepared such that they contain 0.5% (v/v) HNO_3.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 283.3-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be dilated in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of lead standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 If sulfate interference is encountered, add 10 ml of lanthanum solution to each 100 ml of solution.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7471

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 Scope and Application

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis the samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absoption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

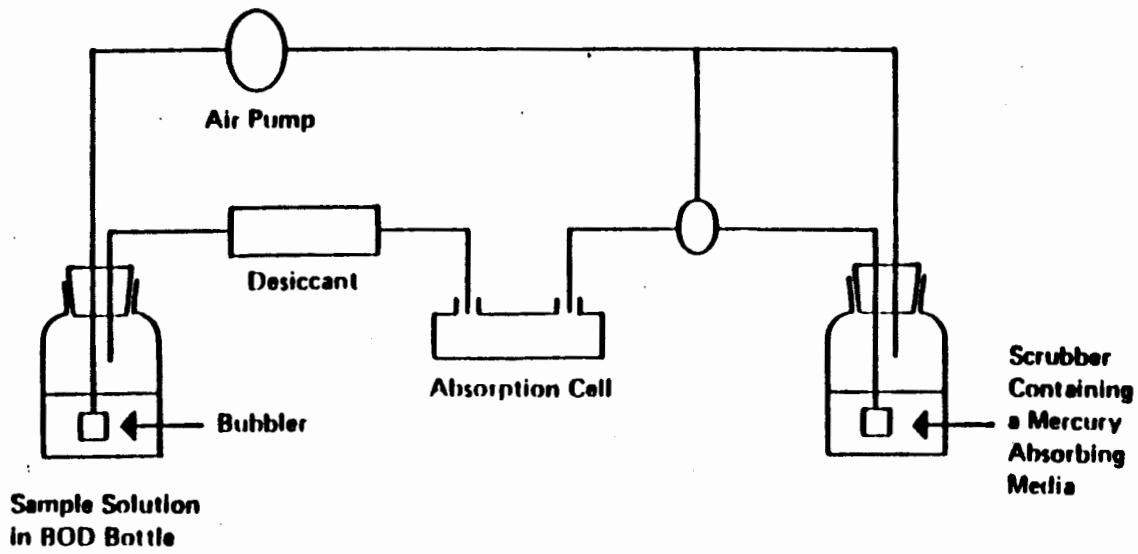

Figure 1. Apparatus for flameless mercury determination.

4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4

2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml (1.0 ml = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before adding the aliquot.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 For solids or semi-solids, moisture may be driven off in a drying oven at a temperature of 60° C.

7.0 Procedure

7.1 Sample preparation: Weigh triplicate 0.2-g portions of dry sample and place in the bottom of a BOD bottle. Add 5 ml of Type II water and 5 ml of aqua regia. Heat 2 min in a water bath at 95° C. Cool, add 50 ml Type II water and 15 ml potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Add 55 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. Add 5 ml of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121° C and 15 lb for 15 min. Cool, dilute to a volume of 100 ml with Type II water and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-ml aliquots of the mercury working standard containing 0 to 1.0 µg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia and heat 2 min in a water bath at 95° C. Allow the sample to cool and add 50 ml Type II water and 15 ml of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate solution and immediately attach to bottle to the aeration apparatus and continue as described in Section 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen

levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass value, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 µg/l.

3.0 Interferences

3.1 Elemental selenium and many of its compounds are volatile and therefore samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction must be employed to avoid erroneously high results.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (more than 800 mg/l) and sulfate (more than 200 mg/l). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000 µl as required.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Selenium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 ml.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2, and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability

of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other instrument parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors

must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 7761

SILVER (ATOMIC ABSORPTION, FURNACE METHOD)

1.0 Scope and Application

1.1 Method 7761 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis by Method 7761, samples must be prepared in order to convert organic forms of silver to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the silver concentration.

2.3 The typical detection limit for this method is 0.2 µg/l.

3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, silver analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Silver nitrate solutions are light sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Silver hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$), analytical reagent grade, in Type II water. Add 5 ml concentrated HNO_3 and bring to volume in a 500-ml volumetric flask.

5.4 Silver working standards: These standards should be be prepared with nitric acid such that the final acid concentration is 0.5% (v/v) HNO_3.

5.5 Concentrated ammonium hydroxide (NH_4OH): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.6 Iodine solution (IN): Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 ml Type II water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 ml. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 ml deionized distilled water add 4.0 ml concentrated NH_4OH, 6.5 g KCN, and 5.0 ml of iodine solution. Mix and dilute to 100 ml with deionized distilled water. Do not keep longer than 2 weeks. CAUTION: This reagent cannot be mixed with any acid solutions since highly toxic hydrogen cyanide will be produced.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Section 7.2; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc. HNO_3. Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc. HNO_3. Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Note, if the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic type samples.

7.2.1 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3, and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. CAUTION: This can only be done after digestion to prevent formation of toxic hydrogen cyanide under acid conditions. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. CAUTION: cyanogen iodide must not be added to the acidified silver standards. New standards must be made as directed in Sections 5.4 and 5.5 except that the acid addition step must be omitted. Transfer 10 ml of stock solution to a small beaker. Add Type II water to make about 80 ml. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 ml cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100-ml volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be used.

7.5 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.6 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.7 Inject a measured µl aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.8 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.9 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.10 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.11 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.12 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.