HANFORD ENVIRONMENTAL ANALYTICAL METHODS
(METHODS AS OF MARCH 1990)

APPENDIX A1-0 AND APPENDIX A1-I

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HEHF Laboratory: Organic

Appendix Number	Lab Number	Method Name	Analytes
A1-0.10	EPA 502.2	Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series	Volatile Organics
A1-0.20	EPA 505	Analysis of Organohalide Pesticides and Aroclors in Water by Microextraction and Gas Chromatography	Organohalide Pesticides Aroclors
A1-0.30	EPA 515.1	Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector	Chlorinated Acids
A1-0.40	EPA 600/4-81/045	The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils	PCBs
A1-0.60	EPA 610	Polynuclear Aromatic Hydrocarbons	PAHs
A1-0.70	NIOSH 5506	Polynuclear Aromatic Hydrocarbons	PAHs
A1-0.80	EHS 0-4	Oil and Grease in Water - Infrared	Oil and Grease
A1-0.90	EPA 508	Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector	Chlorinated Pesticides

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HEHF Laboratory: Organic

<u>Appendix Number</u>	<u>Lab Number</u>	<u>Method Name</u>	<u>Analytes</u>
A1-0.100	EHS G-1	Organic Waste Characterization Using GC/MS Injection	Volatile Organics
A1-0.110	EHS P-2	Phenols in Water Chloroform Extraction	Phenols
A1-0.120	EHS V-2	Volatile Organic Chemical Analysis by Purge and Trap GC	Volatile Organics
A1-0.130	EHS P-8	Polychlorinated Biphenyls in Soil and Sediment	PCBs
A1-0.140	EHS P-9	Polychlorinated Biphenyls in Oil and Waste Liquids	PCBs

METHOD 502.2. VOLATILE ORGANIC COMPOUNDS IN WATER BY
PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY
WITH PHOTOIONIZATION AND ELECTROLYTIC
CONDUCTIVITY DETECTORS IN SERIES

(September, 1986)

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. (1,2) The following compounds can be determined by this method:

<u>Analyte</u>	<u>Chemical Abstract Services Registry Number</u>
- Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane *	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene *	104-51-8
sec-Butylbenzene *	135-98-8
tert-Butylbenzene *	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene *	95-49-8
4-Chlorotoluene *	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane * - extr. Method 504	96-12-8
1,2-Dibromoethane ? - extr. Method 504	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4

* State Specific

----- = not on 601, 602 or in ^{mixes} still currently on order.

<u>Analyte</u>	<u>Chemical Abstract Services Registry Number</u>
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
Ethylbenzene	100-41-4
Hexachlorobutadiene *	87-68-3
Isopropylbenzene *	98-82-8
p-Isopropyltoluene *	99-87-6
Methylene chloride	75-09-2
Naphthalene *	91-20-3
n-Propylbenzene *	103-65-1
Styrene *	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene *	87-61-6
1,2,4-Trichlorobenzene *	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene *	95-63-6
1,3,5-Trimethylbenzene *	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

- 1.2 Method detection limits (MDLs) (3) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e., xylenes) may be hampered by coelution.

- 1.3 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low $\mu\text{g/L}$ level or by experienced technicians under the close supervision of a qualified analyst.

2. SUMMARY OF METHOD

- 2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 5 mL aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components onto a capillary gas chromatography (GC) column. The column is temperature programmed to separate the method analytes which are then detected with a photoionization detector (PID) and a halogen specific detector placed in series.
- 2.2 Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Additional confirmatory information can be gained by comparing the relative response from the two detectors. Each identified component is measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3. INTERFERENCES

- 3.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.1.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Fig. 1). Subtracting blank values from sample results is not permitted.
- 3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be

necessary to wash out the purging device with a soap solution, rinse it with reagent water, and then dry it in an oven at 105°C between analyses.

- 3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4. SAFETY

- 4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.
- 4.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

- 5.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.
- 5.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

5.2.1 The all glass purging device (Fig. 1) must be designed to accept 5-mL samples with a water column at least 5 cm deep. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so that the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point $\leq$ 5 mm from the base of the water column.

5.2.2 The trap (Fig. 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 6 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

5.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the adsorbent from aerosols, and also of insuring that the adsorbent is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

5.2.4 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

5.2.5 Figures 3 and 4 show typical flow patterns for the purge-sorb and desorb modes.

5.3 GAS CHROMATOGRAPH

5.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program

operation. The column oven must be cooled to $<10^{\circ}\text{C}$ (Sect. 5.3.2), therefore, a subambient oven controller is required. The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors. The photoionization and electroconductivity detector are connected with a short piece of uncoated capillary tubing, 0.32 - 0.5mm ID.

5.3.2 Gas Chromatographic Column - 60m long x 0.75mm ID VOCOL (Supelco, Inc.) wide-bore capillary column with 1.5 μm film thickness, or equivalent. The flow rate of helium carrier gas is adjusted to about 6 mL/min. The column temperature is held for 8 minutes at 10°C , then programmed to 180°C at $4^{\circ}\text{C}/\text{min}$, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Fig. 5. This column was used to develop the method performance statements in Section 12.

5.3.3 A high temperature photoionization detector equipped with a 10.2 eV lamp is required (Tracor Model 703 or equivalent).

5.3.4 An electrolytic conductivity or microcoulometric detector is required. These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data. The operating conditions used to collect these data are as follow:

Reactor tube:	Nickel 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

5.4 SYRINGE AND SYRINGE VALVES

5.4.1 Two 5-mL glass hypodermic syringes with Luer-Lok tip.

5.4.2 Three 2-way syringe valves with Luer ends.

5.4.3 One 25- μL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

5.4.4 Micro syringes - 10, 100 μL .

5.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

5.5 MISCELLANEOUS

- 5.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 TRAP PACKING MATERIALS

- 6.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).
- 6.1.2 Methyl silicone packing (optional) - OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.
- 6.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.
- 6.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

6.2 REAGENTS

- 6.2.1 Methanol - Demonstrated to be free of analytes.
- 6.2.2 Reagent water - Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.
- 6.2.3 Hydrochloric acid (1+1) - Carefully add a measured volume of conc. HCl to equal volume of reagent water.
- 6.2.4 Vinyl chloride - 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

- 6.3 STANDARD STOCK SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

- 6.3.1 Place about 9.8 mL of methanol into 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 and weigh to the nearest 0.1 mg.

- 6.3.2 If the analyte is a liquid at room temperature, use a 100- μ L syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.
- 6.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.
- 6.3.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.
- 6.4 SECONDARY DILUTION STANDARDS - Use standard stock solutions to prepare secondary dilution standard solutions that contain the analytes in methanol. The secondary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions (Sect. 8.1) that will bracket the working concentration range. Store the secondary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions from them. Storage times described for stock standard solutions in Sect. 6.3.4 also apply to secondary dilution standard solutions.
- 6.5 INTERNAL STANDARD SPIKING SOLUTION -- Prepare a spiking solution containing fluorobenzene, and 2-bromo-1-chloropropane in methanol using the procedures described in Sect. 6.3 and 6.4. It is recommended that the secondary dilution standard be prepared at a concentration of 5 μ g/mL of each internal standard compound. The addition of 10 μ L of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10 μ g/L.
- 6.6 LABORATORY QUALITY CONTROL CHECK STANDARD CONCENTRATE - Using standard stock solutions, prepare a solution containing each analyte of interest at a concentration of 100 times the maximum contaminant level (MCL) or 1 μ g/mL, whichever is smaller, in methanol.

4/28/88

its reported effectiveness in the analysis of photographic industry effluents. Although the direction given Method 272.1 appears straightforward, caution should be exercised in its use. It is important that the sample is basic ($\text{pH} > 7$) prior to the addition of the CNI reagent to eliminate the possible formation of volatile hydrogen cyanide. Also, the CNI reagent should be added to the sample in an exhaust hood as a precautionary measure. Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided. For the atomic absorption analysis of these samples where the "total metal" digestion is not adequate, the use of an aqueous buffer of sodium thiosulfate and sodium hydroxide should be substituted for the CNI procedure. The conditions for the use of the buffer are described in footnote 28 to Table 1B—List of Approved Inorganic

Test Procedures given on page 33546 of the Federal Register, Vol. 52, No. 171, September 3, 1987. For your convenience that entire footnote as given is restated below:

²⁸ Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halide such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M $\text{Na}_2\text{S}_2\text{O}_3$ and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

Comments concerning this recommendation are welcome.

(Theodore Martin, FTS: 684-7312; COML: 513-569-7312)

Sampling and Field Measurement Section

Intergovernmental Personnel Act (IPA) Assignment

Dr. Fred Kawahara has completed a six-month IPA assignment with the National Bureau of Standards (NBS). During this period Dr. Kawahara has investigated various techniques of coating glass beads using silanes to compliment the work of NBS in developing an analytical method for aromatics with antigens

coated on glass beads. Using C-14 assay techniques, he explored the degree of silanization of glass beads using 4-imino-butyl dimethyl ethoxy silane. Antigens are then acylated on the imino groups for activation of the analytical method.

(Joseph Roesler, FTS: 684-7286; COML: 513-569-7286)

Organic Analyses

Note on Preservation of Drinking Water Samples to be Analyzed for Volatile Organic Chemicals (VOCs) and 1445 Monitoring Compounds

Recipients and users of the September 1986 "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water" should note that a modification to the preservation technique is being made. Continuing use and evaluation of the methods has shown that chlorinated waters must be dechlorinated prior to acidification in order to prevent the chlorination of certain method analytes/aromatic compounds that may be present. The dechlorination step must be added to Methods 502.1, 503.1, 524.1, and 524.2. The methods now being reset for printing have been edited to read as follows:

7.1 Sample Collection

7.1.1 If the sample is expected to contain free or combined chlorine, add ascorbic acid (8) or sodium thiosulfate to the sample to arrest formation of trihalomethanes or other chlorinated artifacts. Ascorbic acid (25 mg/40mL) or sodium thiosulfate (3 mg/40 mL) should be added to the empty sample bottle prior to shipping to the sampling site.

Recent data on preservation of volatiles has shown that thiosulfate cannot be used as a free-chlorine

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

- 7.1.1 Collect all samples in duplicate. Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.
- 7.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.
- 7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the container.

7.2 SAMPLE PRESERVATION

- 7.2.1 Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume.(7) Seal the sample bottles, PFTE-face down, and shake vigorously for one minute.
- 7.2.2 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

7.3 SAMPLE STORAGE

- 7.3.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.
- 7.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 PREPARATION OF CALIBRATION STANDARDS

- 8.1.1 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method or the detection system.

- 8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be discarded after one hour unless sealed and stored as described in Sect. 7.2.

8.2 CALIBRATION

- 8.2.1 Analyze each calibration standard according to Sect. 10, adding 10 μ L of internal standard spiking solution directly to the syringe. Tabulate area response versus the concentration for each analyte and internal standard. Calculate response factors (RF) for each analyte using Equation 1:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \quad \text{Equation 1}$$

where:

A_s = Area for the analyte to be measured;
 A_{is} = Area for the internal standard;
 C_{is} = Concentration of the internal standard, in μ g/L.
 C_s = Concentration of the analyte to be measured, in μ g/L.

The choice of which internal standard to use for an analyte is left to the analyst.

- 8.2.2 Prepare a calibration curve for each analyte. Alternatively, if the RF for an analyte is constant (less than 15% RSD) over the working range, the average RF can be used for that analyte.
- 8.2.3 The working calibration curve or average response factor must be verified on each working day by the measurement of one or more calibration standards. If the area for any analyte varies from the response determined for that standard concentration from the calibration curve or average RF established in Sect. 8.2.2 by more than $\pm 20\%$, repeat steps 8.2.1 and 8.2.2.
- 8.2.4 Calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps. The procedure requires use of a modified purge vessel having a septum seal port in the expanded part of the device.

8.2.4.1 Fill the purging device with 5.0 mL of reagent water or aqueous calibration standard, and add internal standards.

8.2.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 μ L) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 μ L/min. Do not inject the standard through the aqueous sample inlet needle. Inject the gaseous standard before five min of the 11-min purge time have elapsed.

8.2.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard injected in μ g/L, according to Equation 2:

$$S = 0.510 (C)(V) \quad \text{Equation 2}$$

where S = Aqueous equivalent concentration of vinyl chloride standard in μ g/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliters.

9. QUALITY CONTROL

9.1 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 an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2.

- 9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.
- 9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 9.3. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but at least two samples per month.
- 9.1.5 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples. A procedure for low level check samples is described in Section 9.4.
- 9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 9.5.
- 9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.
 - 9.2.1 A quality control (QC) check sample concentrate is required containing each regulated analyte, and any additional analyte which is to be reported, at a concentration of 100 times the MCL or 1 $\mu\text{g/mL}$, whichever is smaller, in methanol. The QC check sample must be prepared by the laboratory using stock standards prepared independently from those used for calibration.
 - 9.2.2 Analyze seven 5-mL QC check samples at 1/5 MCL or 2 $\mu\text{g/L}$ according to the method beginning in Sect. 10. Each sample is produced by injecting 10 μL of QC check sample concentrate into 5 mL of reagent water in a glass syringe through the syringe valve.
 - 9.2.3 Calculate the average recovery ($\bar{X}$) in $\mu\text{g/L}$, and the standard deviation of the recovery (s) in $\mu\text{g/L}$ for each analyte using the seven results. Calculate the MDL for each analyte as specified in Ref. 2. The calculated MDL must be less than the spike level.
 - 9.2.4 For each analyte, ($\bar{X}$) must be between 80% and 120% of the true value. Additionally, s must be $< 30\%$ of $\bar{X}$. If s and $\bar{X}$ for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limit or any $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that analyte.

NOTE: The large number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are determined.

- 9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must repeat the test according to Section 9.2.2 only for the analytes which failed the test.
- 9.3 The laboratory must demonstrate on a regular basis, as outlined in Sect. 9.1.4, that the measurement system is in control by analyzing a quality control sample for all analytes of interest at the MCL or 10 µg/L, whichever is smaller.
 - 9.3.1 Prepare a QC check standard by adding 50 µL of QC check sample concentrate to 5 mL of reagent water in a glass syringe.
 - 9.3.2 Analyze the QC check according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value.
 - 9.3.3 If the recovery for any analyte falls outside the designated range, the analyte has failed the acceptance criteria. A check standard containing each failed analyte must be re-analyzed.
- 9.4 On a weekly basis, the laboratory must demonstrate the ability to analyze low level samples.
 - 9.4.1 Prepare a low level check sample by adding 10 µL of QC check sample concentrate to 5 mL of reagent water in a 5 mL syringe. Analyze according to the method in Sect. 10.
 - 9.4.2 For each analyte, the recovery must be between 60% and 140% of the expected value.
 - 9.4.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.4.1.
- 9.5 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 duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. PROCEDURE

10.1 INITIAL CONDITIONS

10.1.1 Recommended chromatographic conditions are summarized in Section 5.3.2. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Section 9.2 are met.

10.1.2 Calibrate the system daily as described in Section 8.2.

10.1.3 Adjust the purge gas (nitrogen or helium) flow rate to about 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.2 SAMPLE INTRODUCTION AND PURGING

10.2.1 Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Add 10 μ L of the internal calibration standard to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

10.2.2 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 $\pm$ 0.1 min at ambient temperature (Figures 1 and 3).

10.3 SAMPLE DESORPTION - After the 11-min purge, couple the trap to the chromatograph by switching the purge and trap system to the desorb mode (Figure 4), initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas flow of 6 mL/min for 4.0 $\pm$ 0.1 min. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5-mL flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

10.4 TRAP RECONDITIONING - After desorbing the sample for four min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11. CALCULATIONS

11.1 Identify each analyte in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory quality control standard (Sect. 8.2.2) on the appropriate detector. When applicable, determine the relative response of the alternate detector to the analyte. The relative response should agree to within 20% of relative response determined from standards.

11.2 When both detectors respond to an analyte, quantitation is usually performed on the detector which exhibits the greater response. However, in cases where greater specificity or precision would result, the analyst may choose the alternate detector.

11.3 Determine the concentration of the unknowns by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows:

$$C_u = \frac{A_u}{A_{is}} \times \frac{C_{is}}{RF} \quad \text{Equation 3}$$

where: C_u = Concentration of the analyte in sample, in $\mu\text{g/L}$
 C_{is} = Concentration of the internal standard, in $\mu\text{g/L}$
 A_u = Peak area of the analyte
 A_{is} = Peak area of the internal standard
 RF = Relative response factor

11.4 Report the results for the unknown samples in $\mu\text{g/L}$. Round off the results to the nearest 0.1 $\mu\text{g/L}$ or two significant figures.

12. ACCURACY AND PRECISION

12.1 This method was tested in a single laboratory using reagent water spiked at 10 $\mu\text{g/L}$ (8). Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

12.2 Method detection limits for these analytes have been calculated from data collected by spiking reagent water at 0.1 $\mu\text{g/L}$. These data are presented in Table 1.

13. REFERENCES

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4. "Carcinogens—Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August, 1977.
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Table 1. CHROMATOGRAPHIC RETENTION TIMES AND
METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS
ON PHOTOIONIZATION DETECTION (PID) AND
HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time, ^a min.	HECD Ret. Time, min.	PID MDL, µg/L	HECD MDL µg/L
Dichlorodifluoromethane	- ^b	8.47		.05
Chloromethane	-	9.47		.03
Vinyl Chloride	9.88	9.93	0.02	.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	N.D. ^c	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		N.D.
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethyl benzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropyl benzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

Table 1 (Continued)

Analyte	PID Ret. Time, ^a min.	HECD Ret. Time, min.	PID MDL, µg/L	HECD MDL µg/L
n-Propyl benzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethyl benzene } 2-Chlorotoluene } 4-Chlorotoluene }	41.41 41.41 41.60	- 41.45 41.63	0.004 N.D. 0.02	 0.01 0.01
tert-Butyl benzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3 Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	N.D.	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

a. Retention times determined on 60m x 0.75mm ID VOCOL capillary column.
Program: Hold at 10°C for 8 mins, then program at 4°C/min to 180°C, and
hold until all expected compounds have eluted.

b. - Dash indicates detector does not respond.

c. N.D. = Not Determined

Table 2. SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, ^a %	Standard Deviation of Recovery	Recovery, ^a %	Standard Deviation of Recovery
Benzene	99	1.2	- ^b	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	N.D. ^c	N.D.	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	N.D.	N.D.	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

Table 2. (Continued)

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, ^a %	Standard Deviation of Recovery	Recovery, ^a %	Standard Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	-
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

a. Recoveries and standard deviations were determined from seven samples spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

b. Detector does not respond.

c. N.D. = not determined.

Figure 1. Purging device

Figure 2. Trap packings and construction to include desorb capability

Figure 3. Purge and trap system - purge mode.

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

COLUMN: 60 METER X 0.75 MM I.D. VOCOL CAPILLARY

PURGE AND TRAP VOC'S WITH HALL & PID IN SERIES

Figure 5. Gas chromatogram of volatile organics.

Draft Method 505- For Use in WS023 Only

ANALYSIS OF ORGANOHALIDE PESTICIDES AND AROCLORS IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

- 1.1 This method (1,2,3) is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water:

Analyte	CAS No.
Alachlor	19872-80-8
Aldrin	308-00-2
Atrazine	1912-24-9
Chlordane	57-74-9
alpha-Chlorodane	5103-71-9
gamma-Chlorodane	5103-74-2
Dieldrin	60-67-1
Endrin	72-20-8
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-74-4
Lindane	56-88-9
Methoxychlor	72-43-5
cis-Nonachlor	
trans-Nonachlor	39785-80-5
Simazine	122-34-9
Toxaphene	8001-35-2
Aroclor 1016	12874-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53489-21-9
Aroclor 1248	12872-29-6
Aroclor 1254	11087-69-1
Aroclor 1260	11098-82-5

- 1.2 PCBs are determined as Aroclors by this method.
- 1.3 For compounds other than the above mentioned analytes or for other sample sources, the analyst must demonstrate the applicability of the method by collecting precision and accuracy data on actual samples (4) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (5), or by GC analysis using dissimilar columns.
- 1.4 Method detection limits (MDL) (6) for the above organohalides and Aroclors have been experimentally determined (Sect.

12.1). Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used (e.g. column type, age, and proper conditioning; detector condition; and injector mode and condition).

2. SUMMARY OF METHOD

- 2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. Two μ L of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.
- 2.2 The extraction and analysis time is 30 to 50 min per sample depending upon the analytes and the analytical conditions chosen. (See Sect. 5.9)
- 2.3 Confirmatory evidence can be obtained using a dissimilar column. When component concentrations in water samples are sufficiently high, GC/MS may be employed.

3. INTERFERENCES

- 3.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the laboratory reagent blanks (Sect. 9.4). Whenever an interference is noted in the sample blank, the analyst should analyze another solvent blank. Low level interferences generally can be removed by distillation or column chromatography (3); however, it is generally more economical to obtain a new source solvent. An interference-free solvent is a solvent containing non-detectable peaks at the retention times of the analytes of interest.
- 3.2 Caution must be taken in the determination of endrin since it has been reported

that the splitless injector may cause endrin degradation (7). The analyst should be alerted to this possible interference resulting in an erratic response for endrin.

- 3.3 Variable amounts of pesticides and Aroclors from aqueous solutions adhere to glass surfaces. It is recommended that sample transfers and glass surface contacts be minimized.
- 3.4 Aldrin and methoxychlor are rapidly oxidized by chlorine. Dechlorination with sodium thiosulfate at time of collection will retard further oxidation of these compounds.

4. SAFETY

- 4.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (9-10) for the information of the analyst.
- 4.2 The following organohalides have been tentatively classified as known or suspected human or mammalian carcinogens: aldrin, Aroclors, chlordane, dieldrin, heptachlor, hexachlorobenzene, and toxaphene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/ MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. APPARATUS AND EQUIPMENT

- 5.1 SAMPLE CONTAINERS - 40-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a size 24 cap with a flat, disc-like TFE facing backed with a polyethylene film/foam extrusion (Fisher #02-883-3F or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place the vials in a 400°C oven for one hour, then remove and allow to cool in an area known to be free of organics.
- 5.2 VIALS - auto sampler, screw cap with

septa, 1.8 mL, Varian #96-000099-00 or equivalent or any other autosampler vials not requiring more than 1.8 μ L sample volumes.

- 5.3 AUTO SAMPLER - Hewlett-Packard 7671A, or equivalent.
- 5.4 MICRO SYRINGES - 10 and 100 μ L
- 5.5 MICRO SYRINGE - 25 μ L with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.
- 5.6 PIPETTES - 2.0 and 5.0 mL transfer.
- 5.7 VOLUMETRIC FLASKS - 10 and 100 mL glass stoppered.
- 5.8 STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.
- 5.9 GAS CHROMATOGRAPH - Analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.
 - 5.9.1 Three gas chromatographic columns are recommended. Column 1 (Sect. 5.9.2) should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Validation data presented in this method were obtained using this column. Columns 2 and 3 are recommended for use as confirmatory columns when GC/MS confirmation is not available. Alternative columns may be used in accordance with the provisions described in Sect. 9.3.
 - 5.9.2 Column 1 (Primary Column) - 0.32 mm ID x 30 M long fused silica capillary with chemically bonded methyl polysiloxane phase (DB-1, 1.0 μ m film, or equivalent). Helium carrier gas flow is established at 25 cm/sec linear velocity and oven temperature is programmed from 180°C to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted. A sample chromatogram for selected pesticides is presented in Figure 505-1. Chromatograms of the Aroclors, toxaphene, and technical chlordane are presented in Figures 505-2 through 505-10.

5.9.3 Column 2 (Confirmation Column) - 0.32mm ID x 30 M long fused silica capillary with a 1:1 mixed phase of dimethyl silicone and polyethylene glycol (Durawax-DX3, 0.25 μ m film, or equivalent). Helium carrier gas flow is established at 25 cm/sec linear velocity and oven temperature is programmed from 100°C to 210°C at 8°C/min, and held at 210°C until all expected compounds have eluted. Then the post temperature is programmed to 240°C at 8°C/min for 5 min.

5.9.4 Column 3 (Confirmation Column) - 0.32mm ID x 25 M long fused silica capillary with chemically bonded 50:50 Methyl-Phenyl silicone (OV-17, 1.5 μ m film thickness, or equivalent). Helium carrier gas flow is established at 40 cm/sec linear velocity and oven temperature is programmed from 100°C to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted.

Table 1. Retention Times for Method Analytes

Analyte	Primary	Retention Time(a), Min	
		Confirm. 1	Confirm. 2
Hexachlorocyclopentadiene	5.5	(b)	(b)
Simazine	10.9	(b)	(b)
Atrazine	11.2	(b)	(b)
Hexachlorobenzene	11.9	13.4	15.6
Undane	12.3	18.4	18.7
Alachlor	15.1	19.7	21.1
Heptachlor	15.9	17.5	20.0
Aldrin	17.6	18.4	21.4
Heptachlor Epoxide	19.0	24.6	24.6
gamma-Chlordane	20.1	(b)	(b)
alpha-Chlordane	20.9	(b)	(b)
trans-Nonachlor	21.3	(b)	(b)
Dieldrin	22.1	45.1	27.8
Endrin	24.2	33.3	29.2
cis-Nonachlor	24.3	(b)	(b)
Methoxychlor	30.0	(b)	36.4

Primary(c)

Aroclor 1016	13.6, 14.8, 15.2, 16.2, 17.7
Aroclor 1221	7.7, 9.0, 15.9, 19.1, 24.7
Aroclor 1232	11.2, 14.7, 13.6, 15.2, 17.7
Aroclor 1242	11.2, 13.6, 14.7, 15.2, 17.7, 19.8
Aroclor 1248	14.8, 16.2, 17.1, 17.7, 19.8, 22.0
Aroclor 1254	19.1, 21.9, 23.4, 24.9, 26.7
Aroclor 1260	23.4, 24.9, 26.7, 28.2, 29.9, 32.6
Chlordane	15.1, 15.9, 20.1, 20.9, 21.3
Toxaphene	21.7, 22.5, 26.7, 27.2

(a) Columns and analytical conditions are described in Sect. 5.9.2, 5.9.3, and 5.9.4.

(b) Not determined.

(c) Column and conditions described in Sect. 5.9.2. More than one peak listed does not implicate the total number of peaks characteristic of the multi-component analyte. Listed peaks indicate only the ones chosen for quantification.

solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedures:

6.3.1 Prepare stock standard solutions (5000 μ g/mL) by accurately weighing about 0.0500 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 REAGENTS

6.1.1 Hexane extraction solvent - UV Grade, Burdick and Jackson #216 or equivalent.

6.1.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

6.1.3 Sodium chloride, NaCl - ACS Reagent Grade - For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C and hold for 30 min. Place in a bottle and cap.

6.1.4 Sodium thiosulfate, Na₂S₂O₃, ACS Reagent Grade--For preparation of solution (0.04 g/mL), mix 1 g of Na₂S₂O₃ with reagent water and bring to 25-mL volume in a volumetric flask.

6.2 REAGENT WATER - Reagent water is defined as water free of interference when employed in the procedure described herein.

6.2.1 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

6.2.2 Test reagent water each day it is used by analyzing it according to Sect. 10.

6.3 STANDARD STOCK SOLUTIONS - These

samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be maintained at 4°C until arrival at the laboratory.

7.3 SAMPLE STORAGE

- 7.3.1 Store samples and extracts at 4°C until extraction and analysis.
- 7.3.2 Extract all samples as soon as possible after collection. Results of holding time studies suggest that all analytes (aldrin, dieldrin, endrin, heptachlor epoxide, hexachlorobenzene, lindane, and the aroclors) with the possible exception of heptachlor may be extracted within 14 days after collection. In general, heptachlor showed inconsistent results. If heptachlor is to be determined, samples must be extracted within 7 days of collection. Samples from which analytes have not been extracted within these prescribed periods of time must be discarded and replaced.

8. CALIBRATION AND STANDARDIZATION

8.1 CALIBRATION

- 8.1.1 At least three calibration standards are needed. One should contain analytes at a concentration near but greater than the method detection limit for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 µg/L, 0.10 µg/L, and 0.20 µg/L.
- 8.1.2 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard to a 35-mL aliquot of reagent water in a 40-mL bottle. Do not add less than 20 µL of an alcoholic standard to the reagent water. Use a 25-µL micro syringe and rapidly inject the alcoholic standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Mix by inverting and shaking the capped bottle several times. Aqueous standards must be prepared fresh daily.
- 8.1.3 Starting with the standard of lowest concentration, prepare, extract, and analyze each calibration standard beginning with Sect. 10.2 and tabulate

peak height or area response versus the concentration in the standard. The results are to be used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (a relative standard deviation), linearity to the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

- 8.1.4 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 an analyte varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 8.1.5.

- 8.1.5 Single point calibration is an acceptable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close ($\pm 20\%$) to that of the unknowns. Do not use less than 20 µL of the secondary dilution standard solution to produce a single point calibration standard in reagent water.

- 8.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent blanks, standards, duplicate samples, and the laboratory control standard (Sect. 9.6).

- 8.2.1 Significant peak tailing in excess of that shown for the target compounds in the method chromatograms (Figures 1-10) must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or the detector operation.
- 8.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port. If the GC system is apparently performing acceptably but with decreased

sensitivity, it may be necessary to generate a new curve or set of calibration factors to verify the decreased responses.

- 8.2.3 Observed relative area responses of endrin must meet the following criteria: endrin 50% of total area.

9. QUALITY CONTROL

- 9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, analysis of method blanks, instrument QC solution, laboratory control (LC) standards, QC samples, and performance evaluation (PE) samples.

- 9.2 Method Blanks. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a method blank must be analyzed. If within the retention time window of any analyte the method blank produces a peak that is 0.5 EDL for that analyte, determine the source of contamination and eliminate the interference before processing samples.

- 9.3 Initial Demonstration of Capability.

- 9.3.1 Select a representative spike concentration (about 10 times MDL) for each analyte. Prepare a LC sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 35 μ L of the concentrate to each of at least four 35-mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 10.

- 9.3.2 Calculate mean percent recovery (X), and standard deviation of percent recovery (S). For each analyte, X must fall in the range of 70-130% (or within $R \pm 3\text{RSD}$ using the values for R and RSD for reagent water in Table 2) and S must be less than 30% (or less than $3 \times \text{RSD}$ in reagent water in Table 2). If the calculated X and S for every analyte meet the acceptance criteria, performance is acceptable and sample analysis may begin. If any X or S falls outside its acceptance range, initial demonstration procedures for that compound must be repeated.

- 3.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical

costs. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3

9.5 Assessing Laboratory Performance

- 9.5.1 Initial QC criteria are established by using the values for X and S generated above (Sect. 9.3) to establish upper and lower control limits:

$$\begin{aligned}\text{UPPER CONTROL LIMIT} &= X + 3S \\ \text{LOWER CONTROL LIMIT} &= X - 3S\end{aligned}$$

The laboratory must analyze at least one LC sample per sample set (all samples extracted within a 24-h period). The spiking concentration of each analyte in the laboratory control sample should be 10 times EDL. Calculate accuracy as percent recovery (X). If the recovery of any analyte falls outside the control limits, that analyte is judged out of control, and the source of the problem must be identified and resolved before continuing analyses. The control limits should be updated periodically. It is recommended that after each five to ten new recovery measurements that new control limits be calculated using only the most recent 20-30 data points.

- 9.5.2 Each quarter the laboratory must analyze QC check standards (if available). If criteria provided with the QC check standard are not met, corrective action should be taken and documented.

- 9.5.3 At least once a year, the laboratory must analyze a performance evaluation sample (if available), and results for each analyte must be within established acceptance limits.

- 9.6 Analyte Confirmation - When doubt exists about identification of a GC peak, confirmatory techniques such as determination with a mass spectrometer detector or a different GC column must be used.

10. PROCEDURE

10.1 SAMPLE PREPARATION

- 10.1.1 Remove samples from storage and allow them to equilibrate to room temperature.

- 10.1.2 Remove the container caps. Withdraw and discard a 5-mL volume using a transfer pipet. Replace the container caps and weigh the containers with contents to the nearest 0.1 g and record

these weights for subsequent sample volume determinations (Sect. 10.3).

- 10.1.3 Remove the container cap of each sample, and add 6 g NaCl (Sect. 6.1.3) to the sample bottle. Recap and dissolve the NaCl by inverting and shaking the bottles several times (approx. 20 sec).

10.2 EXTRACTION AND ANALYSIS

- 10.2.1 Remove the cap, and using a transfer or automatic dispensing pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Invert the bottle and allow the water and hexane phases to separate.
- 10.2.2 Remove the cap and carefully transfer approximately 0.5 mL of hexane layer into an autosampler vial using a disposable glass pipet.
- 10.2.3 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler vial. Reserve this second vial at 4°C for an immediate reanalysis if necessary.
- 10.2.4 Transfer the first sample vial to an autosampler set up to inject 1-2 mL portions into the gas chromatograph for analysis (See Sect. 5.9 for GC conditions). Alternately, 1-2 mL portions of samples, blanks, and standards may be manually injected, although an autosampler is strongly recommended.

10.3 DETERMINATION OF SAMPLE VOLUME IN BOTTLES NOT CALIBRATED

- 10.3.1 Discard the remaining sample/hexane mixture from the sample bottle. Shake off the remaining few drops using short, brisk wrist movements.
- 10.3.2 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g (Sect. 10.1.2 minus Section 10.3.2). This net weight (in grams) is equivalent to the volume (in mL) of water extracted (Sect. 11.3).

11. CALCULATIONS

- 11.1 Identify the organohalides in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory control standard. Identify the multicomponent compounds using all peaks that are characteristic of the

specific compound from chromatograms generated with individual standards. Select the most sensitive and reproducible peaks for calculation purposes.

- 11.2 Use the calibration curve or calibration factor (Sect. 8.1.3) to directly calculate the uncorrected concentration (C) of each analyte in the sample (e.g., calibration factor x response).

- 11.3 Calculate the sample volume (V_s) as equal to the net sample weight:

$$V_s = \text{gross weight (Sect. 10.1.2)} - \text{bottle tare (Sect. 10.3.2)}.$$

- 11.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu\text{g/L} = \frac{35(C_i)}{(V_s)}$$

- 11.5 Report the results for the unknown samples in $\mu\text{g/L}$. Round off the results to the nearest 0.1 $\mu\text{g/L}$ or two significant figures.

12. ACCURACY AND PRECISION

- 12.1 Single laboratory (EMSL-Cincinnati) accuracy and precision at several concentrations in reagent, ground, and tap water matrices are presented in Table 2.(11) These results were obtained from data generated with a DB-1 column.
- 12.2 This method was tested by 10 laboratories using reagent water and groundwater spiked at three concentration levels. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and virtually independent of the sample matrix. Linear equations to describe the relationships are presented in Table 3.(12)

13. REFERENCES

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Table 2. Single Laboratory Accuracy, Precision and Method Detection Limits (MDLs) for Analytes from Reagent Water, Groundwater, and Tap Water(a)

Analyte	MDL(b) ug/L	Spike Level, ug/L	Reagent R(c)	Water RSD(d)	Ground Water R	RSD	Tap Water R	RSD
Aldrin	0.075	0.15	86	11	100	11	88	13
Alachlor	0.225	0.50	102	13.1	.	.	.	.
Aldrin	0.007	0.05	106	18.9	86	18.9	.	.
Atrazine	2.4	5.0	85	19.1	95	7.7	108	10.1
		20.0	95	5.5	86	10.6	91	3.4
alpha-Chlordane	0.008	0.06	95	3.7	83	5.3	85	8.3
		0.35	86	19.8	94	10.8	91	2.8
gamma-Chlordane	0.012	0.06	95	0.4	86	6.2	83	17.7
		0.35	86	21.5	95	15.3	91	8.8
Chlordane	0.14	0.17	NA	8.0	.	.	105	11.8
		3.4	NA	3.8	.	.	95	10.1
Dieldrin	0.012	0.10	87	19.6	87	15.0	92	17.1
		3.6	114	8.0	94	9.1	81	17.3
Endrin	0.083	0.10	118	25.0	94	21.5	106	13.2
		3.6	99	6.6	100	11.3	85	14.6
Heptachlor	0.003	0.032	77	13.3	37	18.3	200	11.3
		1.2	80	9.3	71	13.8	106	15.8
Heptachlor Epoxide	0.004	0.04	100	15.6	90	15.8	112	6.7
		1.4	115	5.7	103	6.7	81	7.3
Hexachlorobenzene	0.002	0.003	104	13.0	91	12.0	100	15.6
		0.08	103	6.4	101	4.4	88	15.2
Hexachlorocyclopentadiene	0.13	0.15	73	7.0	87	5.9	191	9.7
		0.35	73	16.3	88	7.0	109	13.1
Undane	0.003	0.03	91	7.1	86	6.8	103	7.9
		1.2	111	4.5	108	3.1	93	19.8
Methoxychlor	0.98	2.10	100	21.0	.	.	.	.
		7.03	98	11.1	.	.	.	.
cis-Nonachlor	0.027	0.08	110	13.8	101	7.1	93	15.4
		0.46	82	26.0	83	19.7	87	6.2
trans-Nonachlor	0.011	0.06	98	10.1	83	6.6	73	5.6
		0.35	86	25.3	94	18.3	86	5.9
Simazine	6.8	25	99	8.4	87	9.5	102	13.1
		60	65	5.5	58	30.5	67	9.2
Toxaphene	1.0	10	NA	12.6	.	.	110	8.6
		80	NA	15.3	.	.	114	11.8
Aroclor 1016	0.08	1.0	NA	6.6	.	.	97	7.7
Aroclor 1221	15.0	180	NA	8.3	.	.	92	10.4
Aroclor 1232	0.48	3.9	NA	13.5	.	.	85	6.5
Aroclor 1242	0.31	4.7	NA	6.0	.	.	98	7.7
Aroclor 1248	0.102	3.6	NA	11.5	.	.	.	.
		3.4	.	.	.	.	84	11.8
Aroclor 1254	0.102	1.8	NA	10.4	.	.	.	.
		1.7	.	.	.	.	85	13.9
Aroclor 1260	0.188	2.0	NA	20.7	.	.	.	.
		1.8	.	.	.	.	88	18.0

NA = Not applicable. A separate set of aqueous standards was not analyzed, and the values shown for reagent were used to calculate a recovery for the tap water matrix.

(a) Data corrected for amount detected in blank and represent the mean of 5-6 samples.

(b) MDL = method detection limit in sample in ug/L; calculated by multiplying standard deviation (S) times the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

(c) R = average percent recovery.

(d) RSD = relative standard deviation (percent)

TABLE 3. Method Accuracy and Precision as Functions of Concentration in Reagent Water

Parameter	Applicable Conc. Range (ug/L)	Accuracy as Recovery(X) (ug/L)	Single Analyst Precision(S _r) (ug/L)	Overall Precision(S) (ug/L)
Atrazine	(3.06-45.90)	$1.122C + 0.97$	$0.001x + 1.20$	$0.044x + 2.22$
Simazine	(12.55-50.20)	$0.892C + 1.446$	$-0.125x + 6.412$	$0.193x - 2.716$
Hexachlorobenzene	(0.01-0.37)	$1.028C - 0.00$	$0.108x + 0.00$	$0.227x + 0.00$
Lindane	(0.04-1.39)	$1.009C - 0.00$	$0.057x + 0.01$	$0.142x + 0.00$
Alachlor	(0.50-37.50)	$1.004C - 0.08$	$0.077x + 0.10$	$0.105x + 0.16$
Heptachlor	(0.04-1.41)	$1.002C + 0.02$	$0.107x + 0.01$	$0.211x + 0.02$
Aldrin	(0.04-1.42)	$1.066C + 0.00$	$0.031x + 0.02$	$0.264x - 0.00$
Heptachlor Epoxide	(0.04-1.42)	$0.952C + 0.00$	$0.032x + 0.02$	$0.129x + 0.02$
Dieldrin	(0.10-7.53)	$1.027C + 0.00$	$0.091x + 0.01$	$0.198x + 0.02$
Endrin	(0.10-7.50)	$0.958C + 0.01$	$0.116x + 0.01$	$0.136x + 0.02$
Methoxychlor	(0.20-15.00)	$0.950C + 0.15$	$0.115x + 0.12$	$0.125x + 0.20$
Chlordane	(0.51-50.90)	$1.037C + 0.06$	$0.084x + 0.06$	$0.125x + 0.19$
Toxaphene	(5.63-70.40)	$1.087C + 0.24$	$0.131x - 0.31$	$0.269x + 0.69$
PCB-1016	(0.50-49.80)	$0.856C + 0.31$	$0.106x + 0.31$	$0.147x + 0.45$
PCB-1254	(0.50-50.40)	$0.872C - 0.01$	$0.122x + 0.11$	$0.281x + 0.05$

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 2. Hexane spiked at 11.4 ug/L with Aroclor 1016.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 3. Hexane spiked at 171.4 ug/L with Aroclor 1221.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 4. Hexane spiked at 57.1 ug/L with Aroclor 1232.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 5. Hexane spiked at 57.1 ug/L with Aroclor 1242.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 6. Hexane spiked at 57.1 ug/L with Aroclor 1248.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 7. Hexane spiked at 42.9 ug/L with Aroclor 1254.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 8. Hexane spiked at 34.3 ug/L with Aroclor 1260.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 9. Hexane spiked at 28.6 ug/L with chlordane.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0 μ m
COLUMN DIMENSIONS: 0.32mm ID, 30 M long

Figure 10. Hexane spiked at 57.1 ug/L with toxaphene.

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DETERMINATION OF CHLORINATED ACIDS IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

- 1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water.(1) The following compounds can be determined by this method:

Analyte	CAS No.
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
✓ 2,4-DB	94-75-7
✓ Dalapon	75-89-0
2,4-DB	94-82-6
DCPA acid metabolites	(a)
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-3
✓ DMCa	88-85-7
5-Hydroxydicamba	7600-50-2
4-Nitrophenol	100-02-7
✓ PCP	87-86-5
✓ Aldicarb	1918-02-1
2,4,5-T	93-76-8
✓ 2,4,5-Tp	93-72-1

(a) DCPA acid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies.

- 1.2 This method may be applicable to the determination of salts and esters of analyte acids. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid.
- 1.3 This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for the analytes above (Sect.12). Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.
- 1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate

acceptable results with this method using the procedure described in Sect. 9.3.

- 1.5 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

- 2.1 A measured volume of sample of approximately 1 L is adjusted to pH 12 with 6 N sodium hydroxide and shaken for 1 hour to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed, and the esters are determined by GC using an electron capture detector (ECD).
- 2.2 The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered.

3. INTERFERENCES

- 3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Sect. 9.2.
- 3.1.1 Glassware must be scrupulously cleaned.(2) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap and reagent water. Drain dry.

and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

- 3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.
- 3.2 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with (1+9) hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.
- 3.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.
- 3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.(3,4)
- 3.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and

associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

- 3.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the ground water sampled. The cleanup procedures in Sect. 10 can be used to overcome many of these interferences. Positive identifications should be confirmed using the confirmation column specified in Sect. 5.10.2.

4. SAFETY

- 4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (5-7) for the information of the analyst.
- 4.2 Diazomethane is a toxic carcinogen and can explode under certain conditions. The following precautions must be followed:
 - 4.2.1 Use only a well ventilated hood - do not breath vapors.
 - 4.2.2 Use a safety screen.
 - 4.2.3 Use mechanical pipetting aides.
 - 4.2.4 Do not heat above 90°C - EXPLOSION may result.
 - 4.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirers - EXPLOSION may result.
 - 4.2.6 Store away from alkali metals -- EXPLOSION may result.

- 4.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.
 - 4.2.8 The diazomethane generation apparatus used in the esterification procedures (Sect. 10.4 and 10.5) produces micromolar amounts of diazomethane to minimize safety hazards.
 - 4.3 Ethyl ether is an extremely flammable solvent. If a mechanical device is used for sample extraction, the device should be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.
- 5. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)**
- 5.1 SAMPLING EQUIPMENT**
- 5.1.1 Grab sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in Sect. 3.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.
- 5.2 GLASSWARE**
- 5.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcocks, ground glass or TFE-fluorocarbon stoppers.
 - 5.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.
 - 5.2.3 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.
 - 5.2.4 Evaporative flask, K-D -- 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
 - 5.2.5 Snyder column, K-D -- three-ball macro (Kontes K-503000-0121 or equivalent).
 - 5.2.6 Snyder column, K-D -- two-ball micro (Kontes K-569001-0219 or equivalent).
 - 5.2.7 Flask, round-bottom -- 500-mL with 24/40 ground glass joint.
 - 5.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.
 - 5.2.9 Disposable pipets -- sterile plugged borosilicate glass, 5-mL capacity (Corning 7078-5N or equivalent).
 - 5.3 Separatory funnel shaker -- Capable of holding eight 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI).
 - 5.4 Tumbler -- Capable of holding 4 to 6 tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA).
 - 5.5 Boiling stones -- Teflon, Chemware (Norton Performance Plastics No. 015021).
 - 5.6 Water bath -- Heated, capable of temperature control ($\pm 2^{\circ}\text{C}$). The bath should be used in a hood.
 - 5.7 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.
 - 5.8 Diazomethane generator -- Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen as shown in Figure 515.1-1 (available from Aldrich Chemical Co.). When esterification is performed using diazomethane solution, the diazomethane collector is cooled in an approximately 2-L thermos for ice bath or a cryogenically cooled vessel (Thermoelectrics Unlimited Model SK-12 or equivalent).
 - 5.9 Glass wool -- Acid washed (Supelco 2-0383 or equivalent) and heated at 450°C for 4 hours.
 - 5.10 GAS CHROMATOGRAPH -- Analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.
 - 5.10.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 μm film thickness (available

Table 1. Retention Times for Method Analytes

Analyte	Retention Time (a)	
	Primary	Confirm.
Delapron	3.4	4.7
3,5-Dichlorobenzoic acid	18.6	17.7
4-Nitrophenol	18.6	20.5
DCAA (surrogate)	22.0	14.9
Dicamba	22.1	22.6
Dichlorprop	25.0	25.6
2,4-D	25.5	27.0
DBOH (int. std.)	27.5	27.6
PCP	28.3	27.0
Chloramben	28.7	32.8
2,4,5-TP	29.7	29.5
5-Hydroxydicamba	30.0	30.7
2,4,5-T	30.5	30.9
2,4-DB	32.2	32.2
Dinoseb	32.4	34.1
Bentazon	33.3	34.6

(a) Columns and analytical conditions are described in Sect. 5.10.1 and 5.10.2.

from J&W). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Validation data presented in this method were obtained using this column. Alternative columns may be used in accordance with the provisions described in Sect. 9.2.

5.10.2 Column 2 (Confirmation column) -- 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 µm film thickness (available from J&W). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

5.10.3 Detector -- Electron capture. This detector has proven effective in the analysis of spiked reagent and artificial ground waters. An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Sect. 9.3.

6. REAGENTS AND CONSUMABLE MATERIALS

6.1 Acetone, methanol, methylene chloride, MTBE -- Pesticide quality or equivalent.

6.2 Ethyl ether, unpreserved -- Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. PI126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

6.3 Sodium sulfate, granular, anhydrous, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances. Acidify by slurring 100 g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.1 mL concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. The pH must be below pH 4. Store at 130°C.

6.4 Sodium thiosulfate, granular, anhydrous, ACS grade.

6.5 Sodium hydroxide (NaOH), pellets -- ACS grade.

6.5.1 NaOH, 6 N -- Dissolve 216 g NaOH in 900 mL reagent water.

6.6 Sulfuric acid (H₂SO₄), concentrated, ACS grade -- sp. gr. 1.84.

Figure 515.1-2 Gas Chromatogram of Methyl Esters of Chlorinated Acids on DB-5 Column

- 6.6.1 H_2SO_4 , 12 N -- Slowly add 335 mL concentrated H_2SO_4 to 655 mL of reagent water.
- 6.7 Potassium hydroxide (KOH), pellets -- ACS grade.
 - 6.7.1 KOH, 37% (w/v) -- Dissolve 37 g KOH pellets in reagent water and dilute to 100 mL.
- 6.8 Carbitol (diethylene glycol monoethyl ether), ACS grade -- available from Aldrich Chemical Co.
- 6.9 Diazald, ACS grade -- available from Aldrich Chemical Co.
- 6.10 Diazald solution -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber bottle with a Teflon-lined screw cap.
- 6.11 Sodium chloride (NaCl), crystal, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.
- 6.12 4,4'-Dibromooctafluorobiphenyl (DBOB) -- 99% purity, for use as internal standard (available from Aldrich Chemical Co).
- 6.13 2,4-Dichlorophenylacetic acid (DCAA) -- 99% purity, for use as surrogate standard (available from Aldrich Chemical Co).
- 6.14 Reagent water -- Reagent water is defined as water in which an interferent is not observed at or above the EDL of any analyte. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.
- 6.15 Silicic acid, ACS grade.
- 6.16 Florisil -- 60-100/PR mesh (Sigma No. F-9127). Activate by heating in a shallow container at 150°C for at least 24 and not more than 48 hours.
- 6.17 STOCK STANDARD SOLUTIONS (1.00 $\mu\text{g}/\mu\text{L}$) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

- 6.17.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 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.
- 6.17.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.
- 6.17.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.
- 6.18 INTERNAL STANDARD SPIKING SOLUTION -- Prepare an internal standard spiking solution by accurately weighing approximately 0.0010 g of pure DBOB. Dissolve the DBOB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 25 μL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 $\mu\text{g/L}$. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.
- 6.19 SURROGATE STANDARD SPIKING SOLUTION -- Prepare a surrogate standard spiking solution by accurately weighing approximately 0.0010 g of pure DCAA. Dissolve the DCAA in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 μL of the surrogate standard spiking solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 5 $\mu\text{g/L}$ and, assuming quantitative recovery of DCAA, a surrogate standard concentration in the final extract of 0.5 $\mu\text{g/mL}$. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.
- 6.20 INSTRUMENT QC STANDARD -- Prepare a diluted dinoseb solution by adding 10 μL of the 1.0 $\mu\text{g/mL}$ dinoseb stock solution to MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the instrument QC standard, add 40 μL of the diluted dinoseb solution, 16 μL of the 4-nitrophenol stock solution, 6 μL of the 3,5-dichlorobenzoic acid stock solution, 50 μL of the surrogate standard spiking solution, 25 μL of the internal standard spiking solution, and 250 μL of methanol to a 5-mL volumetric flask and dilute to volume with MTBE. Methylate sample as described in Sect. 10.4. Dilute the sample to 10 mL in MTBE. Transfer the instrument QC standard to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.
7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE
- 7.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be pre-rinsed with sample before collection.
- 7.2 SAMPLE PRESERVATION AND STORAGE
- 7.2.1 Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a 10 mg/mL solution of mercuric chloride in water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.
- 7.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well.
- 7.2.3 After the sample is collected in the bottle containing preservative, seal the bottle and shake vigorously for 1 min.
- 7.2.4 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicate that most of the analytes (measured as total acid) present in samples are stable for 14 days when stored under these conditions. (1) However, analyte stability may be affected by the matrix; therefore, the analyst

should verify that the preservation technique is applicable to the samples under study.

7.3 EXTRACT STORAGE

- 7.3.1 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days(1); however, the analyst should verify appropriate extract holding times applicable to the samples under study.

8. CALIBRATION

- 8.1 Establish GC operating parameters equivalent to those indicated in Sect. 5.10. The GC system may be calibrated using either the internal standard technique (Sect. 8.2) or the external standard technique (Sect. 8.3).

- 8.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. DBOB has been identified as a suitable internal standard.

- 8.2.1 Prepare calibration standards at a minimum of five concentration levels for each analyte 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 250 µL methanol, and dilute to volume with MTBE. Esterify acids with diazomethane as described in Sect. 10.4 or 10.5. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

- 8.2.2 Inject 2 µL of each calibration standard and tabulate the relative response for each analyte (RRa) to an internal standard using the equation:

$$RRa = Aa/Ais$$

where:

Aa = the peak area of the analyte, and

Ais = the peak area of the internal standard.

- 8.2.3 Generate a calibration curve of analyte relative response, RRa, versus analyte concentration in the sample in µL.

- 8.2.4 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

8.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

- 8.3.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest and surrogate compound by adding volumes of one or more stock standards and 250 µL methanol to a volumetric flask. Dilute to volume with MTBE. Esterify acids with diazomethane as described in Sect. 10.4 or 10.5. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

- 8.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

- 8.3.3 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

- 8.3.4 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 analyte varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 8.3.3.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of method blanks, instrument QC solution, laboratory control (LC) standards, QC samples, and performance evaluation (PE) samples.

9.2 Method Blanks. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a method blank must be analyzed. If within the retention time window of any analyte the method blank produces a peak that is 0.5 EDL for that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 Initial Demonstration of Capability.

9.3.1 Select a representative spike concentration (about 10 times EDL) for each analyte. Prepare a LC sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of at least four 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Section 10.

9.3.2 Calculate mean percent recovery (X), and standard deviation of percent recovery (S). For each analyte, X must fall in the range of 70-130% (or within $R \pm 3\text{RSD}$ using the values for R and RSD for reagent water in Table 2) and S must be less than 30% (or less than $3 \times \text{RSD}$ in reagent water in Table 2). If the calculated X and S for every

analyte meet the acceptance criteria, performance is acceptable and sample analysis may begin. If any X or S falls outside its acceptance range, initial demonstration procedures for that compound must be repeated.

9.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.

9.5 Assessing Surrogate Recovery.

9.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors, (2) spiking solutions for degradation, (3) contamination or other obvious abnormalities, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a blank extract reanalysis fails the 70-130% recovery criteria, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis solves the problem, report only data from the analysis with acceptable surrogate recovery. If sample extract reanalysis does not solve the problem, report all data for that sample as suspect.

9.6 Assessing the Internal Standard

9.6.1 For each sample and blank extract, determine if internal standard peak area or height deviates by 30% from the average measured during analysis of calibration standards.

9.6.2 If 30% deviation, optimize instrument performance and inject a second aliquot of that extract. If the reinjected aliquot produces an acceptable internal standard peak area or height, report results for that aliquot. If not, assume that an error was made during addition of internal standard to that extract. Reextract that sample or blank, and analyze that extract.

9.6.3 If 30% deviation continues, analyze a calibration standard (Sect. 8).

9.6.3.1 If the internal standard peak area or peak height fails to meet criteria, then recalibrate, and reanalyze extracts that previously did not meet criteria. If acceptable area or height is measured,

report results. If not, assume an interference from the matrix is affecting the internal standard and use external calibration (Sect. 8).

9.6.3.2 If the internal standard peak area or peak height meets criteria then assume an interference from the matrix is affecting the internal standard in your sample extract and use external calibration.

9.7 Assessing Laboratory Performance

9.7.1 Initial QC criteria are established by using the values for X and S generated above (Sect. 9.3) to establish upper and lower control limits:

$$\begin{aligned}\text{UPPER CONTROL LIMIT} &= X + 3S \\ \text{LOWER CONTROL LIMIT} &= X - 3S\end{aligned}$$

The laboratory must analyze at least one LC sample per sample set (all samples extracted within a 24-h period). The spiking concentration of each analyte in the laboratory control sample should be 10 times EDL. Calculate accuracy as percent recovery (X). If the recovery of any analyte falls outside the control limits, that analyte is judged out of control, and the source of the problem must be identified and resolved before continuing analyses. The control limits should be updated periodically. It is recommended that after each five to ten new recovery measurements that new control limits be calculated using only the most recent 20-30 data points.

9.7.2 Each quarter the laboratory must analyze QC check standards (if available). If criteria provided with the QC check standard are not met, corrective action should be taken and documented.

9.7.3 At least once a year, the laboratory must analyze a performance evaluation sample (if available), and results for each analyte must be within established acceptance limits.

9.8 Assessing Instrument Performance - The instrument QC standard (Sect. 6.12) should be analyzed daily to monitor instrument performance. Inability to demonstrate acceptable instrument performance indicates the need to reevaluate the GC system. If laboratory EDLs differ from listed EDLs (Table 2), concentrations of instrument QC standard compounds may be adjusted as needed.

9.9 Analyte Confirmation - When doubt exists

about identification of a GC peak, confirmatory techniques such as determination with a mass spectrometer detector or a different GC column must be used.

10. PROCEDURE

10.1 AUTOMATED HYDROLYSIS, CLEANUP, AND EXTRACTION METHOD - Validation data presented in this method were generated using the automated extraction procedure with the mechanical separatory funnel shaker.

10.1.1 Add preservative to any samples not previously preserved (Sect. 7.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike sample with 50 μ L of the surrogate standard spiking solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

10.1.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

10.1.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Shake sample for 1 hour using the appropriate mechanical mixing device.

10.1.4 Add 300 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble the sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

10.1.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer,

the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the organic phase. If the tumbler is used, return the aqueous phase to the tumbler bottle.

10.1.6 Add 17 mL of 12 N H₂SO₄ to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H₂SO₄.

10.1.7 Add 300 mL ethyl ether to the sample, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

10.1.8 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the aqueous phase. Collect the extract in a 500-mL round-bottom flask containing about 10 g of acidified anhydrous sodium sulfate. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

10.1.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.2 MANUAL HYDROLYSIS, CLEANUP, AND EXTRACTION METHOD -- Alternative procedure.

10.2.1 Add preservative to any samples not previously preserved (Sect. 7.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Spike sample with 50 µL of the surrogate standard spiking solution.

10.2.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

10.2.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature for 1 hour, shaking the separatory funnel and contents periodically.

10.2.4 Add 60 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

10.2.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

10.2.6 Add 17 mL of 12 N H₂SO₄ to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H₂SO₄.

10.2.7 Add 120 mL ethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min.

If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ethyl ether phase in a 500-mL round-bottom flask containing approximately 10 g of acidified anhydrous sodium sulfate.

10.2.8 Return the aqueous phase to the separatory funnel, add a 60-mL volume of ethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL erlenmeyer flask. Perform a third extraction with 60 mL of ethyl ether in the same manner. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

10.2.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.3 EXTRACT CONCENTRATION

10.3.1 Assemble a K-D concentrator by attaching a concentrator tube to a 500-mL evaporative flask.

10.3.2 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom flask and funnel with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

10.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. 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 and cool for at least 10 min.

10.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether. Add 2 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 250 μ L of methanol. If the gaseous diazomethane procedure (Sect. 10.4) is used for esterification of pesticides, rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. If the pesticides will be esterified using the diazomethane solution (Sect. 10.5), rinse the walls of the concentrator tube while adjusting the volume to 4.5 mL with MTBE.

10.4 ESTERIFICATION OF ACIDS USING GASEOUS DIAZOMETHANE -- Validation results presented in this method were generated using the gaseous diazomethane derivatization procedure.

10.4.1 Assemble the diazomethane generator (Figure 515.1-1) in a hood.

10.4.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.2 grams Diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 1 min. Remove first sample. Rinse the tip of the diazomethane generator with ethyl ether after methylation of each sample. Bubble diazomethane through the second sample extract for 1 min. Diazomethane reaction mixture should be used to esterify only two samples; prepare new reaction mixture in Tube 2 to esterify each two additional samples. Samples should turn yellow after addition of diazomethane and remain yellow for at

least 2 min. Repeat methylation procedure if necessary.

10.4.3 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

10.4.4 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

10.5 ESTERIFICATION OF ACIDS USING DIAZOMETHANE SOLUTION -- Alternative procedure.

10.5.1 Assemble the diazomethane generator (Figure 515.1) in a hood. The collection vessel is a 10- or 15-mL vial, equipped with a Teflon-lined screw cap and maintained at 0-5°C.

10.5.2 Add a sufficient amount of ethyl ether to tube 1 to cover the first impinger. Add 5 mL of MTBE to the collection vial. Set the nitrogen flow at 5-10 mL/min. Add 2 mL Diazald solution (Sect. 6.9) and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the nitrogen flow to purge the diazomethane from the reaction vessel into the collection vial for 30 min. Cap the vial when collection is complete and maintain at 0-5°C. When stored at 0-5°C this diazomethane solution may be used over a period of 48 h.

10.5.3 To each concentrator tube containing sample or standard, add 0.5 mL diazomethane solution. Samples should turn yellow after addition of the diazomethane solution and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

10.5.4 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

10.5.5 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

10.6 FLORISIL CLEANUP

10.6.1 Place a small plug of glass wool into a 5-mL disposable glass pipet. Tare the pipet, and measure 1 g of activated Florisil into the pipet.

10.6.2 Apply 5 mL of 5 percent methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.

10.6.3 Apply 5 mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.

10.6.4 Add 1 mL of 5 percent methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column leaving silicic acid in the tube. Collect eluate in a K-D tube. Repeat with 1-mL and 3-mL aliquots of 5 percent methanol in MTBE, collecting eluates in K-D tube.

10.6.5 If necessary, dilute eluate to 10 mL with 5 percent methanol in MTBE. Spike with 25 μ L of Internal standard solution. Thoroughly mix sample and place aliquot in a GC vial for subsequent analysis.

10.6.6 Seal the vial and store in a refrigerator if further processing will not be performed immediately. Analyze by GC-ECD.

10.7 GAS CHROMATOGRAPHY

10.7.1 Sect. 5.10 summarizes the recommended operating conditions for the GC. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.4 are met.

10.7.2 Calibrate the system daily as described in Sect. 8. The standards and extracts must be in MTBE.

10.7.3 Inject 2 μ L of the sample extract. Record the resulting peak size in area units.

10.7.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.7.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

11. CALCULATIONS

- 11.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 8.
- 11.2 For samples processed as part of a set where the laboratory control standard recovery falls outside of the control limits in Sect. 9, results for the affected analytes must be labeled as suspect.

12. PRECISION AND ACCURACY

- 12.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range. (1) In cases where analytes coeluted using primary analytical conditions, results from confirmatory GC conditions were used. Analyte recoveries at one concentration and EDL results are given in Table 2.
- 12.2 In a single laboratory, analyte recoveries from two artificial ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. (1) Analyte recoveries from the two artificial matrices are given in Table 2.

13. REFERENCES

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Research and Development

The Determination of Polychlorinated Biphenyls in
Transformer Fluid and Waste Oils

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THE DETERMINATION OF POLYCHLORINATED BIPHENYLS IN TRANSFORMER FLUID AND WASTE OILS

1. Scope

- 1.1 This is the EPA preferred method for the determination of polychlorinated biphenyls (PCBs) in waste oils according to PCB regulations.¹ This gas chromatographic (GC) procedure is applicable to the determination of commercial mixtures of PCBs in transformer fluids and certain other hydrocarbon based waste oils. The method can be used to analyze waste oils for individual PCB isomers or complex mixtures of chlorinated biphenyls from monochlorobiphenyl through decachlorobiphenyl only if the isomers have been previously identified by other methods² or by knowledge of the sample history.
- 1.2 The detection limits are dependent upon the complexity of the sample matrix and the ability of the analyst to properly maintain the analytical system. Using a carefully optimized instrument, this method has been shown to be useful for the determination of commercial PCB mixtures spiked into transformer fluid over a range of 5.0 to 500 mg/Kg. Based upon a statistical calculation at 5 mg/Kg for a simple oil matrix, the method detection limit for Aroclors 1221, 1242, 1254, and 1260 is 1 mg/Kg. 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.
- 1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Prior to sample analysis,

each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 10.2.

2. Summary

2.1 The sample is diluted on a weight/volume basis so that the concentrations of each PCB isomer is within capability of the GC system (0.01 to 10 ng/ μ L).

2.2 The diluted sample is then injected into a gas chromatograph for separation of the PCB isomers. Measurement is accomplished with a halogen specific detector which maximizes baseline stability and minimizes interferences normally encountered with other detectors. The electron capture detector (ECD) can normally be substituted for the halogen specific detector when samples contain dichloro through decachlorobiphenyl isomers (Aroclors 1016, 1232, 1242, 1248, 1254, 1260, 1262 and 1268), or when the sample matrix does not interfere with the PCBs. Several cleanup techniques are provided for samples containing interferences. A mass spectrometer operating in the selected ion monitoring mode of data acquisition may also be used as the GC detector when PCB levels are sufficiently high and the PCB m/z ranges are free from interference. Interferences may occur in some waste oil samples even after exhaustive cleanup.

2.3 The concentrations of the PCBs are calculated on a mg/Kg basis, using commercial mixtures of PCBs as standards. The analysis time, not including data reduction, is approximately 35 min/sample.

3. Interferences

3.1 Qualitative misidentifications are always a potential problem in GC

analysis. The use of a halogen specific detector and the analyst's skill in recognizing chromatographic patterns of commercial PCB mixtures minimizes this possibility.

- 3.2 Whenever analyzed samples do not provide chromatographic patterns nearly identical to the standards prepared from commercial PCBs, the analyst must confirm the presence of PCBs by one of three ways: by analysis after column cleanup; by analysis on dissimilar gas chromatographic columns; or, by gas chromatography/mass spectrometry (GC/MS).
- 3.3 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs are to be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified, must demonstrate that the deviation does not affect the validity of the data and alternative test procedure approval must be obtained through the Environmental Monitoring and Support Laboratory, 26 West St. Clair Street, Cincinnati, Ohio 45268 Equivalency Program.³ An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 10.2. In this case, formal approval is not required, but the documented data from Section 10.2 must be on file as part of the overall quality assurance program.
- 3.4 Samples which are diluted at a ratio of 100:1 and are analyzed by electron capture GC, consistently produce results that are 10 to

20% lower than the true value (See Section 12). This is due to quenching of the detector response by high boiling hydrocarbons coeluting with the PCBs. The degree of error is matrix dependent and is not predictable for samples of unknown origin. As the PCB concentration approaches 20% of a control level, for example, 50 mg/kg, the analyst must routinely reanalyze a duplicate spiked sample to determine the actual recovery. Spike the duplicate or diluted sample at 2 times the electron capture observed value and reanalyze according to Section 10.2. Correct the results accordingly.

4. Apparatus

4.1 Gas Chromatograph -- The gas chromatograph should be equipped with on-column 1/4-inch injectors. The oven must be large enough to accept a 1/4" OD 2 meter coiled glass column. —If halogen specific detectors are used, then the column oven should have programming capabilities.

4.2 Gas Chromatographic Detector

4.2.1 A halogen specific detector is used to eliminate interferences causing misidentifications or false-positive values due to non-organohalides which commonly coelute with the PCBs.

a. Electrolytic conductivity detector -- the Hall electrolytic conductivity detector, Model 700-A (HED), available from Tracor, Inc. has been found to provide the sensitivity and stability needed for the current PCB Regulations.¹

b. Other halogen specific detectors, including older model

electrolytic conductivity detectors and microcoulometric titration, may be used. However, the stability, sensitivity, and response time of these detectors may raise the method detection limit and adversely affect peak resolution. Each system must be shown to be operating within requirements of the PCB regulations by collecting single laboratory accuracy and precision data and method detection limits on simple spiked samples as described in Section 10.2.

4.2.2 Semi-specific detectors, such as ECD, may be substituted when sample chromatographic patterns closely match those of the standards. Acid cleanup (See Section 8.1) or Florisil slurry cleanup (See Section 8.7) should be incorporated routinely when the ECD is used.--See Section 3.4 for additional quality control procedures for ECD.

4.2.3 Quantitative GC/MS techniques can be used and the recommended approach is selected ion monitoring (SIM) but the GC/MS data system must have a program that supports this method of data acquisition. The program must be capable of monitoring a minimum of eight ions, and it is desirable for the system to have the ability to change the ions monitored as a function of time. For PCB measurements, several sets of ions may be used depending on the objectives of the study and the data system capabilities. The alternatives are as follows:

Single ions for high sensitivity	154, 188, 222, 256, 292, 326, 360, 394
Short mass ranges which may give enhanced sensitivity, depending on the data system capabilities	154-156, 188-192, 222-226, 256-260, 290-295, 322-328, 356-364, 390-398
Single ions giving decreased sensitivity but are selective for levels of chlorination. ⁽²⁾	190, 224, 260, 294, 330, 362, 394

The data system must have the capability of integrating an abundance of the selected ions between specified limits and relating integrated abundances to concentrations, using the calibration procedures described in this method.

4.3 Gas Chromatographic Columns

4.3.1 The GC columns and conditions listed below are recommended for the analysis of PCB mixtures in oil. If these columns and conditions are not adequate, the analyst may vary the column parameters to improve separations. The columns and conditions selected must be capable of adequately resolving the PCBs in the various Aroclor mixtures so that each

Aroclor is identifiable through isomer pattern recognition. (See Figures 1 through 6 to establish this.) To properly use the calculation procedure described in Section 11.5, the analyst must use the methyl silicone liquid phase column described in Section 4.3.2. Capillary columns and their associated specialized injection techniques are acceptable alternatives; however, due to problems associated with the use of capillary columns the analyst must demonstrate that the entire system will produce acceptable results by performing the operations described in Section 10.2.

4.3.2 Recommended primary analytical column: Glass, 1/4 in. O.D. (2 mm I.D.) 6 ft (180 cm) long, packed with Gas-Chrom Q 100/120 mesh coated with 3% OV-1.

Carrier gas: 40 to 60 mL/min (helium, nitrogen or mixtures of methane in argon as recommended by the manufacturer of the detector).

Temperature Program: 120°C isothermal for 2 minutes, 6°C/min to 220°C and hold until all compounds elute.

Figure 8 shows a chromatogram of the PCB locator mixture (see Section 5.8) analyzed under these conditions. Each PCB peak has been identified by assigning the same relative retention times determined in the isothermal runs Figures 1 through 6.

Isothermal Operation: Aroclor 1221, 1232, or C1₁ through C1₄ isomers -- recommended range 140 to 150°C
Aroclor 1016, 1242, 1254, 1260, 1262, 1268, or C1₃ through C1₁₀ isomers -- recommended range 170 to 200°C

4.3.3 Recommended confirmatory column: Glass tubing 1/4 in. O.D., 2 mm I.D. 6 ft (180 cm) long, packed with Gas-Chrom Q 100/120 mesh coated with 1.5% OV-17 + 1.95% OV-210.

Carrier gas: 40 to 60 mL/min (helium, nitrogen or mixtures of methane in argon as recommended by the manufacturer of the detector).

Column temperatures: Aroclor 1221, 1232, or C1₁ through C1₄ isomers recommended range -- 170 to 180°C.

Aroclor 1016, 1242, 1248, 1254, 1260, 1262, 1268, or C1₃ through C1₁₀ isomers 200°C.

4.4 Volumetric flasks -- 10, 100, 200, and 250-mL.

4.5 Pipets -- 0.10, 1.0, and 5.0 mL Mohr delivery (for viscous oils cut off tip of pipet).

4.6 Micro syringes -- 10.0 µL.

4.7 Sample containers -- 20 mL or larger screw cap bottles with Teflon faced cap liners. (Aluminum foil cap liners can be used for non corrosive samples).

4.8 Chromatographic column -- Chromaflex, 400 mm long x 19 mm ID (Kontes K-420540-9011 or equivalent).

4.9 Gel Permeation Chromatograph -- GPC Autoprep 1002 or equivalent, available from Analytical Bio Chemistry Laboratories, Inc.

4.10 Balance -- Analytical, capable of weighing 99 grams with a sensitivity of ± 0.0001 g.

4.11 Kuderna-Danish (K-D) Evaporative Concentrator Apparatus

4.10.1 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 solvent.

4.11.2 Evaporative flask -- 500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

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

5. Reagents and Materials

5.1 Reagent safety precautions

5.1.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

5.1.2 PCBs have been tentatively classified as known or suspected, human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood.

5.1.3 Diethyl ether should be monitored regularly to determine the peroxide content. Under no circumstances should diethyl ether be used with a peroxide content in excess of 50 ppm as

an explosion could result. Peroxide test strips manufactured by EM Laboratories (available from Scientific Products Co. Cat. No. P1126-8 and other suppliers) are recommended for this test. Procedures for removal of peroxides from diethyl ether are included in the instructions supplied with the peroxide test kit.

5.2 Hexane (mixed hexanes), isooctane, acetonitrile, methylene chloride, cyclohexane, and diethyl ether of pesticide grade.

5.3 Recommended Column Packings

5.3.1 Gas Chrom Q 100/120 mesh coated with 3% OV-1.

5.3.2 Gas Chrom Q 100/120 mesh coated with 1.5% OV-17 + 1.95% OV-210.

5.4 Standards

5.4.1 Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268. Primary dilutions of various Aroclors are available from U.S. EPA, EMSL-Cincinnati Quality Assurance Branch, 26 W. St. Clair Street, Cincinnati, Ohio 45268.

5.4.2 2-Chlorobiphenyl, 3-chlorobiphenyl, and decachlorobiphenyl

5.4.3 Pure individual PCBs as identified in the sample by mass spectrometry or indicated by retention data.

5.4.4 Alumina (Fisher A540 or equivalent).

5.4.5 Silica gel (Davison Grade 950 or equivalent).

5.4.6 Florisil (PR grade or equivalent).

5.4.7 Sulfuric acid A.C.S.

5.4.8 Quality Control Check Sample -- Certified Samples of PCBs in oil matrices are available from U.S. EPA, EMSL-Cincinnati,

Quality Assurance Branch, 26 W. St. Clair Street,
Cincinnati, Ohio 45268.

- 5.5 Standard Stock Solutions -- Prepare primary dilutions of each of the Aroclors or individual PCBs by weighing approximately 0.01 g of material within ± 0.0001 g. Dissolve and dilute to 10.0 mL with isooctane or hexane. Calculate the concentration in $\mu\text{g}/\mu\text{L}$. Store the primary dilutions at 4°C in 10 to 15-mL narrow mouth, screw cap bottles with Teflon cap liners. Primary dilutions are stable indefinitely if the seals are maintained. The validity of inhouse generated or stored primary and secondary dilutions must be verified on a quarterly basis by analyzing EMSL-CI Quality Control Check Samples or certified PCB standards.
- 5.6 Working Standards -- Prepare working standards similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Dilute the mixture to volume with pesticide quality hexane. Calculate the concentration in $\text{ng}/\mu\text{L}$ as the individual Aroclors (Section 11.4) or as the individual PCBs (Section 11.5). Store dilutions at 4°C in 10 to 15-mL narrow mouth, screw cap bottles with Teflon cap liners. If the seals are maintained, these secondary dilutions can be stored indefinitely. (See Section 5.5.)
- 5.7 Laboratory control standard (LCS) -- Prepare a LCS by spiking a PCB free oil typical of the matrix normally analyzed, such as a transformer oil, at 50.0 mg/Kg with a PCB mixture typical of those normally found in the samples, such as Aroclor 1260 at 50.0 mg/Kg.
- 5.8 PCB Locator Mixture -- Prepare a PCB locator mixture containing 0.1 $\text{ng}/\mu\text{L}$ of 2-chlorobiphenyl, 0.1 $\text{ng}/\mu\text{L}$ 3-chlorobiphenyl, 0.5 $\text{ng}/\mu\text{L}$

Aroclor 1242, 0.5 ng/ μ L Aroclor 1260, and 0.2 ng/ μ L Aroclor 1268 in hexane (0.1 ng/ μ L of decachlorobiphenyl can be substituted for Aroclor 1268). Use the chromatogram generated by the PCB locator mixture to help identify the retention times of the various PCB isomers commonly found in commercial PCB mixtures.

6. Sample Collection and Handling

6.1 Sample containers should have a volume of 20 mL or more and have Teflon or foil lined screw caps.

6.2 Sample Bottle Preparation

6.2.1 Wash all sample bottles and seals in detergent solution. Rinse first with tap water and then with distilled water. Allow the bottles and seals to drain dry in a contaminant free area. Then rinse seals with pesticide grade hexane and allow to air dry.

6.2.2 Heat sample bottles to 400°C for 15 to 20 minutes or rinse with pesticide grade acetone or hexane and allow to air dry.

6.2.3 Store the clean bottles inverted or sealed until use.

6.2.4 Sample bottles can be reused. Prior to reuse, rinse the bottles and seals 3 times with hexane, allow to air dry, and then proceed to Section 6.2.1.

6.3 Sample Preservation -- The samples should be stored in a cool, dry, dark area until analysis. Storage times in excess of 4 weeks are not recommended for unknown or undefined sample matrices.

6.4 Sample Collection

6.4.1 Fill a large container such as a 500-mL beaker from a representative area of the sample source. If practical, mix the sample source prior to sampling.

6.4.2 Fill a minimum of two 20-mL sample bottles (Field Sample 1 (FS1) and Field Sample 2 (FS2)) approximately 80% full from the sampling container.

6.4.3 Repeat Sections 6.4.1 and 6.4.2 if there is a need to monitor sampling precision as described in Section 10.6.

7. Procedure

7.1 The approximate PCB concentration of the sample may be determined by X-ray fluorescence (total halogen measurement), microcoulometry (total halogen measurement), density measurements, or by analyzing a very dilute mixture of the sample (10,000:1) according to Section 7.4.

7.2 For samples in the 0 to 100 mg/Kg range, dilute at the rate of 100:1 in hexane.

7.2.1 Pipet 1.0 mL of sample into a 100-mL volumetric flask using a 1.0-mL Mohr pipet. For viscous samples, cut the capillary tip off the pipet. Dilute to volume with hexane. Stopper and mix.

7.2.2 Using the same pipet as in Section 7.2.1, deliver 1.0 mL of sample into a tared 10-mL beaker weighed to $\pm .001$ g. Reweigh the beaker to $\pm .001$ g to determine the weight of sample used in 7.2.1.

7.2.3 As an alternative to Sections 7.2.1 and 7.2.2, weigh approximately 1 gram to $\pm .001$ g of sample in a 100-mL volumetric flask and dilute to volume with hexane.

7.2.4 Analyze the diluted sample according to Section 7.4 or store the diluted sample in a narrow mouth bottle with a Teflon lined screw cap.

7.3 For samples above 100 mg/Kg in concentration, dilute at a rate of 1000:1 in hexane.

7.3.1 Pipet 0.10 mL of sample into a 100-mL volumetric flask using a 0.10 mL-Mohr pipet. Dilute to volume with hexane, stopper and mix.

7.3.2 Using the same pipet as in Section 7.3.1, deliver 0.10 mL of sample into a tared 10 mL beaker to $\pm .0001$ g. Reweigh the beaker to determine the weight of sample used in Section 7.3.1.

7.3.3 As an alternative to Sections 7.3.1 and 7.3.2, weigh approximately 0.1 gram to $\pm .0001$ g of sample and in a 100 mL volumetric flask. Dilute to volume with hexane.

7.3.4 Analyze the diluted sample according to Section 7.4 or store the diluted sample in a narrow mouth bottle with a Teflon lined screw cap.

7.3.5 If the concentration of PCBs is still too high for the chromatographic system, prepare secondary dilutions from Sections 7.3.1 or 7.3.3, until acceptable levels are obtained.

7.4 Analyze the sample by injecting the hexane mixture into the gas chromatograph using auto injectors or the solvent flush technique.⁴

7.4.1 Recommended injection volumes: Halogen specific detector -- 4 to 5 μ L, ECD 2 to 3 μ L. Smaller volumes may be injected when auto injectors are used if the resulting method detection limits are acceptable.

Note: When semi-specific detectors are used, cleanup techniques (see Section 4.2.2) should be routinely incorporated into the analysis scheme prior to injection.

7.5 If the resulting chromatogram shows evidence of column flooding or nonlinear detector responses, further dilute the sample according to Section 7.3.5.

7.6 Determine whether or not PCBs are present in the sample by comparing the sample chromatogram to that of the PCB locator mixture Section 5.8.

7.6.1 If a series of peaks in the sample match some of the retention times of PCBs in the PCB locator mixture, attempt to identify the source by comparing chromatograms of each standard prepared from commercial mixtures of PCBs (see Section 5.6). Proceed to Section 11.4 if the source of PCBs is identified.

7.6.2 If the sample contains a complex mixture of PCBs, proceed to Section 11.5.

7.6.3 If a dilution ratio of 1000:1 (Section 7.3) or higher was analyzed and no measurable PCB peaks were detected, analyze an aliquot of sample diluted to 100:1.

7.6.4 If several PCB interference problems are encountered or if PCB ratios do not match standards, proceed to Section 8, use alternate columns, or use GC/MS² to verify whether or not the nonrepresentative patterns are due to PCBs.

8. Cleanup

Several tested cleanup techniques are described. Depending upon the complexity of the sample, one or all of the techniques may be required to resolve the PCBs from interferences.

8.1 Acid Cleanup

- 8.1.1 Place 5.0 mL of concentrated sulfuric acid into a 40-mL narrow mouth screw cap bottle. Add 10.0 mL of the diluted sample. Seal the bottle with a Teflon lined screw cap and shake for 1 minute.
- 8.1.2 Allow the phases to separate, transfer the sample (upper phase) to a clean narrow mouth screw cap bottle. Seal with a Teflon lined cap.
- 8.1.3 Analyze according to Section 7.4.
- 8.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

NOTE: This cleanup technique was tested over a 6-month period of time using both electron capture and electrolytic conductivity detectors. Care was taken to exclude any samples that formed an emulsion with the acid. The sample was withdrawn well above the sample-acid interface. Under these conditions, no adverse effects associated with column performance and detector sensitivity to PCBs were noted. This cleanup technique could adversely affect the chromatographic column performance for samples containing analytes other than PCBs.

8.2 Florisil Column Cleanup

- 8.2.1 Variances between batches of Florisil may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.
- 8.2.2 Place a 20.0 g charge of Florisil, activated at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70 to 80 mL of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

- 8.2.3 Add 2.0 mL of the undiluted sample to the column with a 2- mL Mohr pipet. For viscous samples, cut the capillary tip off the pipet. Add 225 mL of hexane to the column. Carefully wash down the inner wall of the column with a small amount of the hexane prior to adding the total volume. Collect and discard the first 25.0 mL.
- 8.2.4 Collect exactly 200 mL of hexane eluate in a 200-mL volumetric flask. All the PCBs must be in this fraction.
- 8.2.5 Using the same pipet as in Section 8.2.2, deliver 2.0 mL of sample into a tared 10-mL beaker weighed to ± 0.001 g. Reweigh the beaker to determine the weight of the sample diluted to 200 mL.
- 8.2.6 Analyze the sample according to Section 7.4.
- 8.3 Alumina Column Cleanup
- 8.3.1 Adjust the activity of the alumina by heating to 200°C for 2 to 4 hours. When cool, add 3% water (weight:weight) and mix until uniform. Store in a tightly sealed bottle. Allow the alumina to equilibrate at least 30 minutes before use. Adjust activity weekly.
- 8.3.2 Variances between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Alumina can then be adjusted accordingly.
- 8.3.3 Place a 50.0 g charge of alumina into a Chromaflex column. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate to the top of the alumina. Pre-elute the

column with 70 to 80 mL of hexane. Just before exposing the sodium sulfate layer to air, stop the flow. Discard the eluate.

8.3.4 Add 2.5 mL of the undiluted sample to the column with a 5-mL Mohr pipet. For viscous samples, cut the capillary end off the pipet. Add 300 mL of hexane to the column. Carefully wash down the inner walls of the column with a small volume of hexane prior to adding the total volume. Collect and discard the 0 to 50 mL fraction.

8.3.5 Collect exactly 250 mL of the hexane in a 250-mL volumetric flask. All the PCBs must be in this fraction.

8.3.6 Using the same pipet as in 8.3.4, deliver 2.5 mL of sample into a tared 10-mL beaker ± 0.001 g. Reweigh the beaker to determine weight of sample diluted to 250 mL.

8.3.6 Analyze the sample according to Section 7.4.

8.4 Silica Gel Column Cleanup.

8.4.1 Activate silica gel at 135°C overnight.

8.4.2 Variances between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

8.4.3 Place a 25 g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

- 8.4.4 Preelute the column with about 70 to 80 mL of hexane. Just before exposing the sodium sulfate layer to air, stop the flow. Discard the eluate.
- 8.4.5 Add 2.0 mL of the undiluted sample to the column with a 2-mL Mohr pipet. For viscous samples, cut the capillary tip off the pipet.
- 8.4.6 Wash down the inner wall of the column with 5 mL of hexane.
- 8.4.7 Elute the PCBs with 195 mL of 10% diethylether in hexane volume:volume.
- 8.4.8 Collect exactly 200 mL of the eluate in a 200-mL volumetric flask. All the PCBs must be in this fraction.
- 8.4.9 Using the same pipet as in Section 8.4.5, deliver 2.0 mL of sample into a tared 10-mL beaker (± 0.001 g). Reweigh to determine the weight of sample diluted to 200 mL.
- 8.4.10 Analyze the sample according to Section 7.4.
- 8.5 Gel Permeation Cleanup
- 8.5.1 Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the instruction manual. Use 15% methylene chloride in cyclohexane (volume:volume) as the mobil phase.
- 8.5.2 Place 1.0 mL of sample into a 100-mL volumetric flask, using a 1-mL Mohr pipet. For viscous samples, cut the capillary tip off the pipet.
- 8.5.3 Dilute the sample to volume, using 15% methylene chloride in cyclohexane (volume:volume).
- 8.5.4 Using the same pipet as in Section 8.5.2 deliver 1.0 mL of sample into a tared 10-mL beaker ± 0.001 g. Reweigh the

beaker ± 0.001 g to determine the weight of sample used in Section 8.5.2.

8.5.5 As an alternative to Sections 8.5.2 and 8.5.3 weigh approximately 1 gram ± 0.001 g of sample and dilute to 100.0 mL in 15% methylene chloride in cyclohexane (volume:volume).

8.5.6 Inject 5.0 mL of the diluted sample into the instrument. Collect the fraction containing the Cl_1 through Cl_{10} PCBs (see operator's manual) in a K-D flask equipped with a 10-mL ampul.

8.5.7 Concentrate the Section 8.5.4 fraction down to less than 5 mL, using K-D evaporative concentration techniques.

8.5.8 Dilute to 5.0 mL with hexane, then analyze according to Section 7.4. Be sure to use 100 mL as the dilution volume for the final calculation.

8.6 Acetonitrile Partition

8.6.1 Place 10.0 mL of the previously diluted sample into a 125-mL separatory funnel. Add 5.0 mL of hexane. Extract the sample four times by shaking vigorously for one minute with 30 mL portions of hexane-saturated acetonitrile.

8.6.2 Transfer and combine the acetonitrile phases to a 1-L separatory funnel and add 650 mL of distilled water and 40 mL of saturated sodium chloride solution. Mix thoroughly for 30 to 35 seconds. Extract with two 100 mL portions of hexane by vigorously shaking about 15 seconds.

8.6.3 Combine the hexane extracts in a 1-L separatory funnel and wash with two 100 mL portions of distilled water. Discard the water layer and pour the hexane layer through a

column (Section 4.8) packed with 3 to 4 inches of anhydrous sodium sulfate . Drain the column into a 500-mL K-D flask equipped with a 10-mL ampul. Rinse the separatory funnel and column with three 10 mL portions of hexane.

8.6.4 Concentrate the extracts to 6 to 10 mL in the K-D evaporator in a hot water bath, then adjust the volume to 10.0 mL. Be sure to use the correct dilution volume (see Section 8.6.1) for the final calculation.

8.6.5 Analyze according to Section 7.4.

8.7 Florisil Slurry Cleanup

8.7.1 Place 10 mL of the diluted sample into a 20-mL narrow mouth screw cap container. Add 0.25 g of Florisil. Seal with a Teflon lined screw cap and shake for 1 minute.

8.7.2 Allow the Florisil to settle then decant the treated solution into a second container. Analyze according to Section 7.4.

9. Calibration

9.1 Single Point Calibrations -- Prepare calibration standards from standard stock solutions in hexane that are close to the unknown in composition and in concentration. If when using an electrolytic conductivity detector the sample response is in the low level nonlinear detection area, the calibration point must then be within 20% of the sample. The ECD must be operated only within its linear response range.

9.2 As an alternative to Section 9.1, prepare a calibration curve for each Aroclor or PCB detected in the sample. The standard curve must contain at least 3 points, two of which must bracket the

sample concentration. When using an electrolytic conductivity detector, if the sample response is in a low level nonlinear area of the calibration curve, two of the calibration points must be within 20% of the unknown. The calibration curve must be checked daily, using the Laboratory Control Standard Section 5.7. If the calibration curve is not within 15% of the Laboratory Control Standard, recalibrate the instrument. If an electron capture detector is used then it will be necessary to correct the Laboratory Control Standard value for recovery (see Section 3.4). Use the recovery value determined the same day the calibration curve was generated. The corrected value must be within 15% of the spike value, otherwise the instrument must be recalibrated.

10. Precision and Accuracy

10.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consists 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. After January 1, 1982, ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

10.1.1 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 10.2.

10.1.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 10.2.

10.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 10.4.

10.2 To establish the ability to generate acceptable accuracy and precision in the use of this method, the analyst must perform the following operations.

10.2.1 For each commercial PCB mixture or individual PCB isomer normally measured, select a spike concentration in the range of 25 to 75 mg/kg. Using stock standards, prepare a spiking concentrate in isooctane 1000 times more concentrated than the selected concentration.

10.2.2 Using a microsyringe, add 100 μ L of the PCB concentrate to each of a minimum of four 100 mL aliquots of PCB free oil. A representative waste oil may be used in place of the clean oil, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 7.

10.2.3 Calculate the average percent recovery, (R), and the relative standard deviation(s) of the concentration found.

Waste oil background corrections must be made before R calculations are performed.

10.2.4 Using the appropriate data from Tables 7, 8, and 9, determine the recovery and single operator precision expected for the method and compare these results to the values calculated in Section 10.2.3. If the data are not comparable, the analyst must review and remedy potential problem areas and repeat the test.

10.2.5 After January 1, 1982, the values for R and s must meet method performance criteria provided by the U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, before any samples may be analyzed.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

10.3.1 Calculate upper and lower control limits for method performance:

$$\text{Upper Control Limit (UCL)} = R + 3 s$$

$$\text{Lower Control Limit (LCL)} = R - 3 s$$

where R and s are calculated as in Section 10.2.3.

The UCL and LCL can be used to construct control charts⁴ that are useful in observing trends in performance. After January 1, 1982, the control limits above must be replaced by method performance criteria provided by the U.S. Environmental Protection Agency.

10.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for waste oil samples.

An accuracy statement for the method is defined as $R \pm s$.

The accuracy statement should be developed by the analysis of 4 aliquots of waste oil as described in Section 10.2.2, followed by the calculation of R and s. Alternately, the analyst may use four waste oil data points gathered through the requirement for continuing quality control in Section 10.4. The accuracy statements should be updated regularly.

10.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 10.2.2 at two times the background level. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for the parameter in all samples processed as part of the same set must be qualified as described in Section 11.9. The laboratory should monitoring the frequency of data so qualified to ensure that it remains at or below 5%.

10.5 Before processing any samples, the analyst should demonstrate through the analysis of a PCB free oil sample, that all glassware and reagents are free of interferences. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The most productive specific practices depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor

the precision of the sampling technique. When doubt exists regarding the identification of a peak on the chromatogram, confirmatory techniques such as GC with a dissimilar column, specific element detector, or MS must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

10.7 Analyze the Laboratory Control Standard Section 5.7 daily before any samples are analyzed. Instrument status checks, calibration curve validation and long term precision are obtained from these data. In addition, response data obtained from the Laboratory Control Standard can be used to estimate the concentration of the unknowns. From this information, the appropriate standard dilutions can be determined for single point calibrations.

10.8 Analyze on a quarterly basis an EMSL-Cincinnati Quality Control Sample (Section 5.4.8) of PCBs in oil or whenever new standard dilutions are prepared.

10.8.1 The results of the EMSL Quality Control Sample should agree within 15% of the true value. If they do not, the analyst must check each step in the standard preparation procedure to resolve the problem.

11. Calculations

11.1 Locate each PCB in the sample chromatogram by comparing the retention time of the suspect peak to the retention data gathered from analyzing standards and interference free Quality Control Samples. The width of the retention time window used to make

identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for each PCB can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

- 11.2 If the response for any PCB peak exceeds the working range of the system, dilute according to Section 7.3.5.
- 11.3 If accurate measurement of the peaks in the PCB elution area of the chromatogram is prevented by the presence of interferences, further cleanup is required.
- 11.4 If the parent Aroclors or PCBs are identified in the sample, calibrate according to Section 9. The concentration of the PCBs in the sample are calculated by comparing the sum of the responses for each PCB in the standard to the sum of all of the PCBs in the sample. This is particularly important as sample concentrations approach within 20% of 50 mg/kg or any other EPA regulated concentration. If calculations are based upon a single PCB peak or upon a small percentage of the total PCB peaks, serious errors may result. Peaks comprising less than 50% of the total can be disregarded only if 1) interference problems persist after cleanup; 2) the source of PCBs is obvious; or 3) the concentration of PCBs are not within $\pm 20\%$ of an EPA controlled value such as 50 mg/kg.
 - 11.4.1 Measure the peak height or peak area of each peak identified as a PCB in Section 11.1 in both the sample and the standard.

11.4.2 Use the following formula to calculate the concentration of PCBs in the sample:

$$\text{Concentration mg/Kg} = \frac{B \times V_t}{A \times W}$$

$$A = \frac{\text{Sum of standard Peak Heights (areas)}}{\text{ng of standard injected}} = \text{mm/ng}$$

$$B = \frac{\text{Sum of sample Peak Heights (areas)}}{\mu\text{L injected}} = \text{mm}/\mu\text{L}$$

V_t = dilution volume of sample in mL

W = weight of the sample in grams

11.5 If the parent Aroclors or source of PCBs is not apparent, calculate the concentration according to the procedure of Webb and McCall.⁶ The concentration of the PCBs in each peak is determined individually then added together to determine the total PCB content of the sample. Each PCB identified in the sample must be included in these calculations.

11.5.1 Small variations between Aroclor batches make it necessary to obtain standards prepared from a specific source of Aroclors. Primary dilutions of these reference Aroclors will be available in 1981 from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio 45268.

11.5.2 Analyze a standard mixture of Aroclors 1242, 1254 and 1260 under the conditions shown in Figures 3, 5, and 6. Analyze the sample under the same conditions. Compare the resulting standard chromatograms to those shown in Figures 3, 5, and 6. Each PCB peak must be resolved as well or better than

those shown in the figures. Determine the relative retention time (RRT) of each peak in the standards with respect to p,p'-DDE or assign the RRT shown in the figures to the corresponding peak in the standard. Identify the RRT of each PCB in the sample by comparing the sample chromatogram to the standard chromatograms.

11.5.3 Identify the most likely Aroclors present in the sample, using the Identification Flow Chart Figure 7.

11.5.4 Analyze standards according to Section 9, using the appropriate Aroclors.

11.5.5 Determine the instrument response factor (A) for each individual PCB, using the following formula:

$$A = \frac{\text{Peak Height (area)}}{Ng_i \times \frac{\text{mean weight \%}}{100}}$$

Ng_i = Ng of Aroclor standard injected
Obtain mean weight percent from Tables 1 through 6.

11.5.6 Calculate the concentration of each PCB in the sample using the following formula:

$$\text{Concentration mg/Kg} = \frac{B \times V_t}{A \times W}$$

A = Response factor from 11.5.5

B = $\frac{\text{Peak Height (areas) of sample mm/uL}}{\text{uL injected}}$

V_t = dilution volume of sample in mL

W = weight of sample in grams

The concentration of each PCB must be calculated and added together to obtain the total amount of PCBs present.

11.6 Report all data in mg/Kg.

11.7 Round off all data to 2 significant figures.

11.8 Add all Aroclors and report what was used as the standard. For example, 57 mg/Kg measured as Aroclor 1260 or 57 mg/Kg measured as Aroclors 1242 and 1260.

11.9 Data for the affected parameters of samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 10.4 must be labeled as suspect.

11.10 Determine the actual recovery for electron capture analyses of each sample in the uncorrected 40 to 50 mg/kg concentration range (see Section 3.4). Report the corrected value and the recovery.

12. Precision and Accuracy

12.1 The single laboratory data shown in Tables 7 through 9 were generated using the recommended procedures described in this method to analyze both spiked and nonspiked oil samples of varying degrees of complexity. Data for both the HED and ECD are present. These data were generated by the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

References

1. Federal Register, 40 CFR, Part 761.
2. Eichelberger, J. W., L.E. Harris and W. L. Budde. Anal. Chem., 46, 227 (1974).
3. Federal Register, Vol. 41, No. 232, Wednesday, December 1, 1976.
4. White, L. D., et al., AIHA Journal, 31, 225, (1970).
5. Handbook of Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
6. Webb, R.G. and A.C. McCall. J. Chrom. Sci., 11, 366 (1973).

TABLE 1
Composition of Aroclor 1221^a

RRT ^b	Mean Weight Percent	Relative Std. Dev. ^c	Number of Chlorines ^d
11	31.8	15.8	1
14	19.3	9.1	1
16	10.1	9.7	2
19	2.8	9.7	2
21	20.8	9.3	2
28	5.4	13.9	2 85%
			3 15%
32	1.4	30.1	2 10%
			3 90%
37	1.7	48.8	3
40			3
Total	93.3		

^a Data obtained from.⁶

^b Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

^c Relative standard deviation of 17 analyses.

^d From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 2
Composition of Aroclor 1232^a

RR T ^b	Mean Weight Percent	Relative Std. Dev. ^c	Number of Chlorines ^d
11	16.2	3.4	1
14	9.9	2.5	1
16	7.1	6.8	2
20	17.8	2.4	2
21			2
28	9.6	3.4	2 40%
			3 60%
32	3.9	4.7	3
37	6.8	2.5	3
40	6.4	2.7	3
47	4.2	4.1	4
54	3.4	3.4	3 33%
			4 67%
58	2.6	3.7	4
70	4.6	3.1	4 90%
			5 10%
78	1.7	7.5	4
Total	94.2		

^a Data obtained from.⁶

^b Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

^c Relative standard deviation of four analyses.

^d From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 3
Composition of Aroclor 1242^a

RRT ^b	Mean Weight Percent	Relative Std. Dev. ^c	Number of Chlorines ^d
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2 25%
			3 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3 33%
			4 67%
58	5.6	3.3	4
70	10.3	2.8	4 90%
			5 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	2.3	16.4	5
125	1.6	20.4	5 85%
			6 15%
146	1.0	19.9	5 75%
			6 25%
Total	98.5		

^a Data obtained from.⁶

^b Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

^c Relative standard deviation of six analyses

^d From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 4
Composition of Aroclor 1248^a

RRT ^b	Mean Weight Percent	Relative Std. Dev. ^c	Number of Chlorines ^d
21	1.2	23.9	2
28	5.2	3.3	3
32	3.2	3.8	3
47	8.3	3.6	3
40	8.3	3.9	3 85%
			4 15%
47	15.6	1.1	4
54	9.7	6.0	3 10%
			4 90%
58	9.3	5.8	4
70	19.0	1.4	4 80%
			5 20%
78	6.6	2.7	4
84	4.9	2.6	5
98	3.2	3.2	5
104	3.3	3.6	4 10%
			5 90%
112	1.2	6.6	5
125	2.6	5.9	5 90%
			6 10%
146	1.5	10.0	5 85%
			6 15%
Total	103.1		

^a Data obtained from ⁶

^b Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

^c Relative standard deviation of six analyses.

^d From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

TABLE 6
Composition of Aroclor 1260^a

RRT ^b	Mean Weight Percent	Relative Std. Dev. ^c	Number of Chlorines ^d
70	2.7	6.3	5
84	4.7	1.6	5
98	3.8	3.5	e
104			5 60%
			6 40%
117	3.3	6.7	6
125	12.3	3.3	5 15%
			6 85%
146	14.1	3.6	6
160	4.9	2.2	6 50%
			7 50%
174	12.4	2.7	6
203	9.3	4.0	6 10%
			7 90%
232	9.8	3.4	6 10% ^f
244			7 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

^a Data obtained from.⁶

^b Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

^c Relative standard deviation of six analyses.

^d From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

^e Composition determined at the center of peak 104.

^f Composition determined at the center of peak 232.

TABLE 7
ACCURACY AND PRECISION USING
SPIKED MOTOR OIL

Dilution Ratio	Detector	Method Clean up	Spike mg/Kg	Aroclor Spike	Ave. Conc. Found mg/Kg	(Precision) Rel. Std. Deviation %	(Accuracy) Percent Recovered	Num o Dil
100:1	HED	None	30.3	1242	28.2	4.2	93.1	
100:1	ECD	None	30.3	1242	26.7 ^a	5.7	88.1	
100:1	HED	None	31.1	1260	27.2	2.0	87.5	
100:1	ECD	None	31.1	1260	23.9	2.2	76.8	
100:1	HED	8.1	30.3	1242	28.4	11.5	93.7	
100:1	ECD	8.1	30.3	1242	25.4 ^a	6.1	83.8	
100:1	HED	8.1	31.1	1260	28.1	8.0	90.3	
100:1	ECD	8.1	31.1	1260	24.3	7.8	78.1	
100:1	HED	8.2	30.3	1242	30.7	2.4	101	
100:1	ECD	8.2	30.3	1242	27.3 ^a	10.2	90.1	
100:1	HED	8.2	31.1	1260	30.9	3.6	99.4	
100:1	ECD	8.2	31.1	1260	31.0	8.6	99.7	
100:1	HED	8.3	30.3	1242	30.3	8.6	100	
100:1	ECD	8.3	30.3	1242	28.9 ^a	5.0	95.4	
100:1	HED	8.3	31.1	1260	29.8	4.7	95.8	
100:1	ECD	8.3	31.1	1260	30.8	6.5	99.0	
100:1	HED	8.4	30.3	1242	29.4	5.8	97.0	
100:1	ECD	8.4	30.3	1242	26.4 ^a	5.3	87.1	
100:1	HED	8.4	31.1	1260	29.4	5.2	94.5	
100:1	ECD	8.4	31.1	1260	23.6	4.5	75.9	
100:1	HED	8.5	30.3	1242	31.9	8.5	105	
100:1	ECD	8.5	30.3	1242	23.4 ^a	3.0	77.2	
100:1	HED	8.5	31.1	1260	33.6	9.2	108	
100:1	ECD	8.5	31.1	1260	30.9	5.5	99.4	
100:1	HED	8.6	30.3	1242	34.4	3.8	107	
100:1	ECD	8.6	31.1	1242	23.4 ^a	4.4	77.2	
100:1	HED	8.6	30.3	1260	29.1	4.2	96.7	
100:1	ECD	8.6	31.1	1260	27.0	4.6	86.7	

^a Severe interference problems in elution area of 1242. Measurement based upon only 3 of the 10 normally resolved major peaks. Clean up technique, Sections 8.1, 8.2, 8.3, 8.5, and 8.6 did not improve the quality of the 1242 chromatogram. If this were an unknown sample, it would be impossible to qualitatively identify the presence of Aroclor 1242 using ECD. The HED provided an interference free chromatogram.

TABLE 8
ACCURACY AND PRECISION USING
WASTE TRANSFORMER FLUIDS

Sample	Dilution Ratio	Detector	Method Clean up	1260 Spike mg/Kg	Ave. D Conc. Found	(Precision) Rel. Std. Deviation %	(Accuracy) Percent Recovered	Duplicate
A	100:1	ECD	None	--	22.6	3.6	--	
A	"	HED	None	--	27.0	1.7	--	
A	"	ECD	8.1	--	22.8	2.5	--	
A	"	HED	8.1	--	29.7	1.4	--	
A	"	ECD	8.2	--	22.4	1.0	--	
A	"	HED	8.2	--	28.2	2.2	--	
A	"	ECD	8.3	--	22.7	1.3	--	
A	"	HED	8.3	--	27.8	2.8	--	
A	"	ECD	8.4	--	20.9	--	--	
A	"	HED	8.4	--	30.2	--	--	
A	"	ECD	8.5	--	23.8	0.3	--	
A	"	HED	8.5	--	28.6	4.1	--	
A	"	ECD	None	27.0	45.0	3.3	91	
A	"	HED	None	27.0	55.2	1.5	102	
B	1000:1	ECD	None	--	452	0.8	--	
B	"	HED	"	--	471	1.2	--	
B	"	ECD	"	455	875	0.5	96	
B	"	HED	"	455	916	2.0	99	
C	1000:1	ECD	None	--	284	1.2	--	
C	"	HED	"	--	300	1.4	--	
C	"	ECD	"	300	607	3.6	104	
C	"	HED	"	300	686	3.9	114	

A - dark waste oil

B - black waste oil with suspended solids

C - clear waste oil

D - all samples contained Aroclor 1260

e - duplicate analyses made at each dilution

TABLE 9
Accuracy and Precision and Limit of Detection Data
Results of Analyses of Shell Transformer Fluid
Spiked with PCBs at 5.0 and 27 mg/Kg

Electron Capture Detector (100:1 Dilution)						
Aroclor	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Standard Deviation	% Recovery	MDL ^a (mg/kg)
1221	5.0	7	7.5	0.43	150	1.4
1242	5.0	14	3.8	0.18	76	0.5
1254	5.0	7	4.1	0.08	82	0.2
1260	5.0	14	4.7	0.18	94	0.5

Electrolytic Conductivity Detector (100:1 Dilution)						
Aroclor	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Standard Deviation	% Recovery	MDL ^a (mg/kg)
1221	5.0	6	7.5	0.23	150	0.7
1242	5.0	7	5.9	0.17	118	0.5
1254	5.0	6	5.8	0.16	116	0.5
1260	5.0	7	5.4	0.10	108	0.3

Shell Transformer Oil + 27 ppm Aroclor-1260 (100:1 Dilution)						
Detector	Spike (mg/kg)	Number of Analyses	Avg (mg/kg)	Rel. Std. Deviation %	% Recovery	
ECD	27	14	24.0	.70	89	
HED	27	7	28.3	2.1	105	

^aMDL = Method Detection Limit at 99% confidence that the value is not zero. Note: At these values it would be impossible to identify Aroclor patterns with any degree of confidence. 1 mg/Kg appears to be a reasonable MDL.

$$MDL = t_{(n-1, .99)} (S)$$

where:

MDL = the method detection limit
 $t_{(n-1, .99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
S = standard deviation of the replicate analyses

Column: 3% OV-1
Detector: Electron Capture
Column Temperature: 150° C

Figure 1. Gas chromatogram of Aroclor 1221.

Figure 2. Gas chromatogram of Aroclor 1232.

Figure 3. Gas Chromatogram of Aroclor 1242.

Figure 4. Gas chromatogram of Aroclor 1248.

Column: 3% OV-1
Detector: Electron Capture
Column Temperature: 170° C.

Column: 3% OV-1
Detector: Electron Capture
Column Temperature: 170° C.

Figure 6. Gas chromatogram of Aroclor 1200.

Figure 7. Chromatogram Division Flowchart

Test Method

Polynuclear Aromatic Hydrocarbons — Method 610

1. Scope and Application

1.1 This method covers the determination of certain polynuclear aromatic hydrocarbons (PAH). The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Benzo (a) anthracene	34526	56-55-3
Benzo (a) pyrene	34247	50-32-8
Benzo (b) fluoranthene	34230	205-99-2
Benzo (ghi) perylene	34521	191-24-2
Benzo (k) fluoranthene	34242	207-08-9
Chrysene	34320	218-01-9
Dibenzo (a, h) anthracene	34556	53-70-3
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Indeno (1, 2, 3-cd) pyrene	34403	193-39-5
Naphthalene	34696	91-20-3
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0

1.2 This is a chromatographic method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for many of the parameters listed in Section 1.1, using the extract produced by this method.

1.3 This method provides for both high performance liquid chromatographic (HPLC) and gas chromatographic (GC) approaches to the determination of PAHs. The gas chromatographic procedure does not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo (a) anthracene; benzo (b) fluoranthene and benzo (k) fluoranthene; and dibenzo (a, h) anthracene and indeno (1, 2, 3-cd) pyrene. Unless the purpose for the analysis can be served by reporting the sum of an unresolved pair, the liquid chromatographic approach must be used for these compounds. The liquid

chromatographic method does resolve all 16 of the PAHs listed.

1.4 The method detection limit (MDL, defined in Section 15)⁽¹⁾ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ depending upon the nature of interferences in the sample matrix.

1.5 The sample extraction and concentration steps in this method are essentially the same as in methods 606, 608, 609, 611 and 612.

Therefore, a single sample may be extracted to measure the parameters included in the scope of each of these methods, provided the concentration is high enough to permit selecting aliquots of the extract for cleanup, when required. Selection of the aliquots must be made prior to the solvent exchange steps of this method. The analyst is allowed the latitude, under Gas Chromatography (Section 13), to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.6 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC and GC and in the interpretation of liquid and gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and concentrated to a volume of 10 mL or less. The solvent is exchanged to cyclohexane prior to cleanup. Following cleanup, when using HPLC for determination of the PAHs, the solvent is exchanged to acetonitrile. Ultraviolet (UV) and fluorescence detectors are used with HPLC. When cleanup is not required and when flame ionization detector GC is used for determination, the methylene chloride extract may be analyzed directly. When cleanup is required, the cyclohexane exchange is made. Instrumental conditions are

described which permit the separation and measurement of the PAH compounds⁽²⁾.

2.2 A silica gel column cleanup procedure is provided to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned⁽³⁾. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. It should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not

been fully assessed. Although the HPLC conditions described allow for a unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified⁽⁴⁻⁶⁾ for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens; benzo (a) anthracene, benzo (a) pyrene and dibenzo (a, h) anthracene.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle - Amber glass, one-liter or one-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnel - 2000-mL, with Teflon stopcock.

5.2.2 Drying column - Chromatographic column 400 mm long x 19 mm ID with coarse frit.

5.2.3 Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish - two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials - Amber glass, 10- to 15- mL capacity, with Teflon-lined screwcap.

5.2.8 Chromatographic column - 250 mm long x 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5.3 Boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

5.4 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing 0.0001g.

5.6 High performance liquid chromatographic apparatus (modular):

5.6.1 Gradient pumping system, constant flow.

5.6.2 Reverse phase column, 5 micron HC-ODS Sil-X, 250 mm x 2.6 mm ID (Perkin-Elmer No. 089-0716 or equivalent).

5.6.3 Fluorescence detector, for excitation at 280 nm and emission greater than 389 nm cutoff (Corning 3-75 or equivalent). Fluorometers should have dispersive optics for excitation and can utilize either filter or dispersive optics at the emission detector.

5.6.4 UV detector, 254 nm, coupled to fluorescence detector.

5.6.5 Strip-chart recorder compatible with detectors. Use of a data system for measuring peak areas and retention times is recommended.

5.7 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection or splitless injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder.

A data system is recommended for measuring peak areas.

5.7.1 Column - 1.8 m long x 2 mm ID pyrex glass packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent. This column was used to develop the retention time data in Table 2. Guidelines for the use of alternate column packings are provided in Section 13.

5.7.2 Detector - Flame ionization. This detector has proven effective in the analysis of wastewaters for the compounds listed in the scope excluding the four pairs of unresolved compounds listed in Section 1.3. Guidelines for the use of alternate detectors are provided in Section 12.2.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Sodium thiosulfate - (ACS) Granular.

6.3 Cyclohexane, methanol, acetone, methylene chloride, and pentane - Pesticide quality or equivalent.

6.4 Acetonitrile, high purity HPLC quality, distilled in glass.

6.5 Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

6.6 Silica gel - Grade 923 (100/200 mesh) dessicant (Davison Chemical or equivalent). Before use, activate for at least 16 hours at 130°C in a shallow glass tray, loosely covered with foil.

6.7 Stock standard solutions (1.00 $\mu\text{g}/\mu\text{L}$) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in HPLC quality acetonitrile, dilute to volume in a 10-

mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. Calibration

7.1 Establish liquid or gas chromatographic operating parameters to produce resolution of the parameters equivalent to that indicated in Tables 1 or 2. The chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 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 and diluting to volume with acetonitrile. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Analyze each calibration standard (5 to 25 μL for HPLC and 2 to 5 μL for GC), and tabulate peak height or area responses against the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range ($< 10\%$ relative

standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 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 $\pm 10\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal standard calibration procedure. To use this approach, 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.

7.3.1 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 acetonitrile. One of the standards should be at a concentration near, but above, the MDL and 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 Analyze each calibration standard (5 to 25 μL for HPLC and 2 to 5 μL for GC) and tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

$$\text{Eq. 1 } RF = (A_s C_m) / (A_m C_s)$$

where:

A_s = Response for the parameter to be measured.

A_m = Response for the internal standard.

C_m = Concentration of the internal standard, ($\mu\text{g/L}$).

C_s = Concentration of the parameter to be measured, ($\mu\text{g/L}$).

If the RF value over the working range is a constant ($< 10\%$ RSD), 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_m vs. RF.

7.3.3 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 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.

8. 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 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 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples 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.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in acetonitrile 1000 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 3, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X-R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of inter-laboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

where R and s are calculated as in Section 8.2.3.

The UCL and LCL can be used to construct control charts⁽⁷⁾ that are useful in observing trends in perfor-

mance. The control limits above must be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s . Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly¹⁷.

8.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 14.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a one-liter aliquot of reagent water, that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against 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 duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as chromatography with a dissimilar column or detector must be used. This may include the use of a mass spectrometer. Whenever possible, the

laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹⁸ 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 as free as possible of Tygon tubing and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction. PAHs are known to be light sensitive, therefore, samples, extracts and standards should be stored in amber or foil wrapped bottles in order to minimize photolytic decomposition. Fill the sample bottle and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used for measurement of residual chlorine¹⁹. Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days, and analysis completed within 40 days of extraction¹².

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene

chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle, rinse and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap bottles and protected from light.

10.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%.

11.2 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1- to 10- mL aliquot of sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL cyclohexane and attach a micro-Snyder column. Prewet the micro-Snyder column by adding 0.5 mL methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. 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 the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane. Adjust the extract volume to about 2 mL.

11.3 Silica gel column cleanup for PAHs.

11.3.1 Prepare a slurry of 10g activated silica gel in methylene chloride and place this in a 10-mm ID chromatography column. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

11.3.2 Preequilibrate the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL of cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer.

11.3.3 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL pentane and continue elution of the column. Discard the pentane eluate.

11.3.4 Elute the column with 25 mL of methylene chloride/pentane (4 + 6) (V/V) and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. Elution of the column should be at a rate of about 2 mL/min.

11.3.5 Concentrate the collected fraction to less than 10 mL by K-D techniques as in Section 10.6, using pentane to rinse the walls of the glassware. Proceed with HPLC or GC analysis.

12. High Performance Liquid Chromatography (HPLC)

12.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip, then attach a micro-Snyder column. Increase the temperature of the hot water bath to 95 to 100°C. Concentrate the solvent as in Section 10. After cooling, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL acetonitrile. Adjust the extract volume to 1.0 mL.

12.2 Table 1 summarizes the recommended HPLC column materials and operating conditions for the instrument. This table includes retention times, capacity factors, and MDL that were obtained under these conditions. The UV detector is recommended for the determination of naphthalene, acenaphthylene, acenaphthene, and fluorene, and the fluorescence detector is recommended for the remaining PAHs. Examples of the parameter separations achieved by this HPLC column are shown in Figures 1 and 2. Other HPLC columns, chromatographic conditions or detectors may be used if the requirements of Section 8.2 are met.

12.3 Calibrate the system daily as described in Section 7.

12.4 If the internal standard approach is being used, the internal standard must be added to sample extract and mixed thoroughly, immediately, before injection into the instrument.

12.5 Inject 5 to 25 μ L of the sample extract using a high pressure syringe or a constant volume sample injection loop. Record the volume injected to the nearest 0.1 μ L, and the resulting peak size in height or area units. Re-equilibrate the liquid chromatographic column at the initial gradient conditions for at least 10 minutes between injections.

12.6 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.7 If the peak height or area exceeds the linear range of the system, dilute the extract with acetonitrile and reanalyze.

12.8 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

13. Gas Chromatography

13.1 The packed column GC procedure will not resolve certain isomeric pairs as indicated in Section 1.3 and Table 2. The liquid chromatographic procedure (Section 12) must be used for these materials. Capillary (open-tubular) columns may be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

13.2 To achieve maximum sensitivity with this method, the extract must be concentrated to 1.0 mL. Add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the micro K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus. Drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Table 2 describes the recommended GC column and operating conditions for the instrument. This table includes

retention times that were obtained under these conditions. An example of the parameter separations achieved by this column is shown in Figure 3. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

13.4 Calibrate the GC system daily as described in Section 7.

13.5 If the internal standard approach is being used, add the internal standard to sample extract and mix thoroughly, immediately, before injection into the instrument.

13.6 Inject 2 to 5 μL of the sample extract using the solvent-flush technique⁽¹⁰⁾. Smaller (1.0 μL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL , and the resulting peak size in area or peak height units.

13.7 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

13.8 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

13.9 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

14. Calculations

14.1 Determine the concentration of individual parameters in the sample.

14.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from Equation 2:

$$\text{Eq. 2. Concentration, } \mu\text{g/L} = \frac{(A)(V_i)}{(V_t)(V_s)}$$

where:

A = Amount of material injected, in nanograms.

V_i = Volume of extract injected (μL).

V_t = Volume of total extract (μL).

V_s = Volume of water extracted (mL).

14.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

$$\text{Eq. 3. Concentration, } \mu\text{g/L} = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_s = Volume of water extracted, in liters.

14.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

14.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits established in Section 8.4, data for the affected parameters must be labeled as suspect.

15. Method Performance

15.1 Method detection limits - The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 95% confidence that the value is above zero⁽¹¹⁾. The MDL concentrations listed in Table 1 were obtained using reagent water⁽¹¹⁾. Similar results were achieved using representative wastewaters. MDL for the GC approach were not determined.

15.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL⁽¹¹⁾, with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45% respectively).

15.3 In a single laboratory (Battelle Columbus Laboratories), using spiked wastewater samples, the average recoveries presented in Table 3 were

obtained⁽¹²⁾. Each spiked sample was analyzed in triplicate on two separate days. The standard deviation of the percent recovery is also included in Table 3.

15.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

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11. Cole, T., Riggins, R., and Glaser, J., "Evaluation of Method Detection Limits and Analytical Curve for EPA Method 610 - PNAs," International Symposium on Polynuclear Aromatic Hydrocarbons, 5th, Battelle Columbus Laboratory, Columbus, Ohio (1980).

Table 1. High Performance Liquid Chromatography Conditions and Method Detection Limits

Parameter	Retention Time (min)	Capacity Factor (k')	Method Detection Limit ($\mu\text{g/L}$) ^a
Naphthalene	16.6	12.2	1.8
Acenaphthylene	18.5	13.7	2.3
Acenaphthene	20.5	15.2	1.8
Fluorene	21.2	15.8	0.21
Phenanthrene	22.1	16.6	0.64
Anthracene	23.4	17.6	0.66
Fluoranthene	24.5	18.5	0.21
Pyrene	25.4	19.1	0.27
Benzo(a)anthracene	28.5	21.6	0.013
Chrysene	29.3	22.2	0.15
Benzo(b)fluoranthene	31.6	24.0	0.018
Benzo(k)fluoranthene	32.9	25.1	0.017
Benzo(a)pyrene	33.9	25.9	0.023
Dibenzo(a,h)anthracene	35.7	27.4	0.030
Benzo(ghi)perylene	36.3	27.8	0.076
Indeno(1,2,3-cd)pyrene	37.4	28.7	0.043

HPLC conditions: Reverse phase HC-ODS Sil-X 2.6 mm x 250 mm Perkin-Elmer column; isocratic elution for 5 min using acetonitrile/water (4 + 6), then linear gradient elution to 100% acetonitrile over 25 minutes; flow rate is 0.5 mL/min. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

^aThe method detection limit for naphthalene, acenaphthylene, acenaphthene, and fluorene were determined using a UV detector. All others were determined using a fluorescence detector.

Table 2. Gas Chromatographic Operating Conditions and Retention Times

Parameter	Retention Time (min)
Naphthalene	4.5
Acenaphthylene	10.4
Acenaphthene	10.8
Fluorene	12.6
Phenanthrene	15.9
Anthracene	15.9
Fluoranthene	19.8
Pyrene	20.6
Benzo(a)anthracene	20.6
Chrysene	24.7
Benzo(b)fluoranthene	28.0
Benzo(k)fluoranthene	28.0
Benzo(a)pyrene	29.4
Dibenzo(a,h)anthracene	36.2
Indeno(1,2,3-cd)pyrene	36.2
Benzo(ghi)perylene	38.6

GC conditions: Chromosorb W-AW-DCMS (100/120 mesh) coated with 3% OV-17, packed in a 1.8 m long x 2 mm ID glass column, with nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature was held at 100°C for 4 min, then programmed at 8°/minute to a final hold at 280°C.

Table 3 Single Operator Accuracy and Precision

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (µg/L)	Number of Analyses	Matrix Types
Acenaphthene	88	5.7	11.6-25	24	4
Acenaphthylene	93	6.4	250-450	24	4
Anthracene	93	6.3	7.9-11.3	24	4
Benzo(a)anthracene	89	6.9	0.64-0.66	24	4
Benzo(a)pyrene	94	7.4	0.21-0.30	24	4
Benzo(b)fluoranthene	97	12.9	0.24-0.30	24	4
Benzo(ghi)perylene	86	7.3	0.42-3.4	24	4
Benzo(k)fluoranthene	94	9.5	0.14-6.2	24	4
Chrysene	88	9.0	2.0-6.8	24	4
Dibenzo(a,h)anthracene	87	5.8	0.4-1.7	24	4
Fluoranthene	116	9.7	0.3-2.2	24	4
Fluorene	90	7.9	6.1-23	24	4
Indeno(1,2,3-cd)pyrene	94	6.4	0.96-1.4	24	4
Naphthalene	78	8.3	20-70	24	4
Phenanthrene	98	8.4	3.8-5.0	24	4
Pyrene	96	8.5	2.3-6.9	24	4

Column: HC-ODS SIL-X

Mobile phase: 40% to 100% Acetonitrile in water

Detector: Ultra violet at 254nm

Figure 1. Liquid chromatogram of polynuclear aromatic hydrocarbons.

Column: HC-ODS SIL-X
 Mobile phase: 40% to 100% Acetonitrile
 in water
 Detector: Fluorescence

Figure 2. Liquid chromatogram of polynuclear aromatic hydrocarbons.

Column: 3% OV-17 on Chromosorb W-AW-DCMS
 Program: 100°C. 4 min., 8° per min. to 280°C.
 Detector: Flame ionization

Figure 3. Gas chromatogram of polynuclear aromatic hydrocarbons.

FORMULA: Table 1

POLYNUCLEAR AROMATIC HYDROCARBONS

M.W.: Table 1

METHOD: 5506

ISSUED: 5/15/85

OSHA: proposed for B[a]P: 0.2 $\mu\text{g}/\text{m}^3$
 ACGIH: suspect carcinogen (B[a]P)

PROPERTIES: Table 1

COMPOUNDS: acenaphthene	benzo[ghi]perylene	fluorene
acenaphthylene	benzo[a]pyrene	indeno[1,2,3-cd]pyrene
anthracene	benzo[e]pyrene	naphthalene
benz[a]anthracene	chrysene	phenanthrene
benzo[b]fluoranthene	dibenz[a,h]anthracene	pyrene
benzo[k]fluoranthene	fluoranthene	

SYNONYMS: PAH; PNA; also see Table 2.

SAMPLING	MEASUREMENT
SAMPLER: FILTER + SORBENT (2- μm , 37-mm PTFE + washed XAD-2, 100 mg/50 mg)	! METHOD: HPLC, FLUORESCENCE/UV DETECTION !
FLOW RATE: 2 L/min	! ANALYTE: compounds above !
VOL-MIN: 200 L -MAX: 1000 L	! EXTRACTION: 5 mL organic solvent appropriate to ! sample matrix (step 7) !
SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C	! COLUMN: 15 cm x 4.6 mm, reverse phase, 5- μm C ₁₈ !
SAMPLE STABILITY: unknown; protect from heat and UV radiation	! INJECTION VOLUME: 10 to 50 μL !
FIELD BLANKS: 10% (≥ 3) of samples MEDIA BLANKS: 6 to 10	! MOBILE PHASE: H ₂ O/CH ₃ CN gradient @ ambient ! temperature !
AREA SAMPLES: 8 replicates on preweighed filters for solvent selection	! FLOW RATE: 1.0 mL/min !
	! DETECTORS: UV @ 254 nm; fluorescence @ 340 nm ! (excitation), 425 nm (emission) !
	! CALIBRATION: external standards in CH ₃ CN !
	! RANGE, LOD AND PRECISION (s_p): EVALUATION OF ! METHOD !
ACCURACY	!
RANGE STUDIED, BIAS, AND OVERALL PRECISION (s_p): not measured	!

APPLICABILITY: The working range for B[a]P is 1 to 50 $\mu\text{g}/\text{m}^3$ for a 400-L air sample. Specific sample sets may require modification in filter extraction solvent, choice of measurement method, and measurement conditions (see EVALUATION OF METHOD).

INTERFERENCES: Any compound which elutes at the same HPLC retention time may interfere. Heat, ozone, NO₂, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 206 and 251 [1]. The spectrophotometric methods, P&CAM 184 and 186 [1], have not been revised. Also see Method 5515 (GC).

5/15/85

5506-1

REAGENTS:

1. Filter extraction solvent: benzene,* cyclohexane, methylene chloride, or other appropriate solvents, pesticide grade (step 7).
2. Water, distilled, deionized, degassed.
3. Acetonitrile, HPLC grade, degassed.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with acetonitrile. Stable six months if refrigerated and protected from light.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filter. PTFE-laminated membrane filter, 2- μ m pore size, 37-mm diameter (ZEFLOUR, Membrana, Pleasanton, CA or equivalent), backed by a gasket (37-mm OD, 32-mm ID) cut from a cellulose support pad, in cassette filter holder.
NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
NOTE 2: Take filters to be preweighed from the filter package and allow to equilibrate 24 hrs with laboratory atmosphere before taring.
 - b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H₂O).
2. Personal sampling pump capable of operating for 8 hrs at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Filters, 0.45- μ m, PTFE or nylon (for filtering sample solutions).
9. Pipet, 5-mL.
10. Syringe or micropipets, 1- to 100- μ L.
11. Ultrasonic bath.
12. HPLC, with gradient capability, fluorescence (excitation @ 240 nm, emission @ 425 nm) and UV (254 nm) detectors in series, electronic integrator, and column [HC-ODS-SILX (Perkin-Elmer Corp.), Vydac 201TP (The Separations Group) or equivalent; see page 5506-1].
13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.
15. Kuderna-Danish extractor.

SPECIAL PRECAUTIONS: Treat benzene and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L. Take a concurrent set of eight replicate area samples at 2 to 4 L/min on preweighed, 2- μ m PTFE filters in an area of highest expected PAH concentration.
NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a scintillation vial. Hold filter at edge to avoid disturbing the deposit. Cap the scintillation vial and wrap it in aluminum foil.
NOTE: This step is necessary to avoid loss of analytes due to sublimation and degradation by light.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAH. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
 - a. Allow the preweighed area filter samples to equilibrate 24 hrs with the laboratory atmosphere.
 - b. Weigh the area filters. Determine total weight collected on each.
 - c. Extract the first pair of area filters with acetonitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and adsorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [2,3] and benzene:ethanol (4:1 v/v) [4] have been recommended for extraction of PAH from diesel exhaust particulate.
 - d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
 - e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
 - a. Add 5.0 mL of the solvent chosen in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
 - b. Cap and let sit 15 to 20 min in an ultrasonic bath.
NOTE 1: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.
NOTE 2: The sample must be dissolved in acetonitrile for chromatography. If needed, perform solvent exchange as follows:
CAUTION: To avoid loss of volatile components, do not allow the sample to go to dryness at any time.
 - (1) After filtration (step 10), take the sample to near dryness in a Kuderna-Danish extractor.
 - (2) Add ca. 1 mL acetonitrile, take to near dryness, and adjust final volume to 1.0 mL with acetonitrile and filter again.
9. Desorb PAH from sorbent.
 - a. Score each sorbent tube with a file in front of the front (larger) sorbent section. Break tube at score line.

- b. Transfer glass wool plug and front sorbent section to a culture tube. Discard the foam plug. Transfer back sorbent section to a second culture tube.
 - c. Add 5.0 mL acetonitrile to each culture tube. Cap the culture tubes.
 - d. Allow samples to sit for 30 min. Swirl occasionally.
10. Filter all sample extracts through an 0.45- μ m membrane filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least five working standards.
 - a. Dilute aliquots of calibration stock solution with acetonitrile in 10-mL volumetric flasks (e.g., to 2.5, 0.5, 0.1, 0.02, and 0.002 μ g/mL).
 - b. Intersperse working standards and samples in the measurements.
 - c. Prepare calibration graphs (peak area vs. μ g of each PAH per sample).
12. Recovery and desorption efficiency.
 - a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
 - (1) Filters. Using a microliter syringe or micropipette, spike four filters at each of five concentration levels with a mixture of the analytes. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.

NOTE: This step may not be used for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.
 - (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. Prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blanks in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight. Analyze (steps 9, 10, and 14 through 16). Prepare graphs of DE vs. amounts found.
 - b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R and DE graphs if checks do not agree to within $\pm 5\%$ of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set HPLC according to manufacturer's recommendations and to conditions on page 5506-1. Equilibrate column at 60% CH₃CN/40% H₂O at 1.0 mL/min for 15 min before injecting first sample.
15. Inject sample aliquot. Start mobile phase gradient:
 - a. Linear gradient 60% CH₃CN to 100% CH₃CN, 20 min.
 - b. Hold at 100% CH₃CN for 20 min.

NOTE: Hold longer if necessary to prevent carryover of background, e.g., from coal dust.
 - c. Linear gradient to initial condition, 5 min.
16. Measure peak areas.

NOTE 1: Approximate retention times appear in Table 3.

NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.

NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [5,6] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. Read the mass, μg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
18. Calculate concentration, C ($\mu\text{g}/\text{m}^3$), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

$$C = \frac{(W - B + W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \mu\text{g}/\text{m}^3.$$

NOTE: W_f and W_b include analyte originally collected on the filter as particulate, then volatilized during sampling. This can be a significant fraction for many PAH (e.g., fluoranthene, naphthalene, fluorene, anthracene, phenanthrene).

EVALUATION OF METHOD:

The fluorescence detector used in this method is both sensitive and selective. The detector can "see" as little as 50 pg of many PAH injected on the column. LODs for the 17 analytes range from 50 to 350 ng per sample. It does not respond to non-fluorescent molecules such as aliphatics. The method is, therefore, most amenable to determination of trace amounts of PAH in mixtures of aliphatic compounds. Successful applications include: aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

This method has been evaluated by analyzing spiked filters, spiked sorbent tubes, and complete spiked sampling trains through which were drawn 500 L of air [7]. Each of the three groups was spiked with each analyte at two concentration levels in sextuplicate. Particular note should be made that the effect of particulate matter has not been evaluated, and every sampling matrix is unique. The data on the following page were obtained on spiked samplers stored refrigerated in the dark for three months followed by measurement with HPLC.

COMPOUND	CALIBRATION RANGE (μg per sample)	LOD (μg per sample)	MEASUREMENT PRECISION	
			SPIKED ^a	SPIKED + AIR ^b
1. ACENAPHTHENE	2.0 - 13	0.8	.058 S	.093 (50)
2. ACENAPHTHYLENE	1.0 - 100	0.35	.032 S	.075 (100)
3. ANTHRACENE	0.4 - 13	0.05	.039 S	.037 (5)
4. BENZ[a]ANTHRACENE	0.4 - 13	0.15	.032 F	.084 (5)
5. BENZO[b]FLUORANTHENE	0.4 - 12	0.1	.027 F	.028 (10)
6. BENZO[k]FLUORANTHENE	0.4 - 13	0.15	.025 F	.027 (1)
7. BENZO[ghi]PERYLENE	0.5 - 25	0.2	.031 F	.029 (10)
8. BENZO[a]PYRENE	0.4 - 14	0.2	.027 F	.029 (5)
9. BENZO[e]PYRENE	0.5 - 13	0.2	(c)	(c)
10. CHRYSENE	0.4 - 12	0.15	.039 F	.024 (5)
11. DIBENZ[a,h]ANTHRACENE	0.5 - 25	0.2	.026 F	.029 (10)
12. FLUORANTHENE	0.4 - 13	0.15	.026 S	.050 (10)
13. FLUORENE	0.7 - 13	0.25	.031 S	.090 (10)
14. INDENO[1,2,3-cd]PYRENE	0.5 - 12	0.2	.044 F	.032 (10)
15. NAPHTHALENE	0.6 - 13	0.25	.041 S	.125 (50)
16. PHENANTHRENE	0.4 - 13	0.1	.036 S	.070 (2)
17. PYRENE	0.5 - 13	0.2	(c)	(c)

^aRSR for filter (F) where volatilization is nil or for sorbent (S) where substantial volatilization may occur during sampling.

^bRSR determined at the μg level shown in parenthesis for a spiked filter followed by a sorbent tube. After spiking, laboratory air was drawn through the sampling train at 2 L/min for 4 hrs.

^cNot determined.

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METHOD REVISED BY: B. R. Belinky and E. J. Slick, NIOSH/DPSE.

Date: _____

OIL AND GREASE IN WATER - INFRARED

Reference

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., 1985, pp. 496-499.

Principles

Dissolved or emulsified oil and grease are extracted from water using organic solvents. Since various solvents differ in their ability to extract oil and grease, it is important to be consistent in the solvents used. 1,1,2-trichlorotrifluoroethane was chosen to conform with the procedure used by the Environmental Protection Agency. After the oil and grease have been extracted, the amount present is quantified using infrared spectroscopy at 2930 cm^{-1} .

Limitations

Low boiling fractions such as kerosene and gasoline can be determined reliably by this method as can other oil and grease fractions. This must be taken into account when comparing results obtained by this method to those obtained gravimetrically as that method does not detect low boiling fractions. Since no organic solvent is known to selectively dissolve only oil and grease, other organic substances present may be dissolved as well. Only those showing infrared absorption in the 2930 cm^{-1} hydrocarbon region will cause interferences. To aid in breaking up saponified oil and grease, samples should be acidified to about pH 1. The addition of saturated sodium chloride may also be helpful.

Equipment

1. 1-liter separatory funnels with teflon stopcocks.
2. Recording infrared (IR) spectrophotometer for use in the 3200 to 2700 cm^{-1} range.
3. 1 cm IR cell (quartz windows).
4. 25, 50 & 100 mL volumetric flasks.
5. Whatman IPS phase separating paper.

Reagent (Stock)

1. 1,1,2-Trichlorotrifluoroethane (TCTFE) - spec quality.
2. Sodium chloride - NaCl.
3. Sulfuric acid conc. - H_2SO_4 .
4. Isooctane
5. Hexadecane
6. Benzene - CLASS I HUMAN CARCINOGEN

Reagents (Prepared)

1. Saturated NaCl - add NaCl to deionized H₂O with stirring until no more NaCl will dissolve and a slight excess remains (approximately 100g/250mL). Prepare annually.

Standards

1. Stock Standard - Pipet 250 μ L benzene, 375 μ L isooctane and 375 μ L hexadecane into a tightly sealed 1 mL vial. This represents a reference oil of density = 0.77 mg/ μ L. Refrigerate and prepare monthly.
2. Working Standards - Prepare three working standards monthly as follows:
 - a. Pipet 10 μ L of stock standard reference oil to 50 mL of TCTFE. 1 mL = 154 μ g oil and grease. (Working standard "A")
 - b. Pipet 3.5 mL of working standard "a" (154 μ g/mL) to a 50 mL volumetric and dilute to volume with TCTFE. 1 mL = 10.8 μ g oil and grease.
 - c. Pipet 10.0 mL of working standard "a" (154 μ g/mL) to a 50 mL volumetric and dilute to volume with TCTFE. 1 mL = 30.8 μ g oil & grease.

Also prepare a zero standard by filling a 25 mL volumetric flask with TCTFE.

ProcedureA. Sample collection

1. Preclean 1-liter glass sample bottles with 1:1 HNO₃ and deionized H₂O.
2. Collect approximately 1 liter of sample, acidify with 2.5 mL conc. H₂SO₄ within 6 hours of collection and refrigerate.
3. Analyze within 24 hours of collection.

B. Analysis

1. If the sample has not been acidified, add 2.5 mL conc. H₂SO₄ per liter.
2. Transfer the sample to a 1-liter separatory funnel.
3. Rinse the sample container with 15 mL 1,1,2-trichlorotrifluoroethane (TCTFE) and add this to the separatory funnel along with an additional 25 mL TCTFE.
4. Shake the separatory funnel vigorously for 2 minutes and allow the layers to separate. If an emulsion forms add 10 mL saturated NaCl solution and mix gently to break the emulsion.

5. Draw off the lower TCTFE layer through Whatman IPS filter paper into a dry 100 mL volumetric flask.
6. Rinse the original sample container with 15 mL TCTFE and add this to the separatory funnel along with an additional 25 mL TCTFE.
7. Shake the separatory funnel vigorously for 2 minutes as before and allow the layers to separate.
8. Draw off the lower TCTFE layer and add it to the 100 mL volumetric containing the first TCTFE extract, again, filtering through Whatman IPS filter paper.
9. Drain the upper aqueous phase into a 1000 mL graduated cylinder and record the volume (v).
10. Rinse the separatory funnel with 20 mL TCTFE and add this washing to the 100 mL volumetric, filtering as above.
11. Prepare a blank by filtering 10-20 mL TCTFE into a stoppered flask.
12. Set up the IR spectrophotometer according to the manufacturer's instructions. Zero the instrument and run a styrene spectrum to be sure the instrument is operating properly.
13. Fill a 1 cm IR cell with the zero standard and scan from 3200-2700 cm^{-1} .
14. Rinse the cell with each successive standard and sample and scan the same wavelength region.
15. Clean the IR cell with TCTFE and acetone, dry and return it to a desiccator for storage.

Calculations

1. Measure the absorbance of the standards and samples by constructing a straight baseline over the scan range and measuring the absorbance of the peak maximum at 2930 cm^{-1} and subtracting the baseline absorbance at that point.
2. Using the standards data, prepare a calibration curve by plotting $\mu\text{g/mL}$ oil and grease vs absorbance.
3. Use the calibration curve to determine the oil and grease concentration of the sample TCTFE extracts.
4. Calculate the original sample oil and grease concentration as follows:

$$\text{mg/L oil and grease} = \frac{A \times 100}{V}$$

A = $\mu\text{g/mL}$ oil and grease in TCTFE extract

100 = mL of TCTFE

V = mL of H_2O extracted

Draft Method 508- For Use in WS023 Only

DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

- 1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated pesticides in ground water and finished drinking water.(1) The following compounds can be determined using this method:

Analyte	CAS No.
Aldrin	309-00-2
Chlordane-alpha	5103-71-9
Chlordane-gamma	5103-74-2
Chlomeb	2675-77-6
Chlorobenzilate	501-15-6
Chlorothalonil	2921-88-2
DCPA	1897-45-6
4,4'-DDD	72-54-6
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-83-4
Ethridazole	2583-15-9
HCH-alpha	319-84-6
HCH-beta	319-85-7
HCH-delta	319-86-8
HCH-gamma	58-89-9
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Methoxychlor	72-43-5
cis-Permethrin	52845-53-1
trans-Permethrin	52845-53-1
Propachlor	1918-16-7
Trifluralin	1582-09-8

- 1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for the analytes above (Sect. 12). Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.
- 1.3 This method is restricted to use by or

under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Sect. 9.3.

- 1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

- 2.1 A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by GC with an electron capture detector (ECD).
- 2.2 An alternative manual liquid-liquid extraction method using separatory funnels is also described.

3. INTERFERENCES

- 3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Sect. 9.2.

- 3.1.1 Glassware must be scrupulously cleaned.(2) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap

and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

- 3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.
- 3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. (3,4)
- 3.3 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.
- 3.4 Matrix Interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the ground water sampled. Cleanup of sample extracts may be necessary. Positive identifications must be confirmed using the confirmation column specified in Sect. 5.8.2.

4. SAFETY

- 4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (5-7) for the information of the analyst.

5. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)

5.1 SAMPLING EQUIPMENT

- 5.1.1 Grab sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle #219820), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in Sect. 3.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce #012736) and extracted with methanol overnight prior to use.

5.2 GLASSWARE

- 5.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.
- 5.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce #012736) and extracted with methanol overnight prior to use.
- 5.2.3 Flask, Erlenmeyer -- 500-mL
- 5.2.4 Concentrator tube, Kuderna-Danish (K-D) 10- or 25-mL, graduated (Kontes K-570050-1025 or K-570050-2525 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

- 5.2.5 Evaporative flask, K-D 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- 5.2.6 Snyder column, K-D three-ball macro (Kontes K-503000-0121 or equivalent).
- 5.2.7 Snyder column, K-D two-ball micro (Kontes K-569001-0219 or equivalent).
- 5.2.8 Vials - Glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.
- 5.3 Separatory funnel shaker -- Capable of holding eight 2-L. separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI).
- 5.4 Tumbler -- Capable of holding four to six tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA.).
- 5.5 Boiling stones carborundum, #12 granules (Arthur H. Thomas Co. #1590-033). Heat at 400°C for 30 min prior to use. Cool and store in a dessicator.
- 5.6 Water bath -- Heated, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 5.7 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 5.8 GAS CHROMATOGRAPH - Analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.
- 5.8.1 Column 1 (Primary column) - 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 μm film thickness (available from J&W). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. A sample chromatogram obtained with this column is presented in Fig. 508-1. Validation data presented in this method were obtained using this column. Alternative columns may be used in accordance with the provisions described in Sect. 9.4.
- 5.8.2 Column 2 (Confirmation column) - 30

Table 1. Retention Times for Method Analytes

	Retention Time(a)	
	Primary	Confirmatory
Ethridiazole	23.48	22.78
Chlomeb	25.50	26.18
Propachlor	28.90	30.94
Trifluralin	31.62	(b)
HCH-alpha	31.62	32.98
Hexachlorobenzene	31.98	(b)
HCH-beta	33.32	40.12
HCH-gamma	33.68	35.36
PCNB (internal std.)	34	34
HCH-delta	35.02	41.48
Chlorthalonil	35.36	39.78
Heptachlor	37.74	36.72
Aldrin	40.12	38.08
DCEA	41.14	41.14
Heptachlor epoxide	42.16	42.16
Chlordane-gamma	43.52	43.86
Endosulfan I	44.20	43.52
Chlordane-alpha	44.54	44.54
4,4'-DDE	45.90	44.88
Dieldrin	45.90	45.90
Endrin aldehyde	46.92	46.92
Endosulfan sulfate	47.60	49.30
Chlorobenzilate	47.94	48.28
4,4'-DDD	48.28	46.92
Endosulfan II	48.62	51.68
Endrin	49.98	(b)
4,4'-DDT	50.32	50.32
Methoxychlor	53.38	53.72
cis-Permethrin	58.48	(b)
trans-Permethrin	58.82	(b)

(a) Columns and analytical conditions are described in Sect. 5.8.1 and 5.8.2.

(b) Data not available.

m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 μm film thickness (available from J&W). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

- 5.8.3 Detector - Electron capture. This detector has proven effective in the analysis of spiked reagent and artificial ground waters. An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Sect. 9.4.

Figure 508-1 Gas Chromatogram of Selected Analytes
on Primary Column

6. REAGENTS AND CONSUMABLE MATERIALS

- 6.1 Acetone, methylene chloride, MTBE -- Distilled-in-glass quality or equivalent.
- 6.2 Phosphate buffer, pH7 -- Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.
- 6.3 Sodium chloride, crystal, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.
- 6.4 Sodium sulfate, granular, anhydrous, ACS grade -- Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.
- 6.5 Sodium thiosulfate, granular, anhydrous, ACS grade.
- 6.6 Pentachloronitrobenzene (PCNB) -- 98% purity, for use as internal standard.
- 6.7 4,4'-Dichlorobiphenyl (DCB) -- 96% purity, for use as surrogate standard (available from Chemicals Procurement Inc.).
- 6.8 Reagent water -- Reagent water is defined as water in which an interferent is not

observed at or above the EDL of any analyte. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

- 6.9 STOCK STANDARD SOLUTIONS (1.00 $\mu\text{g}/\mu\text{L}$) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

6.9.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 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.

6.9.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap

vials. Store at room temperature and protect from light.

6.9.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.

6.10 INTERNAL STANDARD SPIKING SOLUTION

-- Prepare an internal standard spiking solution by accurately weighing approximately 0.0010 g of pure PCNB. Dissolve the PCNB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 5 μ L of the internal standard spiking solution to 5 mL of sample extract results in a final internal standard concentration of 0.1 μ g/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

6.11 SURROGATE STANDARD SPIKING SOLUTION

-- Prepare a surrogate standard spiking solution by accurately weighing approximately 0.0050 g of pure DCB. Dissolve the DCB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 μ L of the surrogate standard spiking solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 25 μ g/L and, assuming quantitative recovery of TDBP, a surrogate standard concentration in the final extract of 5.0 μ g/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

6.12 INSTRUMENT QC STANDARD -- Prepare instrument QC standard stock solutions by accurately weighing 0.0010 g each of chlorothalonil, chlorpyrifos, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10-mL volumetric flasks. Combine 2 μ L of the chlorpyrifos stock solution, 50 μ L of the DCPA stock solution, 50 μ L of the chlorothalonil stock solution, and 40 μ L of the HCH-delta stock solution to a 100-mL volumetric flask and dilute to volume with MTBE. Transfer the instrument QC standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be prerinsed with sample before collection.

7.2 SAMPLE PRESERVATION

7.2.1 Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a 10 mg/mL solution of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

7.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well.

7.2.3 After adding the sample to the bottle containing preservative, seal the sample bottle and shake vigorously for 1 min.

7.2.4 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results indicate that most of the target analytes present in the samples are stable for 14 days when stored under these conditions.(1) However, analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

7.3 EXTRACT STORAGE

7.3.1 Sample extracts should be stored at 4°C away from light. A 14-day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore the analyst should verify appropriate extract holding times applicable to the samples under study.

8. CALIBRATION

8.1 Establish GC operating parameters equivalent to those indicated in Sect. 5.8. The GC system may be calibrated using either the internal standard technique (Sect. 8.2)

or the external standard technique (Sect. 8.3).

8.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. PCNB has been identified as a suitable internal standard.

8.2.1 Prepare calibration standards at a minimum of five concentration levels for each analyte 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 MTBE. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

8.2.2 Inject 2 μL of each calibration standard and tabulate the relative response for each analyte (RRa) to an internal standard using the equation:

$$RRa = Aa/Ais$$

where:

Aa = the peak area of the analyte, and
Ais = the peak area of the internal standard.

8.2.3 Generate a calibration curve of analyte relative response, RRa, versus analyte concentration in the sample in μL . Data presented in Sect. 12.2 were generated using TPP for quantification calculations.

8.2.4 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

8.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

8.3.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest and surrogate

compound by adding volumes of one or more stock standards to a volumetric flask. Dilute to volume with MTBE. One of the calibration standards should be representative of an analyte concentration near, but above, the EDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

8.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 10 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range ($< 10\%$ relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

8.3.3 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close ($\pm 20\%$) to that of the unknowns.

8.3.4 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 analyte varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 8.3.3.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of method blanks, instrument QC solution, laboratory control (LC) standards, QC

- samples, and performance evaluation (PE) samples.
- 9.2 **Method Blanks.** Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a method blank must be analyzed. If within the retention time window of any analyte the method blank produces a peak that is 0.5 EDL for that analyte, determine the source of contamination and eliminate the interference before processing samples.
- 9.3 **Initial Demonstration of Capability.**
- 9.3.1 Select a representative spike concentration (about 10 times EDL) for each analyte. Prepare a LC sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of at least four 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Section 10.
- 9.3.2 Calculate mean percent recovery (X), and standard deviation of percent recovery (S). For each analyte, X must fall in the range of 70-130% (or within $R \pm 3RSD$ using the values for R and RSD for reagent water in Table 2) and S must be less than 30% (or less than $3 \times RSD$ in reagent water in Table 2). If the calculated X and S for every analyte meet the acceptance criteria, performance is acceptable and sample analysis may begin. If any X or S falls outside its acceptance range, initial demonstration procedures for that compound must be repeated.
- 9.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3
- 9.5 **Assessing Surrogate Recovery.**
- 9.5.1 When surrogate recovery from a sample or method blank is <70% or 130%, check (1) calculations to locate possible errors, (2) spiking solutions for degradation, (3) contamination or other obvious abnormalities, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.
- 9.5.2 If a blank extract reanalysis fails the 70-130% recovery criteria, the problem must be identified and corrected before continuing.
- 9.5.3 If sample extract reanalysis solves the problem, report only data from the analysis with acceptable surrogate recovery. If sample extract reanalysis does not solve the problem, report all data for that sample as suspect.
- 9.6 **Assessing the Internal Standard**
- 9.6.1 For each sample and blank extract, determine if internal standard peak area or height deviates by 30% from the average measured during analysis of calibration standards.
- 9.6.2 If 30% deviation, optimize instrument performance and inject a second aliquot of that extract. If the reinjected aliquot produces an acceptable internal standard peak area or height, report results for that aliquot. If not, assume that an error was made during addition of internal standard to that extract. Reextract that sample or blank, and analyze that extract.
- 9.6.3 If 30% deviation continues, analyze a calibration standard (Sect. 8).
- 9.6.3.1 If the internal standard peak area or peak height fails to meet criteria, then recalibrate, and reanalyze extracts that previously did not meet criteria. If acceptable area or height is measured, report results. If not, assume an interference from the matrix is affecting the internal standard and use external calibration (Sect. 8).
- 9.6.3.2 If the internal standard peak area or peak height meets criteria then assume an interference from the matrix is affecting the internal standard in your sample extract and use external calibration.
- 9.7 **Assessing Laboratory Performance**
- 9.7.1 Initial QC criteria are established by using the values for X and S generated above (Sect. 9.3) to establish upper and lower control limits:
- UPPER CONTROL LIMIT = $X + 3S$
 LOWER CONTROL LIMIT = $X - 3S$
- The laboratory must analyze at least one LC sample per sample set (all samples extracted within a 24-h period). The spiking concentration of each analyte in the laboratory control sample should be

10 times EDL. Calculate accuracy as percent recovery (X). If the recovery of any analyte falls outside the control limits, that analyte is judged out of control, and the source of the problem must be identified and resolved before continuing analyses. The control limits should be updated periodically. It is recommended that after each five to ten new recovery measurements that new control limits be calculated using only the most recent 20-30 data points.

9.7.2 Each quarter the laboratory must analyze QC check standards (if available). If criteria provided with the QC check standard are not met, corrective action should be taken and documented.

9.7.3 At least once a year, the laboratory must analyze a performance evaluation sample (if available), and results for each analyte must be within established acceptance limits.

9.8 Assessing Instrument Performance - The instrument QC standard (Sect. 6.12) should be analyzed daily to monitor instrument performance. Inability to demonstrate acceptable instrument performance indicates the needs to reevaluate the GC-NPD system. If laboratory EDLs differ from listed EDLs (Table 2), concentrations of instrument QC standard compounds may be adjusted as needed.

9.9 Analyte Confirmation - When doubt exists about identification of a GC peak, confirmatory techniques such as determination with a mass spectrometer detector or a different GC column must be used.

10. PROCEDURE

10.1 AUTOMATED EXTRACTION METHOD Validation data presented in this method were generated using the automated extraction procedure with the mechanical separatory funnel shaker.

10.1.1 Add preservative to any samples not previously preserved (Sect. 7.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike sample with 50 μ L of the surrogate standard spiking solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

10.1.2 Adjust sample to pH 7 by adding 50 mL of phosphate buffer.

10.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

10.1.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

10.1.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask containing approximately 5 g anhydrous sodium sulfate. Swirl flask to dry extract; allow flask to sit for 15 min.

10.1.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.2 MANUAL EXTRACTION METHOD Alternative procedure.

10.2.1 Add preservative to any samples not previously preserved (Sect. 7.2). Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Spike the sample with 50 μ L of the surrogate standard spiking solution. Pour the entire sample into a 2-L separatory funnel.

10.2.2 Adjust sample to pH 7 by adding 50 mL of phosphate buffer.

- 10.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.
- 10.2.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask containing approximately 5 g anhydrous sodium sulfate.
- 10.2.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Swirl flask to dry extract; allow flask to sit for 15 min.
- 10.2.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.3 EXTRACT CONCENTRATION

- 10.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Decant methylene chloride extract into K-D concentrator. Rinse remaining sodium sulfate with two 25-mL portions of methylene chloride and decant rinses into the K-D concentrator.
- 10.3.2 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 65 to 70°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot 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 will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

- 10.3.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 10 mL MTBE and a boiling stone to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

- 10.3.4 Add 5 μ L of internal standard spiking solution to the sample extract, seal, and shake to distribute the internal standard. Transfer extract to an appropriate-sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-ECD.

10.4 GAS CHROMATOGRAPHY

- 10.4.1 Sect. 5.8 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.4 are met.
- 10.4.2 Calibrate the system daily as described in Sect. 8. The standards and extracts must be in MTBE.
- 10.4.3 Inject 2 μ L of the sample extract. Record the resulting peak sizes in area units.
- 10.4.4 The width of the retention time window used to make identifications should be based upon measurements of actual

retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

- 10.4.5 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

11. CALCULATIONS

- 11.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 8.
- 11.2 For samples processed as part of a set where laboratory control standard measurements fall outside of the control limits in Sect. 9, data for the affected analytes must be labeled as suspect.

12. PRECISION AND ACCURACY

- 12.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range.(1) Analytes were divided into two spiking groups for recovery studies. Analyte recoveries at one concentration and EDL data are given in Table 2.
- 12.2 In a single laboratory, analyte recoveries from two artificial ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices.(1) Analyte recoveries from the two artificial matrices are given in Table

2.

13. REFERENCES

1. Battelle/NPS Method 2
- 2.ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation", American Society for Testing and Materials, Philadelphia, PA, p. 86, 1986.
- 3.Giam, C. S., Chan, H. S., and Nef, G. S. "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," Analytical Chemistry, 47, 2225 (1975).
- 4.Giam, C. S., and Chan, H. S. "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.
- 5."Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.
- 6."OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
- 7."Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
- 8.ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 130, 1986.

Table 2. Single Laboratory Accuracy, Precision and Estimated Detection Limits (EDLs) for Analytes from Reagent Water and Synthetic Groundwaters(a)

Analyte	EDL(b) ug/L	Spike Level, ug/L	Reagent R(c)	Water RSD(d)	Synthetic Water 1		Synthetic Water 2	
					R	RSD	R	RSD
Aldrin	0.075	0.15	88	11	100	11	88	13
Chlordane-alpha	0.0015	0.15	99	12	96	13	99	8
Chlordane-gamma	0.0015	0.15	99	12	96	13	99	7
Chlornel	0.5	5	97	12	95	7	75	11
Chlorobenzilate	5	10	108	5	98	11	102	9
Chlorthalonil	0.025	0.25	91	9	103	10	71	13
DCPA	0.025	0.25	103	12	100	13	101	6
4,4'-DDD	0.0025	0.25	107	8	96	9	101	7
4,4'-DDE	0.01	0.1	99	12	96	13	99	7
4,4'-DDT	0.06	0.6	112	15	98	12	84	10
Dieldrin	0.02	0.2	87	10	103	9	82	9
Endosulfan I	0.015	0.15	87	10	102	8	84	10
Endosulfan sulfate	0.015	0.15	102	15	94	12	72	17
Endrin	0.015	0.15	88	10	98	10	104	9
Endrin aldehyde	0.025	0.25	88	9	103	11	84	11
Endosulfan II	0.024	0.15	92	11	98	11	76	9
Ethionazole	0.025	0.25	103	6	91	7	98	4
HCH-alpha	0.025	0.05	92	11	108	7	86	9
HCH-beta	0.01	0.1	95	7	92	6	100	6
HCH-delta	0.01	0.1	102	11	99	12	103	6
HCH-gamma	0.015	0.15	89	11	115	6	85	9
Heptachlor	0.01	0.1	98	12	85	13	85	9
Heptachlor epoxide	0.015	0.15	87	10	103	7	82	12
Hexachlorobenzene	0.0077	0.06	99	22	82	12	68	7
Methoxychlor	0.05	0.5	105	13	101	10	104	6
cis-Permethrin	0.5	5	91	10	96	12	86	11
trans-Permethrin	0.5	5	111	6	97	10	102	7
Propachlor	0.5	5	103	9	116	4	95	8
Trifluralin	0.025	0.25	103	5	86	12	87	11

(a) Data corrected for amount detected in blank and represent the mean of 7-8 samples.

(b) EDL = estimated detection limit in sample in ug/L; calculated by multiplying standard deviation (S) times the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

(c) R = average percent recovery.

(d) RSD = relative standard deviation (percent)

Date: _____

ORGANIC WASTE CHARACTERIZATION USING DIRECT GC/MS INJECTION

References

Method developed by HEHF's Environmental Health Sciences Laboratory.

Principles

Identification and semi-quantitative analysis of major components of organic liquid waste samples is possible by direct injection of the sample into a gas chromatograph/mass spectrometer (GC/MS) equipped with a capillary column and split injection system. GC conditions and column of choice are determined by the type of sample being characterized. In general, components present at concentrations above 0.5-1% and chromatographable at column temperatures below 250°C can be detected. Halogenated hydrocarbons can be detected at concentrations as low as 1000 mg/Kg (ppm). Semi-quantitative concentration values are determined using relative component abundances.

This technique, when combined with sample density information, can also be used for the determination of percent levels of glycols in aqueous solutions.

Limitations

Not all GC/MS instruments are compatible with this technique. Suitable instruments must be capable of producing a large split ratio (up to ~200:1) when the sample is injected to avoid ion source contamination and column overloading problems. When use of this technique on a new instrument is being considered, it should be tried cautiously to avoid damage to or contamination of the instrument.

Complete resolution or identification of all components in samples consisting of complex mixtures may not always be possible and concentrations determined are quite approximate. For many waste samples, however, this is all the information that is necessary for adequate characterization for disposal purposes. This is a good screening tool which should be supplemented by additional analyses as needed.

Equipment

1. GC/MS equipped with capillary column and split injection system. Instruments known to be compatible with this method include:
 - a. Hewlett Packard 5992A bench top GC/MS
 - b. Hewlett Packard 5890 GC with 5970B mass selective detector
2. DB-5 0.25 μ film, 0.25 mm x 30 m capillary column or equivalent
3. 1 μ L syringe for manual injections or autosampler
4. Mass spectral library & software to perform "reverse" library searches

Reagents

Isooctane, acetone and deionized water or other appropriate solvents for syringe rinsing.

Procedure

1. Autotune the GC/MS and make sure the instrument is functioning properly.
2. Select an appropriate temperature program. The following programs have been found satisfactory when using the DB-5 capillary column:
 - a. HP5992A--30°C initial, 10°C/min. ramp, 250°C final, run time 45 minutes
 - b. HP5890/5970B--30°C initial, 10°C/min. ramp, 300°C final, run time 35 minutes
3. Establish the appropriate split ratio of -15:1 for the HP5992A or -150:1 for the HP5890/5970B.
4. Inject the sample and collect the chromatographic and mass spectral data. Data collection parameters should be set to yield a Total Ion Chromatogram containing approximately 100 peaks in a complex oil sample.
 - a. HP5992A - manually inject 0.1 µL using a 1 µL syringe.
 - b. HP5890/5970B - manually or with an autosampler inject 1 µL using a 10 µL syringe (viscous samples must be injected manually).
5. Produce a printout of the sample chromatogram and the mass spectra for each chromatographic peak.
6. Identify the sample constituents by comparing sample spectra to mass spectra of known compounds. The following mass spectral data bases are available:
 - a. NIH/EPA Mass Spectral Data Base, NSRDS-NBS 63, 1983, 6 volumes hard copy.
 - b. Chemical Information Systems, Inc. Mass Spectral Search System for searching the NIH/EPA/MSDC Mass Spectral Data Base and Wiley Mass Spectral Search System for searching the 1982 Registry of Mass Spectral Data from John Wiley & Sons, Inc. (See Lab Operating Procedure L-8.10 for accessing these computer data bases.)
 - c. NBS-Rev.F Mass Spectral Library, resident on the HP5890/5970B GC/MS. (Instrument has capability of automatically searching all spectra in a sample against this library.)

Calculations

Approximate concentrations of sample components are determined by summing the abundances of all components and dividing that sum into the abundance of the component of interest. This assumes equivalent responses for all compounds, which is not true; however, the information obtained is adequate for the gross characterizations provided by this method.

The following guidelines are used when characterizing organic liquids, especially oil matrices:

1. Aliphatic hydrocarbons are grouped as to those with molecular weights less than or equal to 10 and those greater than 10. (Decane has a flash point of -60°C , the critical temperature for flammable or nonflammable waste designation.)
2. Low molecular weight solvents (ketones, alcohols, benzene, toluene, xylene, etc.) are characterized and reported individually when possible.
3. Halogenated solvents and other halogenated materials are identified and reported separately as much as possible.
4. Aromatic compounds heavier than xylene are grouped as substituted benzenes, subs. naphthalenes, subs. phenols, etc. If polynuclear aromatics with three or more rings are found, they are identified separately as much as possible. At a minimum they are grouped by the number of rings present.

The following procedure is used to determine ethylene and propylene glycols in water when no other major components are present:

1. Identify the glycol or glycols present.
2. Determine the sample density.
3. Using charts of density versus percent glycol or solution of two equations with two unknowns, determine the amount of glycol present.

Example: Sample identified as ethylene glycol and water.
density = 1.065

$$A + B = 1$$

$$A = \% \text{ water}/100$$

$$B = \% \text{ ethylene glycol}/100$$

$$1.000A + 1.113B = 1.065$$

$$1.000 = \text{approximate density of water}$$

$$1.113 = \text{density of ethylene glycol}$$

$$1.065 = \text{measured density of the sample}$$

$$\text{solution: } A = 0.42 = 42\% \text{ water}$$

$$B = 0.58 = 58\% \text{ ethylene glycol}$$

Wm H. Hamilton
1/9/90

Method No. EHS P-2

Title: PHENOLS IN WATER - CHLOROFORM EXTRACTION

Date Issued: Before 12/82

Approved by: M K Hamilton *mk*

Written by: M K Hamilton

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

PHENOLS IN WATER - CHLOROFORM EXTRACTION

Reference

Standard Methods for the Examination of Water and Wastewater, 16th Ed., 1985, pp. 556-560.

Principle

After a preliminary distillation, the steam-distilled phenols in alkaline solution are reacted with 4-aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye. The dye is then extracted into chloroform and the absorbance is measured at 460 nm.

Limitations

Some interferences must be removed before the phenols may be determined. H_2S and SO_2 interference is eliminated by acidifying the sample to pH4 or less with 1.5 mL conc. H_3PO_4 per liter and aerating immediately after collection. To inhibit biochemical oxidation, 1.0 g $CuSO_4 \cdot 5H_2O$ is added per liter and the sample is stored at 4°C until analysis (no more than 24 hours). A preliminary distillation is performed to separate the phenols from any non-volatile impurities. Many different phenolic compounds may be present in the sample, all of which produce the colored antipyrine dye. To achieve uniformity, all results are reported in terms of mg/L phenol which gives the minimum concentration of phenolic compounds present.

Equipment

1. All glass distillation apparatus as shown or equivalent.

2. 500 mL graduated cylinders
3. Spectrophotometer for use at 460 nm with 1.0 cm cells
4. Whatman #41 filter paper - 11cm
5. Long-stemmed glass funnels
6. pH meter
7. 1-liter separatory funnels

Reagents (Stock)

1. Phosphoric acid - conc. 85% H_3PO_4
2. Cupric sulfate pentahydrate - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
3. Reagent grade phenol
4. Ammonium chloride - NH_4Cl
5. Ammonium hydroxide - conc. NH_4OH
6. 4-aminoantipyrine
7. Potassium ferricyanide - $\text{K}_3\text{Fe}(\text{CN})_6$
8. Chloroform - CHCl_3 - CLASS 2 SUSPECT HUMAN CARCINOGEN

Reagents (Prepared)

1. Ammonium chloride solution - Dissolve 25g NH_4Cl in deionized H_2O and dilute to 500 mL. Prepare annually.
2. Aminoantipyrine solution - Dissolve 2.0 g of 4-aminoantipyrine in deionized H_2O and dilute to 100 mL. Prepare fresh daily.
3. Potassium ferricyanide solution - Dissolve 8.0 g $\text{K}_3\text{Fe}(\text{CN})_6$ in deionized H_2O and dilute to 100 mL. Filter if necessary. Prepare fresh weekly.

Standards

1. Stock phenol solution - Dissolve 1.00 g reagent grade phenol in freshly boiled and cooled deionized H_2O and dilute to 1-liter. (If extreme accuracy is desired, see Standard Methods, page 559, for standardization.) 1 mL = 1.0 mg phenol. Prepare weekly.
2. Standard phenol solution - Dilute 1.0 mL of the stock phenol to 100 mL with freshly deionized H_2O . Prepare fresh daily. 1 mL = 10.0 μg phenol.

Procedure

1. Transfer a 500 mL aliquot of sample that has been acidified and treated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to the distillation flask and begin distilling into a 500 mL graduated cylinder. (Also carry a standard containing 10 μg phenol/500 mL and a reagent blank through the distillation.)
2. When about 450 mL has been distilled, stop the distillation. After boiling ceases, add 50 mL of deionized H_2O to the distillation flask and continue distilling until 500 mL has been collected. Transfer the distillate to a 1-Liter separatory funnel.
3. In 1-liter separatory funnels, prepare a 500 mL deionized H_2O blank and a series of standards containing 1, 5, 10, and 20 μg phenol in 500 mL. (0.1, 0.5, 1.0 and 2.0 mL of 10 $\mu\text{g}/\text{mL}$ phenol standard.) Carry all samples and standards through the remainder of the procedure.
4. Add 10 mL NH_4Cl solution and adjust to $\text{pH } 10.0 \pm 0.2$ using conc. NH_4OH .
5. Add 3.0 mL of aminoantipyrine solution and mix well.
6. Add 3.0 mL of $\text{K}_3\text{Fe}(\text{CN})_6$ solution, mix well and allow pale yellow color to develop for three minute.
7. Extract immediately with 25 mL of CHCl_3 . Shake separatory funnel at least 10 times, let phases separate and shake again. NOTE: ALL WORK WITH CHLOROFORM SHOULD BE DONE WITH GLOVES IN A HOOD.
8. After the phases separate, filter the CHCl_3 extract through 1PS filter paper to remove any H_2O .
9. Measure absorbance of samples and standards at 460 nm, using chloroform as a reference.
10. Discard CHCl_3 solutions in waste can marked for organic carcinogens.

Calculation

1. Plot μg phenol in 500 mL vs. absorbance.
2. Determine μg phenol in the samples from the curve.

$$\text{mg/L phenol} = \frac{\text{aliquot } \mu\text{g phenol}}{500 \text{ mL sample}}$$

Use the standard carried through the distillation to determine % recovery. Make necessary correction in results if recovery is less than 100%.

VOLATILE ORGANIC CHEMICAL (VOC) ANALYSIS
BY PURGE AND TRAP GC WITH
PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to the determination of at least 58 VOC's in finished drinking water, raw source water, or drinking water in any treatment stage. A list of the determinable compounds is given in Reference 1 and show in Attachment A.
- 1.2 Method detection limits are very compound dependent and are variable. Each analyst as part of the quality control associated with this method must determine the precision of his or her own technique and thereby a personalized set of detection limits.

The analytical range of this method is currently defined by the equipment we are using to perform it. The span of the data processing equipment and the spans of the two detectors used combine to effectively limit the working range to approximately 0.2 to 20 $\mu\text{g/L}$.

Co-elution of some compounds effectively prohibits their direct determination by this method; meta and para xylene, 1,2,3-trichloropropane and 1,1,2,2-tetrachloroethane are the two problem pairs on the column system used in this method. The identities of all other co-eluting compounds can be distinguished by the particular detector responding to them; i.e., in all other cases each of the co-eluting compounds only responds on one detector.

- 1.3 It is highly recommended that this method only be used by analysts experienced in the measurement of purgeable organics at low $\mu\text{g/L}$ concentrations. As mentioned above, part of the quality control for this method includes a demonstration of analyst performance. Before proceeding further it is mandatory that the analyst read Reference 1 thoroughly.

2. METHOD PRINCIPLES

- 2.1 Volatile organic compounds with low water solubility are removed (purged) from a 5 ml volume of the aqueous sample contained in a sparging cell by passing helium through the sample. The purged compounds are carried with the gas through a stainless steel tube packed with several adsorbent materials, on which the compounds are trapped. After completion of sample purging the sorbent tube is heated and backflushed with helium. The trapped compounds are carried onto a megabore fused silica capillary column which is held at subambient temperatures. The column is then temperature programmed to separate the method analytes which are then detected by the photoionization detector (PID) and the electrolytic conductivity detector (ELCD) in series.

- 2.2 Tentative identifications are based on retention time comparison between sample peaks and standard peaks as well as a comparison of response from each detector if the compound responds on both. Internal standard calibration is used to enhance the precision of the technique and to provide "reference" peaks which can then be used to more positively identify the analyte peaks by adjusting the identification windows to account for minor fluctuations in predicted retention times.

3. INTERFERENCES

- 3.1 The primary interferences for this method are common laboratory solvents such as methylene chloride and Freon 113 which are used in our facility. Isolating, as much as possible, the area in which any work related to VOC analysis is to be performed is the ultimate solution.
- 3.2 There are several compounds which are known to be chromatographic interferences. Those which are known at this time are: 1-chlorohexane and chlorobenzene, Freon 113 and 1,1-dichloroethylene, trichlorobromomethane and one of the middle eluting chlorinated compounds, and a dichlorotoluene coelutes with one of the later eluting aromatics. As can be seen, identification is far from foolproof so great care needs to be exercised.
- 3.3 Carryover from a high to a low sample may also be a source of contamination, but with the use of the ALS-10 it is more important that the sparging cells be thoroughly cleaned after each use to prevent any carryover problems.

4. METHOD PITFALLS

- 4.1 Analyte volatility represents the major source of both sample and calibration standard instability.

As regards samples, any air space above aqueous samples renders them invalid. Samples must also be kept cold (ca. 4 °C) from the time of collection to the time of analysis and they must be analyzed within 14 days of collection to avoid losses of volatile components.

Calibration standards also suffer from stability problems. Methanolic working standard solutions last about 1 week during normal usage; a drop in response, especially in the gaseous compounds indicates standard decomposition. Working standards must be replaced when the response observed differs from that of the initial calibration curve by 20% or more (see Section 11., Quality Control). It is highly recommended that stock and working standard solutions be stored after preparation in a number of small autosampler vials to maximize the amount of time that a batch of standards will last. Minimizing the amount of time a standard spends at room temperature is also highly advised. Stock standard solutions last approximately one month if stored in a freezer.

A final problem arising from analyte volatility involves sample and standard storage. Samples should be stored refrigerated, with a holding blank, in a refrigerator free of volatile contaminants. Standards should be stored in a freezer. This will minimize the amount of cross

contamination that will occur. An additional precaution that can be taken to prevent contamination is storage of standards and/or samples in closed containers with activated carbon to adsorb any atmospheric contaminants.

5. SAFETY

- 5.1 A number of the analytes dealt with in this method have toxic and/or carcinogenic properties which mandates that all standards be prepared in a fume hood and that proper protective equipment be utilized. For further information the analyst is referred to the safety references cited in Reference 1. Also refer to EHS Lab Operating Procedure L-4.10, "Laboratory Policy Guide - Use of Carcinogens."

6. APPARATUS AND EQUIPMENT

- 6.1 SAMPLE CONTAINERS-- 40 ml glass screw cap vials equipped with PTFE-faced silicone septa (I-Chem # S-3360040 or equivalent). IF I-Chem pre-cleaned bottles will not be used, wash vials and septa with detergent and rinse with tap and deionized water.

Allow vials and septa to air dry at room temperature, place in a GC oven at 105 °C for one hour, allow to cool in the GC lab and replace caps and septa. Vials should be prepared as close to their usage as possible to prevent any contamination during storage.

- 6.2 PURGE AND TRAP SYSTEM-- The basic operating principles of the Tekmar LSC 2 and the ALS-10 units, utilized by EHS, are covered in their respective operating manuals (Reference 2 & 3. It is highly recommended that these be read thoroughly before beginning any work with this equipment. Of special concern are the flow patterns utilized in the system. This equipment satisfies the criteria of EPA method 502.2 and other EPA methods involving purge and trap equipment.

There are minimal problems with this equipment, and routine maintenance consists of cleaning the sparging cells and periodically (perhaps monthly) pressure checking the ALS-10 sparging positions for leaks, as is detailed in the Tekmar manual for the ALS-10. Sparging cells are cleaned after each use by sucking a weak detergent solution through the cells in a reverse direction to the normal flow, followed by a thorough rinsing with deionized water and baking at 110 °C in a GC oven until dry. Periodic flow checks are also required and flows must be verified whenever a new trap is installed. Appropriate flows are a purge flow of 40 cc/min. (at the sparge cell inlet), and a desorb (column carrier gas) flow rate of approximately 6 cc/min. Helium is the gas utilized.

The trap utilized for this method is the one specified in Section 5.2.2 of EPA method 502.2 (Tekmar #142366-003 or equivalent). The trap cycle listed below is a modification of the EPA recommended purge cycle. It is one recommended by Lowell Wright of OI corporation as one which will minimize ELCD signal suppression and premature catalytic tube failure due to desorbed water.

Purge time is 11 min., purge temperature is 30 °C or less (in deference to the room temperature). Desorb preheat temperature is 17 °C, desorb time and temperature are 2 min. and 180 °C respectively (to minimize water deposition onto the column). Bake time and temperatures are 11 min. and 180 °C. Prior to using a new trap or using one which has been idle for an extended period, it should be conditioned by subjecting it to at least one bake cycle and more if necessary. The traps are susceptible to premature failure if any sample foams and is carried into the tubing beyond the sparge cell. It is also advisable not to bake the trap unless it is being sparged with helium (with the ALS-10 this means a sparge cell must be in place) since this does seem to shorten the life of the trap.

Trap life is highly variable; some indicators of a failing trap are an increased number of artifact peaks in the PID chromatogram, perhaps a decrease in bromoform sensitivity (but there are many causes for this phenomena), an increase in back pressure required to maintain flow across the trap, and perhaps also problems with sensitivity of the gaseous compounds especially vinyl chloride since this compound is barely retained on the trap.

- 6.3 GAS CHROMATOGRAPHIC SYSTEM -- The basic requirements of the gas chromatographic system are detailed sufficiently in Reference 4 so no further discussion will be made here of general requirements. Rather, the specific conditions under which our particular system has been found to operate best are given.

Gas Chromatograph: HP 5880
Column: J & W Scientific DB-624, 0.53mm i.d.
Column Length: 30 m.
Film Thickness: Approx. 3 μ m.
Start Temp-Time: -15 °C, 1 min.
Program Rate: 3 °C / min.
End Temp-Time: 140 °C, 5 min.
Post Temp-Time: 175 °C, 2 min.
Det 1-Type & Temp: PID, 180 °C, Range = 100.
Det 2-Type & Temp: ELCD, 180 °C, "S" Mode.
PID Lamp: 10.2 ev.
ELCD Tube Temp & H₂ Flow: 900 °C, 100 +/- 10 cc/min.
ELCD Flow and Eluent: 50 μ l/min, n-Propanol.
ELCD Pump Setting: 3-4 turns (10 turn pot.)
Carrier Flow & Gas: 6 cc/min He @ 140C.
Make-Up Gas-Flow: He, 24 cc/min.

Special Notes

PID Intensity should be set at ~30%. The two detectors are connected in series with a short piece of deactivated, uncoated, 0.53 mm i.d. fused silica tube.

A copy of a correct printout of the various conditions, run tables, and the short keystroke program which needs to be entered in order to operate the instrument from the 5880 terminals is contained in Attachment B. A current copy of this is also kept in the GC laboratory. Understanding this information is critical to successful operation of this instrument.

A listing of each of the methods used on the Hewlett-Packard (HP) data system are also contained in Attachment B. The analyst is referred to Reference 7 for detailed instructions on the use of the data system.

The instrument utilizes liquid nitrogen (LN2) cryogenics as the means to lower the column oven temperature to -15 °C. Two 25 L dewar flasks of LN2 are used to fill the instrument dewar, which is then pressurized to 20 psi with nitrogen. It is important to remember when using the ALS-10 to make a clock table entry such that after the last run of a series the oven temperature is raised above 50 °C so that the cryogenic cooling is not activated unnecessarily for an extended period.

A troubleshooting guide which has more specific information about what to do when things go wrong is kept in the Laboratory Operating Procedures Manual (see Proc. #L-8.11).

- 6.4 MISCELLANEOUS EQUIPMENT-- A number of small items will be required to perform this method; a variety of microliter syringes for dilutions etc., as well as a 5 ml gas tight syringe with a luer lock valve for loading of standards and samples into the 5 ml sparging cells.

7. REAGENTS

- 7.1 METHANOL-- Methanol which is free from any analyte contaminants must be used to prepare standard solutions. Burdick and Jackson Purge and Trap grade methanol (product #232) is highly recommended.
- 7.2 n-Propanol--The n-propanol used as eluent in the ELCD cell must be a high purity glass distilled type (Burdick and Jackson product # 322 or equivalent).
- 7.3 Gases--Three gases are used to perform this analysis; helium, hydrogen, and LN2. Ultra high purity helium and hydrogen are required for the proper operation of the ELCD. The LN2 used for the cryogenic system is obtained from Battelle's tank outside the whole body counter. Its purity is really an unknown but it also has no bearing on the performance of the method.
- 7.4 REAGENT WATER-- Analyte-free reagent water is prepared by passing deionized water through two Millipore activated carbon organic removal cartridges (Millipore #CC1512000) using a vacuum flask apparatus (Rainin #38-181). This water is then sparged in a large impinger with high purity nitrogen for 1/2 hr and stored in a closed container in the GC laboratory.
- 7.5 SAMPLE PRESERVATIVE-- Hydrochloric acid (1+1) is prepared using ACS reagent grade HCL and the reagent water prepared above.
- 7.6 STANDARD STOCK SOLUTIONS-- These solutions are prepared from commercially available stock solutions (Supelco) or from ampulated stock solutions provided by the EPA Quality Assurance Materials Bank (QAMB). The stock solutions can also be prepared from neat materials following the directions in Sections 6.3.1-6.3.4 in Reference 1. Typically stock solutions are at concentrations of 1000 to 10,000 ug/mL. Refer to

Section 4.1 for storage conditions and shelf life of these solutions.

- 7.7 WORKING STANDARD SOLUTION-- The working standard solution is prepared from the commercial stock solutions by additions of appropriate microliter volumes of the stock solutions to methanol. The working solution concentration is 5 ug/mL of each analyte. Additions of 1 μ L to 20 μ L of this solution to 5 ml of reagent water in a 5 ml glass syringe yield calibration standard concentrations of 1-20 μ g/L in the aqueous solution. Refer to Section 4.1 for storage conditions and standard shelf life.
- 7.8 INTERNAL STANDARD WORKING SOLUTION--The internal standard working solution is prepared from EPA stock solutions by dilution into methanol. The two internal standards are fluorobenzene (PID) and 1,4-Dichlorobutane (ELCD). 2-Bromo-1-chloropropane is not used because it cannot be separated from another analyte on the DB-624 column or on the VOCOL column recommended in Reference 1. The internal standard in EPA method 502.1 is 1,4-dichlorobutane and this compound was adopted for this methodology. The internal standard working solution is prepared at a concentration of 10 μ g/mL of each standard compound by dilution of the stock solutions. Addition of 5 μ L of this solution to 5 mL of aqueous sample or reagent water in a 5 mL glass syringe to yields a final aqueous concentration of 10 μ g/L.
- 7.9 SURROGATE WORKING SOLUTION-- Surrogate compounds are added to each sample to yield recovery information on each sample. The two surrogates used (one for each detector) are 2-chlorobutane and p-difluorobenzene. Stock surrogate spiking solutions are prepared from either neat material as per Sections 6.3.1-6.3.4 of EPA method 502.2 (2-chlorobutane) or from available EPA standard solutions (p-difluorobenzene). The surrogate working solution is prepared at a concentration of 10 μ g/mL. This solution is used for calibration and for sample spiking. Calibration standards are prepared by addition of 1, 2, 5, 10 and 20 μ L of this working solution to 5 mL of reagent water in a glass syringe to which the internal standard and calibration standard solutions have already been added. This results in aqueous concentration levels of 2, 4, 10, 20, and 40 μ g/L. A 5 μ L aliquot of the surrogate working solution is used to spike the samples at a 10 μ g/L level.
- 7.10 LABORATORY QC CHECK SOLUTIONS-- Two different kinds of QC check solutions are prepared in our laboratory. A check solution is currently being made from EPA standard solution mixes to check the comparability of our standards to those of the EPA. This EPA QC Check solution does not contain all of the analytes covered by method 502.2 but it does contain a substantial number of them. EPA currently does not have a standard solution mix or even several standard solution mixtures which have all of the analytes covered under method 502.2. Currently we are using this EPA solution to function as the "Laboratory Quality Control Check Standard" referred to in method 502.2.

A source of standard solution mixes different from that used to prepare the calibration standards has been found (Ultra Scientific) from which a second QC check solution will be prepared to cover all of the analytes. The EPA QC check solution will continue to be analyzed in addition to the

normal QC check solution in order to validate comparability with EPA standards. More will be said on this subject later in Section 11.

8. SAMPLE COLLECTION, PRESERVATION, STORAGE

- 8.1 SAMPLE COLLECTION--The analyst is referred to Reference 1 for adequate details concerning sample collection. All samples are collected in duplicate. If samples are to be composited it must be done according to the guidelines contained in Reference 8.
- 8.2 SAMPLE PRESERVATION--Samples are held at 4 °C from the time of collection to receipt at the laboratory by the use of biomailers and cold packs. Upon receipt at the laboratory lower the sample pH to <2 by addition of 200 µL of 1:1 HCl (see Section 7.3) to the sample through the septum using a syringe equipped with a narrow gauge needle.
- 8.3 SAMPLE STORAGE--Store samples in a refrigerator free of organic solvent vapors (see Section 4.1) at 4 °C until analysis. All samples must be analyzed within 14 days of collection. Samples not analyzed within this time period must be discarded and replaced.

9. CALIBRATION AND STANDARDIZATION

- 9.1 CALIBRATION STANDARD PREPARATION--Calibration standards are prepared by adding 5 mL of reagent water to a 5 mL glass gas-tight syringe. Five microliters of internal standard working solution are then added quickly through the luer valve to the syringe. Then the appropriate volumes of surrogate working solution and the calibration standard working solution are added in the same fashion. The contents of the syringe are then loaded into a sparge cell and analyzed according to Section 12.

Calibration standards are prepared at concentrations of 1, 2, 5, 10, and 20 µg/L by addition of 1, 2, 5, 10, and 20 µL of the 5 ug/ml standard working solution. Surrogate levels are twice this concentration because the same volumes are added but the concentration of the surrogate working solution is 10 µg/mL.

- 9.2 INTERNAL STANDARD INSTRUMENT CALIBRATION--The internal standard method of calibration is used. Response factors are calculated and a calibration curve generated using the Extrachrom II Data system. For a discussion of how this is performed and the pertinent equations used the analyst is referred to Reference 7. A first order (linear) or second order (quadratic) fit must be used to generate the calibration curve, the one yielding the highest correlation coefficient should normally be chosen. The % RSD of the response factors must be less than 20% for all of the analytes or another calibration curve must be prepared.

10. METHOD PERFORMANCE DEMONSTRATION

- 10.1 METHOD PERFORMANCE AND MDL DETERMINATION--In order to demonstrate acceptable method performance and to determine the method detection limits (MDL) each analyst is required to analyze seven samples at a concentration of 0.5 µg/L. These samples are prepared using the

laboratory QC check solution.

For each analyte the mean recovery must be between 80% and 120% of the true value and the relative standard deviation of the values must be < 30%. If either of these tests fail, system performance is unacceptable and corrective action must be taken. Corrective action can be a repeat of the test, preparation of fresh QC check solution, recalibration of the instrument or other means. The method detection limit at the 99% confidence level is determined as $3.143 \times s$ where s is the standard deviation of the concentrations observed above.

11. QUALITY CONTROL

- 11.1 DAILY METHOD BLANKS--Each day before any standards or samples are analyzed a method blank consisting of 5 mL of reagent water containing 5 μ L of internal standard working solution, and 5 μ L of surrogate working solution must be analyzed and found to contain less than the MDL of any of the 502.2 analytes. If any compounds are found above the MDL corrective action must be taken. Corrective action could include preparation of fresh reagent water, re-cleaning of the sparging cells, replacement of the trap, and replacement of the purge gas hydrocarbon traps, or all of the above.
- 11.2 DAILY STANDARD VALIDATION--Each day after analysis of the method blank two standard check solutions must be analyzed. First, a calibration standard solution must be analyzed and the concentrations obtained must be within 20% of their true values. Standard concentration levels used should alternate to cover all standard levels over a period of several days. Standards should be run at the end of each sample batch as well, if possible. Second, a solution prepared to be 5 μ g/L using the Laboratory QC Check Solution must be analyzed and the recoveries obtained must be within 40% of their expected values. If either of these solutions fails the test for no obvious reason, then corrective action must be taken in the form of fresh standards or a recalibration of the instrument.
- 11.3 DAILY EPA QC STANDARD CHECK--Each day of analysis a solution prepared to be 5 to 20 μ g/L using the EPA QC check solution must be analyzed and the recovery must be within 40% of the expected value. Corrective action for a failure of this test must be taken in the form of fresh standards or a recalibration of the instrument.
- 11.4 SURROGATE RECOVERY CHECK--Surrogates are added to each sample and blank to yield a concentration of 10 μ g/L. Surrogate recovery must be within 80-120%.
- 11.5 INTERNAL STANDARD AREA CHECK--Internal standard areas must be recorded and each day must be within 50% of the areas observed for the daily calibration standards and within 50% of the prior day's daily calibration standard values. Failure of this test invalidates all samples it affects. Corrective action may include replacement of internal standard solution, a repair of a particular detector, or a recalibration of the instrument.

- 11.6 WEEKLY LOW LEVEL STANDARD CHECK--At least once each week a calibration standard at the 0.5 $\mu\text{g/L}$ must be analyzed and the analyte recovery must be within 40% of the expected value. If this test is failed, corrective action must be taken. Corrective measures might include a simple repetition of the test, preparation of fresh standards, instrument repair, or recalibration of the instrument.
- 11.7 WEEKLY EPA PE SAMPLE ANALYSIS--Performance Evaluation (PE) samples are available from EPA EMSL-Cincinnati and one of these must be analyzed at least once each week at a concentration that is within the range of the calibration curve. The analyte concentration values must be within 20% of those provided by EPA EMSL-Cincinnati or within the acceptance limits provided, whichever is applicable.
- 11.8 SAMPLE DUPLICATE ANALYSIS--Any samples in which a positive result is obtained for any analytes other than trihalomethanes must be analyzed in duplicate, duplicate analyses should agree to within 40%.
- 11.9 RESPONSE FACTOR CHECK--When analytes are found in the samples for which responses are observed on both detectors the analyte concentrations obtained on both detectors should be within 40% of each other.
12. SAMPLE ANALYSIS
 - 12.1 INSTRUMENTAL CONDITIONS--The instrumental conditions to be used are described fully in Sections 6.2 and 6.3. Approximate retention times and example chromatograms are contained in Attachment B.
 - 12.2 QUANTITATION--The analyte concentrations are calculated by the internal standard method by comparison of the response factors observed in the samples with those of the calibration standards. More information on the calculation methods used is contained in Reference 7. Results are reported in $\mu\text{g/L}$ and rounded off to two significant figures or 0.1 $\mu\text{g/L}$.
13. DOCUMENTATION
 - 13.1 QUALITY CONTROL--Quality control results are recorded to verify acceptable method performance on a series of forms prepared for this purpose, copies of these forms are contained in Attachment C.
 - 13.2 QUANTITATION--The analytical quantitative results obtained from analysis of the samples are recorded on a form established for this purpose, a copy of this form is contained in Attachment C.
14. REFERENCES
 1. Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series, Method 502.2, EPA, as shown in 52 CFR 12879 (April 17, 1987).

2. Tekmar Company Liquid Sample Concentrator Model LSC-2 operating manual.
3. Tekmar Company Automatic Liquid Sampler Model ALS-10 operating manual.
4. Hewlett-Packard Gas Chromatograph Model 5880 operating manual.
5. HNU Photoionization Detector (PID) Model PI-52 operating manual.
6. OI Corporation Electrolytic Conductivity Detector (ELCD) Model 4420 operating manual.
7. Extrachrom II Data System Operators manual.
8. Federal Register, Vol. 52, No. 130, Wednesday July 8, 1987.

ATTACHMENT A

Entry	Time	Component Name
1	3.480	CCl2F2
2	4.460	CHLOROMETHANE
	5.220	VINYL CHLORIDE
	7.070	BROMOMETHANE
	7.850	CHLOROETHANE
	9.220	TRICHLOROFLUOROMETHANE
7	11.750	1,1-DICHLOROETHYLENE
8	14.290	METHYLENE CHLORIDE
9	15.260	TRANS-1,2-DICL ETHYLENE
10	16.970	1,1-DICHLOROETHANE
11	18.420	2-CHLOROBUTANE
12	19.020	2,2-DICHLOROPROPANE
13	19.230	cis-1,2-DICHLOROETHENE
14	20.060	CHLOROBROMOMETHANE
15	20.610	CHLOROFORM
16	20.790	1,1,1-TRICHLOROETHANE
17	21.370	CCL4 & 1,1-DiCl-PROPENE
18	22.420	1,2-DICHLOROETHANE
19	24.590	TRICHLOROETHYLENE
20	25.390	1,2-DICHLOROPROPANE
21	25.870	DIBROMOMETHANE
22	26.640	BROMODICHLOROMETHANE
23	28.260	trans-1,3-DICHLOROPROPENE
24	30.500	cis-1,3-DICHLOROPROPENE
25	31.120	1,1,2-TRICHLOROETHANE
26	31.260	TETRACHLOROETHYLENE
27	31.650	1,3-DICHLOROPROPANE
28	32.500	CHLORODIBROMOMETHANE
	32.710	1,2-DIBROMOETHANE (EDB)
	34.680	CHLORBENZ&1-Cl-HEXANE (NC)
	35.160	1112-TETRACHLOROETHANE
32	38.140	BROMOFORM
33	39.440	1,4-DICHLOROBUTANE (ISTD)
34	39.940	BROMOBENZENE
35	40.530	1122-TCEANE & 123-3CL-PRO
36	40.830	o-CHLOROTOLUENE
37	41.340	P-CHLOROTOLUENE
38	44.000	M-DICHLOROBENZENE
39	44.430	1,4-DICHLOROBENZENE
40	45.960	1,2-DICHLOROBENZENE
41	49.540	1,2-DiBr-3-CHLOROPROPANE
42	53.060	1,2,4-TRICHLOROBENZENE
43	53.980	HEXACHLORO-1,3-BUTADIENE
44	55.250	1,2,3-TRICHLOROBENZENE

entry	Time	Component Name
1	5.180	VINYL CHLORIDE
2	11.720	1,1-DICHLOROETHYLENE
3	15.240	TRANS-1,2-DICHLOROETHYLENE
4	19.210	CIS-1,2-DICHLOROETHYLENE
5	21.400	1,1-DICHLOROPROPENE
6	22.100	BENZENE
7	23.270	FLUOROBENZENE (ISTD)
8	23.870	P-DIFLUOROBENZENE
9	24.570	TRICHLOROETHYLENE
10	28.240	trans-1,3-DICHLOROPROPENE
11	29.270	TOLUENE
12	30.470	CIS-1,3-DICHLOROPROPENE
13	31.240	TETRACHLOROETHYLENE
14	34.660	CHLOROBENZENE
15	35.230	ETHYL BENZENE
16	35.730	M & P XYLENE
17	37.300	O-XYLENE
18	37.420	STYRENE
19	38.900	ISOPROPYLBENZENE
20	39.900	BROMOBENZENE
21	40.640	N-PROPYL BENZENE
22	40.810	O-CHLOROTOLUENE
23	41.320	P-CHLOROTOLUENE
24	41.470	1,3,5-TRIMETHYLBENZENE
25	42.760	T-BUTYL BENZENE
26	43.000	1,2,4-TRIMETHYLBENZENE
27	43.710	SEC-BUTYL BENZENE
28	43.980	1,3 DICHLOROBENZENE
29	44.430	1,4-DCB & ISOPROPTOL
30	45.940	1,2-DICHLOROBENZENE
31	46.230	N-BUTYL BENZENE
32	53.030	1,2,4-TRICHLOROBENZENE
33	54.000	NAPHTHALENE & HEXA-CL-BUTA
34	55.230	1,2,3-TRICHLOROBENZENE

POLYCHLORINATED BIPHENYLS IN SOIL AND SEDIMENT

I. References

- A. "Test Methods for Evaluating Solid Waste," EPA SW 846 Methods 3540, 3660, and 8080.
- B. "Determination of Pesticides and PCB's in Sediments (Gas Chromatographic Method)," Region 10 Laboratory Surveillance and Analysis Division U.S. Environmental Protection Agency, Seattle, Washington.
- C. The analytical chemistry of PCBs, M. D. Erickson, Butterworth Publishers, Boston, 1986.

II. Principles and Limitations

The dried soil is extracted with acetone/hexane in a Soxhlet extractor. The extract is evaporated to a low volume and then solvent exchanged into isooctane. The resulting solution is treated by a cleanup procedure (routinely: acid wash/florisil slurry) to remove interfering substances. Analysis is by capillary gas chromatography using an electron capture (EC) detector. The method is made qualitative and quantitative by comparing peak patterns, area counts, and retention times of the sample chromatogram with chromatograms of known quantity and type of aroclor standards, obtained under the same conditions. Results can be confirmed by running the samples and standards using a second dissimilar column.

Occasionally, sample chromatograms indicate the presence of PCBs; however, no aroclor or mixture of aroclors are indicated by the pattern. This is often the case with weathered or otherwise degraded aroclor mixtures or when a non-aroclor material is the PCB source. In these cases the Dry Color Manufacturers Associations' (DCMA) method for PCB identification is employed, (see Section IV.F "Non-aroclor and partial aroclor PCB mixture").

Electron capture detectors respond to chlorine containing compounds other than PCBs and to certain other electrophilic materials containing other halogens, nitrogen, oxygen, and sulfur. Most common interferences can be removed by sulfuric acid washing. The chromatogram of each analyzed sample should be carefully compared with those of the standards. The response of an EC detector to PCBs is reduced by high boiling hydrocarbons that co-elute with the PCBs. This suppression can be compensated for by running spiked samples to determine the actual recovery.

Residual oxygen in carrier and makeup gas can react with components of samples to give oxidation products to which EC detectors will respond. Purity of these gases should be assured.

III. Materials

A. Equipment:

1. Extraction apparatus, Soxhlet, Allihn Condenser (250 mL flask, 40mm I.D. ext. tube, 73mm Ht siphon tube)
2. Controlled heating mantle
3. Extraction thimbles (Whatman cellulose 35mm x 80mm)
4. 1 x 12 cm screw cap tubes
5. Teflon lined caps
6. 10 mL repipetors for solvent and acid measurement and transfer
7. 0.5 mL, 1 mL, and 2 mL Class A or better glass pipets
8. Volumetric flasks, isooctane washed
9. Analytical balance with 0.1 mg sensitivity
10. Analytical balance with 0.1 g sensitivity
11. SE-54 or DB-5 fused silica capillary column 30 meter length, 0.250mm I.D., 0.25 μ m film thickness
12. DB1-30m megabore column 30 meter length, 0.53mm I.D., 1.5 μ m film thickness
13. Gas chromatograph fitted for capillary column and equipped with electron capture detector and auto sampler
14. Vortex
15. Centrifuge
16. Pasteur Pipets
17. Autosampler vials with teflon caps
18. Mechanical rotary extractor
19. Three ball Snyder Column .
20. Oven capable of maintaining temperature of 50-55°C
21. Carborundum boiling chips, soxhlet extracted
22. Aluminum foil

23. Lambda pipets

B. Reagents:

1. Pesticide grade 2,2,4-trimethylpentane (isooctane)
2. Pesticide grade hexane
3. Pesticide grade acetone
4. Reagent grade (conc.) Sulfuric Acid
5. Activated Florisil, 60/100 mesh, reagent grade, suitable for pesticide-residue analysis. Available from Floridin Company and treated per AOAC (1980) 29.002 before use
6. EPA standards (1000 to 5000 ppm) of aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268
7. Hexabromobenzene (PCB surrogate)
8. Ultra high purity helium
9. 90 percent argon--10 percent methane (P10) or 95 percent argon--5 percent methane (P5)
10. Tetrabutylammonium hydrogen sulfate, reagent grade
11. Sodium sulfite, reagent grade
12. Ethanol, USP 95%
13. Potassium hydroxide, anhydrous pellets
14. Dry Color Manufactures Association mixture of PCB isomers in hexane. Available from Ultra scientific.
15. Sodium sulfate, anhydrous, certified A.C.S.
16. 2-propanol, reagent grade

C. Standards & Prepared Reagents:

Note: All glassware should be dedicated for the preparation of aroclor standards.

1. Stock Aroclor solutions. EPA Aroclor standards range from 5000 $\mu\text{g/mL}$ to 1000 $\mu\text{g/mL}$ and are received in 1 mL glass ampules. The appropriate amount of standard is volumetrically transferred to a 25 or 50 mL volumetric flask and diluted in isooctane so that a 10 to 20 $\mu\text{g/mL}$ solution is produced.

Transfer the stock solution to a brown glass bottle fitted with a teflon lined cap. Transfer remaining EPA standard material to a 1 mL auto sampler vial. The stock solution and the EPA standard are stable indefinitely if their seals are maintained and they are stored at or below 0°C.

2. Working standards - (0.5, 0.1, 0.05, 0.01 $\mu\text{g/mL}$). Add appropriate amount of stock standard (depending on stock standard concentration) to screw cap test tubes and make up with isooctane so that a 0.5 $\mu\text{g/mL}$ solution results. Serially dilute the 0.5 $\mu\text{g/mL}$ to make up the remaining standards (0.01, 0.05, and 0.1 $\mu\text{g/mL}$). Total volume of each working standard should be approximately 10 mL. Prepare monthly or as needed.
3. DCMA mixture, stock and serial dilutions. The DCMA mixture ampule is opened and an aliquot diluted 100 fold. Serial dilutions of 2, 10, and 20 fold are made up of this solution. The remaining original DCMA mixture is transferred to an auto sampler vial, sealed with a teflon backed cap and stored at or below 0°C.
4. Hexabromobenzene (HBB) surrogate-working standard. The neat HBB standard is removed from the freezer and a 10 mg aliquot volumetrically made up into 100 mL of isooctane. The resulting 100 $\mu\text{g/mL}$ solution, the HBB working standard, is subdivided into 10 mL vials, secured with a teflon lined screw cap. These materials are stable indefinitely if their seals are maintained and they are stored at or below 0°C.
5. 1:1 acetone/hexane extraction solution-mix equal volumes of hexane and acetone. Use the same "batch" of extraction solvent for a given set of samples, spikes and controls.

IV. Methods

Note: This procedure is intended to qualitatively and quantitatively analyze samples for the nine specific aroclors listed on page 3. This method is not adequate for qualitative and/or quantitative analysis of partial aroclors or individual congeners which may result from aroclor degradation or by products of chemical reactions. For non-aroclor samples see Section IV.F for the analysis of these partial or non-aroclor containing samples.

- A. Extraction: (Soxhlet extraction, based on: "Test Methods for Evaluating Solid Waste," EPA SW 846 Method 3540.
 1. Empty the majority of the sample from its container on to a sheet of aluminum foil. Pick through the sample and remove larger stones, roots and other non-homogeneous material. Place 10 g of cleaned, homogeneous material into a cellulose thimble. Add 10 g of sodium sulfate and mix.

Alternately, place approximately 100 g of soil sample in a 250 mL beaker and place in an oven to dry at 50-55°C for 6-8 hours. Cool to room temperature. Sieve soil through 20 mesh, Standard Sieve (A.S.T.M. Designation E11). Weigh 10 g of sieved sample into a cellulose extraction thimble. Do not add sodium sulfate. This is the preferred method when working with exceptionally wet materials (i.e. sludges with standing liquid phase).

2. Prepare blank, spike and other QC samples in accordance with Section IV.C.
 3. Spike every sample, sample duplicate, sample spike, EPA QC, and blank with 100 μ L of the HBB surrogate.
 4. Place 150 mL of 1:1 acetone/hexane solution into the 250 mL round-bottom flask containing several carborundum boiling chips. Attach the flask to the soxhlet extractor, and extract the sample for 18 hours.
 5. Allow the extract to cool after the extraction is completed. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask.
 6. Attach three-ball Snyder column to the flask and reduce solvent to a volume of approximately 25 mL.
 7. Rinse down Snyder column with isooctane and add an additional 25 mL isooctane to sample flask. Add a new boiling chip and reduce solution volume to approximately 10 mL. It may be necessary to wrap the Snyder column in aluminum foil to speed evaporation.
 8. Allow the extract to cool. Rinse down the Snyder column with isooctane and quantitatively transfer extract to a 50 mL volumetric flask and adjust to volume with isooctane.
 9. Transfer 10 mL of the extract to a screw cap tube.
- B. Cleanup techniques
1. Acid wash/florisil cleanup (Primary procedure)
 - a. Add 3 mL concentrated sulfuric acid to each of the 10 mL sample aliquots, including blanks, QC samples, etc.
 - b. Shake by hand for 30 seconds and Vortex for 30 seconds.
 - c. Transfer all test tubes containing samples, blanks, quality control and spiked samples to the rotary extractor. Run extractor for 1 hour.
 - d. Label test tubes for each sample, blank, quality control and spiked sample being run. Add ~0.2 g florisil to each empty test tube.

- e. Remove sample test tubes from the extractor and centrifuge for approximately 5 minutes at 3000 rpm. Transfer each isooctane layer to its corresponding florisisil-containing test tube.
- f. Place sample test tubes in extractor for 1 hour.
- g. If the isooctane extract appears colored or cloudy additional/alternative cleanup procedures may be necessary, otherwise the extract is ready for analysis (Section IV.D.).

2. Sulfur removal (Based on EPA SW 846 Method 3660)

This procedure is used routinely with sediment and sludge samples or when sulfur interference is indicated on the chromatogram.

- a. Prepare TBA-sulfite reagent: Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL of deionized water. Extract 3 times with 20 mL portions of isooctane. Discard the isooctane extracts and add 25 g of sodium sulfite to the water solution. Resulting solution is saturated with respect to sodium sulfite and is stable for 1 month at room temperature.
- b. Transfer 2 mL of extract from Section IV.B.1.g (Acid wash/florisisil cleanup) to a new test tube.
- c. Add 1 mL of TBA-sulfite reagent and 1 mL 2-propanol to the test tube. Shake test tube for at least 1 minute and look for clear crystals from precipitation of sodium sulfite. If crystals are not present, add crystalline sodium sulfite in 100 mg portions until solid material remains (one portion is usually enough).
- d. Add 5 mL of deionized water and shake for at least 1 minute. Let stand for 5 minutes for phase separation. Collect top, isooctane, layer in an auto sampler vial. The extract is ready for analysis (Section IV.D.).

3. Ethanol/potassium hydroxide cleanup

This procedure is used when hydroxyl containing species such as pentachlorophenol and glycols are present. Additionally, fats are made more water soluble through saponification. Certain chlorinated pesticides undergo dehydrochlorination.

- a. Prepare 2% potassium hydroxide/ethanol solution: Dissolve 2 g KOH into 100 mL of 95% ethanol.
- b. Prepare 50% ethanol/water solution: add equal volumes of ethanol and deionized water.

- c. Pipet up to 4 mL of extract from Section IV.B.1.g. (Acid wash/florisil cleanup) into a pyrex test tube and reduce to dryness under N_2 .
- d. Add 2 mL of ethanol/KOH reagent and 1 boiling chip.
- e. Reflux test tube contents over boiling water bath for 20 minutes. During first 5 minutes the test tube should be immersed only in the steam of the water bath. This gentle refluxing is to prevent the loss of analytes along with the solvent stream. The steam refluxing should reduce the sample to near dryness. Continue refluxing with the tube immersed in the water bath for the remaining 15 minutes.
- f. Remove test tube from water bath. Following cooling add 2 mL of ethanol/water solution. Note: if a precipitate forms during the refluxing step it should be dissolved before adding the ethanol/water solution. To dissolve the precipitate, reheat the test tube and add a few drops of the ethanol/KOH reagent. Swirl, to dissolve the precipitate and then add the 2 mL of ethanol/water.
- g. Add isooctane in a 1 to 1 ratio of the amount of extract used in step "c" above and shake for 1 minute.
- h. If a clear separation of isooctane from the ethanol/water phase is achieved, the extract is ready for analysis, otherwise a second iteration of the acid wash/florisil slurry cleanup is recommended.

C. Analyte Recovery and quality control

1. Preparation of spiked samples

- a. In order to determine the effect of matrix suppression on the electron capture detector every 10th sample is spiked with aroclor material. If a given sample set contains a variety of widely different matrixes, each type should be spiked.
- b. Samples to be spiked are cut in duplicate. A small amount (1.0 to 0.5 mL) of aroclor stock solution (10 to 20 $\mu\text{g/mL}$) is added to the sample in the extraction thimble. The resulting concentration of the added spiked sample after extraction is in the range of 0.1 to 0.5 $\mu\text{g/mL}$.
- c. The sample spike is handled as any other sample beginning with Step 4 of the extraction procedure, IV.A.

2. Preparation of quality control samples

- a. There are currently no PCB containing sediments or soil available from the EPA.

3. Preparation of blank sample

- a. Place 10 g of sodium sulfate in a cellulose extraction thimble and handle as any other sample beginning with Step 4 of the extraction procedure, IV.A.

D. Gas chromatography analysis (splitless mode)

1. Instrument parameters:

H.P. 5880A	Initial Oven Temperature	150°C
	Initial Time	0.5 minute
	Temperature Profile:	
	Rate	10°C/minute
	Final Temperature	225°C
	Final Time 1	0 minutes
	Rate 2	8°C
	Final temperature 2	260°C
	Final time 2	15 minutes
	Post temperature	300°C
	Post time	1 minute
	Injector Temperature	250°C
	Detector Temperature	300°C
	Detector	Electron Capture
	Chart Speed	1 cm/minute
	Attenuation	3
	Threshold	2
	Peak Width	0.04
	Flows:	
	Capillary Column (He)	1 mL/minute
	Septum Purge	2 mL/minute
	Split Vent	65-70 mL/minute
	Make Up Gas	30-40 mL/minute
	(90% Argon 10% Methane)	
	Split valve opens:	0.5 min

2. Operation

- a. Transfer aliquots of samples to auto sampler vials and load them into 7672A auto sampler tray while entering autosampler vial data into "sample table."
- b. Run interspersed sets of standards and controls with samples. Also include isooctane washes on a regular basis. Average set of runs should contain 40 percent analytical standards, controls, spikes, and blanks to 60 percent samples.
- c. Start resident program: "PCBs". This program provides for summing of peak areas occurring between discrete time windows. These windows correspond to the major peaks of specific aroclors. Program also provides for selecting individual vials for double injection. See Appendix I for

- d. Double inject all quality control samples, all spikes, at least one analytical standard from each set of a given aroclor, and isooctane washes that follow a high concentration injection.
- e. Inspect the results of the initial run of samples and assess the following:
 1. the need for further dilutions and or cleaning,
 2. the identity of the aroclor contaminant(s), (if present at all), and
 3. the correct selection of aroclor standards to run along with the samples. (Standards must be of the same aroclor type as the samples and the standards' area counts must bracket the samples' area counts).
- f. If there is doubt as to the aroclor identity or there are other reasons for needing confirmation of the results, the analysis can be repeated using the DB1-30m megabore column, or other dissimilar columns.
- g. When necessary, dilute samples, perform any additional cleanup, or reselect appropriate aroclor formulations for standards. Then return to Section IV.D.2.a. for reanalysis. When a sample is subjected to additional cleanup, a spiked sample must also be similarly treated.

E. Calculations

1. Single Aroclor Samples

PCB concentrations in single aroclor samples are calculated by summing the total area of all the peaks due to that aroclor and comparing to the total area of those same peaks found in the standards.

- a. Determine which aroclor is present in the sample by comparing retention times and peak patterns of the sample to those of the standards.
- b. Plot concentration versus area count for the aroclor standards. Using the method of least squares, calculate the regression equation for the best line, using the analytical standards data. Calculate the correlation coefficient (must be 0.999 or better). Regression analysis may be done using a hand calculator such as the HP11C or a computer program such as LOTUS 123.
- c. Determine the concentration of aroclor present in the sample from the calibration curves.

- d. Use the spiked sample(s) to determine percent recovery of PCB material in the sample(s). If a sample set is large, and of similar matrix, then the recovery data can be averaged. Check the quality control charts to confirm that this level of recovery is within the acceptable range. (See Section V on quality control.)
- e. Use the EPA control sample(s) to confirm that the method is under control. Use the area counts of the analytical standards to confirm that the instrument is operating correctly.
- f. Use the HBB surrogate data to determine percent recovery on all non aroclor spiked samples.
- g. Calculation: $\text{ppm PCB in Oil} = \frac{C \times D}{R \times W}$
where:
C the observed PBC concentration in $\mu\text{g/mL}$
D the dilution ratio of the sample
R the recovery correction factor as determined by spikes or surrogates
W the weight of the sample aliquot in g
- h. Round off all data to 2 significant figures and report all data in ppm on a $\mu\text{g/g}$ ratio in the soil/sediment.

2. Mixed aroclor samples

PCB concentrations in mixed aroclor samples are calculated from individual congener peak areas or peak grouping sums. These peaks are chosen from non-overlapping regions of the chromatogram. These areas are compared with the same areas on the chromatograms of the analytical standards. A concentration is determined for each aroclor present and a total concentration calculated.

- a. Look at the sample's chromatogram and also at those of aroclor standards to determine which aroclors comprise the mixture. Determine which peaks from each aroclor have the least contribution from the other aroclors present.
- b. Using the area of the selected non-overlapping peaks determine the concentration of each aroclor by standard ratios:

Calculation: $X = (A \times c) / a$

where:

X	concentration of aroclor "X"
A	area of selected peaks in sample
a	area of selected peaks in standard
c	concentration of standard in $\mu\text{g/mL}$

- c. The total PCB concentration is determined by the summation of each of the individual aroclor concentrations. This value is substituted into "the observed PCB concentration in $\mu\text{g/mL}$ " in step "g" of the above section.
- d. See Appendix 2 for an example of a calculation for determining total PCB concentration in a mixed aroclor sample.

F. Analysis of non-aroclor and partial aroclor PCB mixtures

Samples that contain PCBs from non-aroclor formulations or from aroclors that have been altered through chemical or biological action are best analyzed using the Dry Color Manufacturers Association (DCMA) method.

Essentially, this method divides the distribution of PCB congener peaks into 10 regions. Each region is centered around the retention time of each PCB homologous series (i.e. pentachlorobiphenyl, hexachlorobiphenyl, etc.). In each homologous series one congener has been selected that has an average response factor for that series. These 10 congeners are prepared at different concentrations and run on the GC as outlined above in Section IV.D. (note "final time 2" may have to be extended in order to see decachlorobiphenyl). Regression equations are calculated for each of the 10 congeners as described in Section IV.E.1.B. Samples are cleaned up as needed and run as described in Sections IV.A through IV.D. Sample peaks are summed for each PCB congener region. Sample data for each region is compared against the appropriate DCMA regional standards to determine individual congener concentrations.

Total PCB concentration in a given sample is determined by summing the individual regional/congener concentrations.

V. Quality Control

Quality control data relating to PCBs are kept on the following matrix types: aqueous, solid, surface, air, and non-aqueous fluids. Quality control data relating to samples analyzed using this method are recorded under the category "Wastes" in our QC records. Since there are no PCB containing soils or sediments available from the EPA, quality control data for this matrix consists of spike and surrogate recovery data. Results of the analyses of the quantitation standards are also maintained. See the record categories "Environmental" and "Industrial Hygiene" for other PCB QC records.

- A. The following data are recorded for each sample set:
1. The spiking aroclor, its concentration, the amount spiked, and the dilution factor.
 2. The date of analysis and run number.
 3. The calculated true value of the spiked sample and the observed value(s).
 4. The percent recovery of the observed value as compared to the calculated true value. This is plotted for an estimate of method accuracy.
 5. The percent difference between the low and high observed values. This is plotted for an estimate of instrument precision.
- . Currently, this data is entered into a LOTUS 123 spreadsheet which determines means and standard deviations and plots results against these descriptive statistics.
- B. The area counts of the aroclor standards are monitored as an estimate of detector sensitivity. Likewise the HBB peak is used to determine theoretical plate height as an indicator of degradation in chromatography.

DWD

Appendix 1. PCB program for HP 5880 gas chromatograph

```

LIST PRGM
PROGRAM:      (ANNOTATION OFF)
8      M=0
9      DIM C(100)
10     INPUT "WHICH SAMPLES DO YOU WANT INJECTED (FIRST, LAST)?", S1, S2
13     INPUT "PRIMARILY SINGLE(1) OR DOUBLE(2) INJECTION?", F
14     LET D1=0
15     IF F=1 THEN 450
16     LET D2=0
17     IF F=2 THEN 500
18     IF S1>S2 THEN 600
20     FOR I=S1 TO S2
40     WAIT
50     VALVE 5 ON
60     START AUTO SEQ I, I
70     GOSUB 100
73     FOR J=1 TO D1
75     IF I=C(J) THEN 82
76     NEXT J
77     FOR J=1 TO D2
78     IF I=C(J) THEN 90
79     NEXT J
80     IF F=1 THEN 90
82     WAIT
84     VALVE 5 ON
86     START AUTO SEQ I, I
88     GOSUB 100
90     NEXT I
92     IF M=1 THEN 650
95     VALVE 5 OFF
98     STOP
100    REM THIS SUBROUTINE GENERATES THE PEAK SUMMED TABLES
105    REPORT ANNOTATION OFF
110    FOR K=1 TO 3
120    DATA "1016/1232/1242/1248", 10, 15, "1254", 12.4, 17, "1260", 14.5, 23.5
130    READ N$, T1, T2
140    EXECUTE X, "REPORT TIME "&VAL$(T1)&" AREA SUM ON "
170    EXECUTE Y, "REPORT TIME "&VAL$(T2)&" AREA SUM OFF "
175    REPORT TIME 5 AREA SUM ON
180    EXECUTE W1, "REPORT TIME "&VAL$(T1-0.01)&" AREA SUM OFF "
190    EXECUTE Z1, "REPORT TIME "&VAL$(T2+0.01)&" AREA SUM ON "
195    REPORT TIME 17.59 AREA SUM OFF
220    PRINT "PEAKS SUMMED FROM RT";T1;" TO ";T2;" FOR AROCLOR ";N$
230    LIST REPORT
240    EXECUTE X1, "DELETE REPORT TIME "&VAL$(T1)
250    EXECUTE Y1, "DELETE REPORT TIME "&VAL$(T2)
255    DELETE REPORT TIME 5
260    EXECUTE W2, "DELETE REPORT TIME "&VAL$(T1-0.01)
270    EXECUTE Z2, "DELETE REPORT TIME "&VAL$(T2+0.01)
275    DELETE REPORT TIME 17.59

```

```
300 NEXT K
310 REPORT ANNOTATION ON
315 RESTORE
320 RETURN
450 LET D1=0
460 INPUT "HOW MANY DO YOU WANT DOUBLE INJECTED?",D1
461 FOR N=1 TO 20
463 NEXT N
470 IF D1=0 THEN 16
475 FOR L=1 TO D1
480 INPUT "WHICH SAMPLE?",C(L)
485 NEXT L
490 GOTO 16
500 LET D2=0
510 INPUT "HOW MANY DO YOU WANT SINGLE INJECTED?",D2
520 IF D2=0 THEN 18
525 FOR L=1 TO D2
530 INPUT "WHICH SAMPLE?",C(L)
535 NEXT L
540 GOTO 18
600 S3=S2
610 S2=99
620 M=1
630 GOTO 20
650 S1=1
660 S2=S3
670 M=0
680 GOTO 20
```

Appendix 2. Determination of PCBs in mixed aroclor samples

The attached figure includes three chromatograms: A) a mixed aroclor waste sample containing aroclors 1242/1248 and 1260; B) a 0.1 µg/mL aroclor 1242 standard; C) a 0.01 µg/mL 1260 standard.

Some of the peaks from the 1242/1248 region that are not overlapped by 1260 peaks occur at retention times (RT): 7.73, 8.61, 9.01, 9.56, and 9.78 minutes. Similarly, non-overlapped peaks for the 1260 region occur at retention times: 18.58, 18.97, and 19.24 minutes. The area counts for these peaks are as follows:

<u>R.T.</u>	<u>Region</u>	<u>Area from standards</u>	<u>Area from sample</u>
7.73	1242	159.0	93.11
8.61	1242	302.8	261.83
9.01	1242	155.6	129.8
9.56	1242	408.13	325.8
9.78	1242	<u>204.2</u>	<u>165.8</u>
Sum:		1229.7	976.34
18.58	1260	43.63	74.76
18.97	1260	18.74	31.10
19.24	1260	<u>24.70</u>	<u>39.94</u>
Sum:		87.07	145.80

Calculation:

The concentration of each aroclor is determined from the ratio of peak areas in the sample to that of the standard. The 1260 contribution is therefore:

$$(0.01 \times 145.8)/87.07 = 0.0167 \mu\text{g/mL}$$

and the 1242 contribution is:

$$(0.1 \times 976.34)/1229.7 = 0.0794 \mu\text{g/mL}$$

The total concentration of PCBs in the sample extract is 0.096 µg/mL. This value is then substituted for "the observed PCB concentration in µg/mL" in the equation for calculating ppm PCB in oil found in Section IV.E.1.g.

C

RT: VALUE 5 - OFF ON: START PRGM RATE !

B

ATT: VALUE 5 - OFF OV: START FROM RATE !

A

Method No. EHS P-9

Title: Polychlorinated Biphenyls in Oil and Waste Liquids

Date Issued: 9-23-85

Approved by: M. K. Hamilton,

Written by: H. L. Boorse

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

POLYCHLORINATED BIPHENYLS IN OIL AND WASTE LIQUIDS

I. References

- A. "EPA (Environmental Protection Agency) Method Study 28, PCB's (Polychlorinated Biphenyls) in Oil," Versar, Inc., Springfield, VA. Prepared for Environmental Monitoring and Support Lab.- Cincinnati, OH October 1984.
- B. "Analysis of Polychlorinated Biphenyls in Mineral Insulating Oils by Gas Chromatography," ASTM D4059-83. Vol. 10.03 Electrical Insulation Liquids, Gases, Protective Equipment.
- C. "The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils", EPA-600/4-81-045, T. A. Bellar and J. J. Lichtenberg. Environmental Monitoring and Support Laboratory.
- D. The analytical chemistry of PCBs, M. D. Erickson, Butterworth Publishers, Boston, 1986.
- E. "Test Methods for Evaluating Solid Waste," EPA SW 846, Methods 3660 & 8080.

II. Principles and Limitations

The sample is diluted with isooctane and the resulting solution is treated by a cleanup procedure (routinely: acid wash/florisil slurry) to remove interfering substances. Analysis is by capillary gas chromatography using an electron capture (EC) detector. The method is made qualitative and quantitative by comparing peak patterns, area counts, and retention times of the sample chromatogram with chromatograms of known quantity and type of aroclor standards, obtained under the same conditions. Results can be confirmed by running the samples and standards using a second dissimilar column.

Occasionally, sample chromatograms indicate the presence of PCBs; however, no aroclor or mixture of aroclors are indicated by the pattern. This is often the case with weathered or otherwise degraded aroclor mixtures or when a non-aroclor material is the PCB source. In these cases the Dry Color Manufacturers Associations' (DCMA) method for PCB identification is employed. (See Section IV.F "Non-aroclor and partial aroclor PCB mixture.")

Electron capture detectors respond to chlorine-containing compounds other than PCBs and to certain other electrophilic materials containing other halogens, nitrogen, oxygen, and sulfur. Most common interferences can be removed by sulfuric acid washing. The chromatogram of each analyzed sample should be carefully compared with those of the standards. The response of an EC detector to PCBs is reduced by high boiling hydrocarbons that co-elute with the PCBs. This suppression can be compensated for by running spiked samples to determine the actual recovery.

Residual oxygen in carrier and makeup gas can react with components of samples to give oxidation products to which EC detectors will respond. Purity of these gases should be assured.

III. Materials

A. Equipment:

1. 1 x 12 cm screw cap tubes
2. Teflon lined caps
3. 10 mL repipetors for solvent and acid measurement and transfer
4. 0.5 mL, 1 mL, and 2 mL Class A or better glass pipets
5. Volumetric flasks, isooctane washed
6. Analytical balance with 0.1 mg sensitivity
7. SE-54 or DB-5 fused silica capillary column 30 meter length, 0.250mm I.D., 0.25 μ m film thickness
8. DB1-30m megabore column 30 meter length, 0.53mm I.D., 1.5 μ m film thickness
9. Gas chromatograph fitted for capillary column and equipped with an electron capture detector and auto sampler
10. Vortex
11. Centrifuge
12. Pasteur Pipets
13. Autosampler vials with teflon caps
14. Mechanical rotary extractor
15. Lambda pipets as needed
16. Carborundum boiler chips

B. Reagents:

1. Pesticide grade 2,2,4-trimethylpentane (isooctane)
2. Reagent grade (conc.) Sulfuric Acid

3. Activated Florisil, 60/100 mesh, reagent grade, suitable for pesticide-residue analysis. Available from Floridin Company and treated per AOAC (1980) 29.002 before use.
4. EPA standards (1000 to 5000 ppm) of aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268
5. EPA controls of aroclors in oils (transformer, hydraulic, and capacitor)
6. Hexabromobenzene (PCB surrogate standard)
7. Ultra high purity helium
8. 90 percent argon--10 percent methane (P10) or 95 percent argon--5 percent methane (P-5)
9. Tetrabutylammonium hydrogen sulfate, reagent grade
10. Sodium sulfite, reagent grade
11. Ethanol, USP 95%
12. Potassium hydroxide, anhydrous pellets
13. Dry Color Manufactures Association mixture of PCB isomers in hexane. Available from Ultra scientific.
14. 2-propanol, reagent grade

C. Standards & Prepared Reagents:

Note: All glassware should be dedicated for the preparation of aroclor standards.

1. Stock Aroclor solutions. EPA Aroclor standards range from 1000 to 5000 $\mu\text{g/mL}$ and are received in 1 mL glass ampules. The appropriate amount of standard is volumetrically transferred to a 25 or 50 mL volumetric flask and diluted in isooctane so that a 10 to 20 $\mu\text{g/mL}$ solution is produced. Transfer the stock solution to a brown glass bottle fitted with a teflon lined cap. Transfer remaining EPA standard material to a 1 mL auto sampler vial. The stock solution and the EPA standards are stable indefinitely if their seals are maintained and they are stored at or below 0°C.
2. Working standards--(0.5, 0.1, 0.05, 0.01 $\mu\text{g/mL}$). Add appropriate amount of stock standard (depending on stock standard concentration) to screw cap test tubes and make up with isooctane so that a 0.5 $\mu\text{g/mL}$ solution results. Serially dilute the 0.5 $\mu\text{g/mL}$ to make up the remaining standards (0.01, 0.05, and 0.1 $\mu\text{g/mL}$). Total volume of each working standard should be approximately 10 mL. Prepare monthly or as needed.

3. DCMA mixture, stock and serial dilutions. The DCMA mixture ampule is opened and an aliquot diluted 100 fold. Serial dilutions of 2, 10, and 20 fold are made up of this solution. The remaining original DCMA mixture is transferred to an auto sampler vial, sealed with a teflon backed cap and stored at or below 0°C.
4. Hexabromobenzene (HBB) surrogate-working standard. The neat HBB standard is removed from the freezer and a 10 mg aliquot volumetrically made up into 100 mL of isooctane. The resulting solution, the HBB working standard, is subdivided into 10 mL vials, secured with a teflon lined screw cap. These materials are stable indefinitely if their seals are maintained and they are stored at or below 0°C.

IV. Methods

Note: This procedure is intended to qualitatively and quantitatively analyze samples for the nine specific aroclors listed on Page 3. This method is not adequate for qualitative and/or quantitative analysis of partial aroclors or individual congeners which may result from aroclor degradation or by products of chemical reactions. For non-aroclor samples see Section IV.F for the analysis of these partial or non-aroclor containing samples.

A. Dilution:

1. Pipet approximately 0.10 g sample using a pasteur pipet into a tared screw top test tube.
2. Reweigh the test tube to ± 0.0001 g and record the weight of the sample.
3. Prepare blank, spike, and other QC samples in accordance with Section IV.C.
4. Dilute to 10 mL with isooctane and mix well.
5. Spike every sample, sample duplicate, sample spike, EPA QC, and blank with 2 μ L of the HBB surrogate.

B. Cleanup techniques

1. Acid wash/florisil cleanup (Primary procedure)
This procedure is used for all samples received at the laboratory.
 - a. Add 3 mL concentrated sulfuric acid to each of the samples, including blanks, QC samples, etc.
 - b. Shake by hand for 30 seconds and Vortex for 30 seconds.

- c. Transfer all test tubes containing samples, duplicate samples, blanks, quality controls and spiked samples to the rotary extractor. Run extractor for 1 hour.
- d. Label test tubes for each sample, blank, quality control and spiked sample being run. Add -0.2 g florisisl to each empty test tube.
- e. Remove sample test tubes from the extractor and centrifuge for approximately 5 minutes at 3000 rpm. Transfer each isooctane layer to its corresponding florisisl-containing test tube.
- f. Place sample test tubes in extractor for 1 hour.
- g. If the isooctane extract appears colored or cloudy, additional/alternative cleanup procedures may be necessary; otherwise the extract is ready for analysis. (Section IV.D.)

2. Sulfur removal (Based on EPA SI0846 Method 3660)

This procedure is used routinely with sediment and sludge samples or when sulfur interference is indicated on the chromatogram.

- a. Prepare TBA-sulfite reagent: Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL of deionized water. Extract 3 times with 20 mL portions of isooctane. Discard the isooctane extracts and add 25 g of sodium sulfite to the water solution. Solution is saturated with respect to sodium sulfite and is stable 1 month at room temperature.
- b. Transfer 2 mL of extract from Section IV.B.1.g. ("Acid wash/florisisl cleanup") to a new test tube.
- c. Add 1 mL of TBA-sulfite reagent and 1 mL 2-propanol to the test tube. Shake test tube for at least 1 minute and look for clear crystals from precipitation of sodium sulfite. If crystals are not present, add crystalline sodium sulfite in 100 mg portions until solid material remains (one portion is usually enough).
- d. Add 5 mL of deionized water and shake for at least 1 minute. Let stand for 5 minutes for phase separation. Collect top, isooctane, layer in an auto sampler vial. The extract is ready for analysis (Section IV.D).

3. Ethanol/potassium hydroxide cleanup

This procedure is used when hydroxyl-containing species such as pentachlorophenol and glycols are present. Additionally, fats are made more water soluble through saponification. Certain chlorinated pesticides undergo dehydrochlorination.

- a. Prepare 2% potassium hydroxide/ethanol solution: Dissolve 2 g KOH into 100 mL of 95% ethanol.
- b. Prepare 50% ethanol/water solution: add equal volumes of ethanol and deionized water.
- c. Pipet up to 4 mL of extract from Section IV.B.1.g ("Acid wash/florisil cleanup") into a pyrex test tube and reduce to dryness under N₂.
- d. Add 2 mL of ethanol/KOH reagent and 1 boiling chip.
- e. Reflux test tube contents over boiling water bath for 20 minutes. During first 5 minutes the test tube should be immersed only in the steam of the water bath. This gentle refluxing is to prevent the loss of analytes along with the solvent stream. The steam refluxing should reduce the sample to near dryness. Continue refluxing with the tube immersed in the water bath for the remaining 15 minutes.
- f. Remove test tube from water bath, cool and add 2 mL of ethanol/water solution. Note: if a precipitate forms during the refluxing step it should be dissolved before adding the ethanol/water solution. To dissolve the precipitate, reheat the test tube and add a few drops of the ethanol/KOH reagent. Swirl, to dissolve the precipitate and then add the 2 mL of ethanol/water.
- g. Add isooctane in a 1 to 1 ratio of the amount of extract used in Step "c" above and shake for 1 minute.
- h. If a clear separation of isooctane from the ethanol/water phase is achieved, the extract is ready for analysis, otherwise a second iteration of the acid wash/florisil slurry cleanup is recommended.

C. Analyte Recovery and quality control

1. Preparation of spiked samples

- a. In order to determine the effect of matrix suppression on the electron capture detector, every 10th sample is spiked with aroclor material. If a given sample set contains a variety of widely different matrixes, each type should be spiked.

- b. Samples to be spiked are cut in duplicate. A small amount (0.1 to 0.2 mL) of aroclor stock solution (10 to 20 $\mu\text{g/mL}$) is added to one of the sample aliquots. The sample aliquot with added aroclor material is made up to 10 mL in isooctane and shaken. The resulting concentration of the added spiked sample is in the range of 0.1 to 0.5 $\mu\text{g/mL}$.
- c. The sample spike is handled as any other sample beginning with the acid wash/florisil slurry cleanup.

2. Preparation of quality control samples

- a. Available from the EPA are PCBs in transformer, hydraulic, and capacitor oils. They are available at approximately 10, 50, and 500 ppm concentrations. A typical oil would be identified as: "Aroclor 1260 transformer oil, concentration 1, WP# 683." Starting with an approximately 0.1 g aliquot, quality control oils are treated as any sample.

3. Preparation of blank sample

- a. Dispense 10 mL of isooctane into a screw top test tube and treat as any sample extract.

D. Gas chromatography analysis (splitless mode)

1. Instrument parameters:

H.P. 5880A	Initial Oven Temperature	150°C
	Initial Time	0.5 minute
	Temperature Profile:	
	Rate	10°C/minute
	Final Temperature	225°C
	Final Time 1	0 minutes
	Rate 2	8°C
	Final temperature 2	260°C
	Final time 2	15 minutes
	Post temperature	300°C
	Post time	1 minute
	Injector Temperature	250°C
	Detector Temperature	300°C
	Detector	Electron Capture
	Chart Speed	1 cm/minute
	Attenuation	3
	Threshold	2
	Peak Width	0.4
	Flows:	
	Capillary Column (He)	1 mL/minute
	Septum Purge	2 mL/minute
	Split Vent	65-70 mL/minute
	Make Up Gas	30-40 mL/minute
	(90% Argon 10% Methane)	
	Split valve opens:	0.5 minute

2. Operation

- a. Transfer aliquots of sample extracts to autosampler vials and load them into 7672A auto sampler tray while entering auto sampler vial data into "run table."
- b. Run interspersed sets of standards and controls with samples. Also include isooctane washes on a regular basis. Average set of runs should contain 40 percent analytical standards, controls, spikes, and blanks to 60 percent samples.
- c. Start resident program "PCBs." This program provides for summing of peak areas occurring between discrete time windows. These windows correspond to the major peaks of specific aroclors. Program also provides for selecting individual vials for double injection. See Appendix 1 for listing of program.
- d. Double inject all quality control samples, all spikes, at least one analytical standard from each set of a given aroclor, and isooctane washes that follow a high concentration injection.
- e. Inspect the results of the initial run of samples and assess the following: (1) the need for further dilutions and or cleaning, (2) the identity of the aroclor contaminant(s), (if present at all), and (3) the correct selection of aroclor standards to run along with the samples. (Standards must be of the same aroclor-type as the samples and the standards' area counts must bracket the samples' area counts.)
- f. If there is doubt as to the aroclor identity or there are other reasons for needing confirmation of the results, the analysis can be repeated using the DB1-30m megabore column, or other dissimilar columns.
- g. When necessary, dilute samples, perform any additional cleanup, or reinject with appropriate aroclor formulations for standards. Then return to Part "a" above for reanalysis. When a sample is subjected to additional cleanup, a spiked sample must also be similarly treated.

E. Calculations

1. Single Aroclor Samples

PCB concentrations in single aroclor samples are calculated by summing the total area of all the peaks due to that aroclor and comparing to the total area of those same peaks found in the standards.

- a. Determine which aroclor is present in the sample by comparing retention times and peak patterns of the sample to those of the standards.
- b. Plot concentration versus area count for the aroclor standards. Using the method of least squares, calculate the regression equation for the best line using the analytical standards data. Calculate the correlation coefficient (must be 0.999 or better). Regression analysis may be done using a hand calculator such as the HP11C or a computer program such as LOTUS 123.
- c. Determine the concentration of the aroclor present in the sample from the calibration curves.
- d. Use the spiked sample(s) to determine percent recovery of PCB material in the sample(s). If an sample set is large, and of similar matrix, then the recovery data can be averaged. Check the quality control charts to confirm that this level of recovery is within the acceptable range. (See Section V on quality control.)
- e. Use the EPA control sample(s) to confirm that the method is under control. Use the area counts of the analytical standards to confirm that the instrument is operating correctly.
- f. Use the HBB surrogate data to determine percent recovery on all non-aroclor spiked samples.
- g. Calculation:

$$\text{ppm PCB in Oil} = \frac{C \times D}{R \times W}$$

where:

- C the observed PBC concentration in $\mu\text{g/mL}$
- D the dilution ratio of the sample
- R the recovery correction factor as determined by spikes or surrogates
- W the weight of the sample aliquot in g

- h. Round off all data to 2 significant figures and report all data in ppm on a $\mu\text{g/g}$ ratio in the oil.

2. Mixed aroclor samples

PCB concentrations in mixed aroclor samples are calculated from individual congener peak areas or peak grouping sums. These peaks are chosen from non-overlapping regions of the chromatogram. These areas are compared with the same areas on the chromatograms of the analytical standards. A concentration is determined for each aroclor present and a total concentration calculated.

- a. Look at the sample's chromatogram and also at those of aroclor standards to determine which aroclors comprise the mixture. Determine which peaks from each aroclor have the least contribution from the other aroclors present.
- b. Using the area of the selected non-overlapping peaks determine the concentration of each aroclor by standard ratios:

Calculation: $X = (A \times c) / a$

where:

X concentration of aroclor "X"
A area of selected peaks in sample
a area of selected peaks in standard
c concentration of standard in $\mu\text{g/mL}$

- c. The total PCB concentration is determined by the summation of each of the individual aroclor concentrations. This value is substituted into "the observed PCB concentration in $\mu\text{g/mL}$ " in Step "g" of the above section.
- d. See Appendix 2 for an example of a calculation for determining total PCB concentration in a mixed aroclor sample.

F. Analysis of non-aroclor and partial aroclor PCB mixtures

Samples that contain PCBs from non-aroclor formulations or from aroclors that have been altered through chemical or biological action are analyzed using the Dry Color Manufacturers Association (DCMA) method.

Essentially this method divides the distribution of PCB congener peaks into 10 regions. Each region is centered around the retention time of each PCB homologous series (e.g. pentachlorobiphenyl, hexachlorobiphenyl, etc.). In each homologous series one congener has been selected that has an average response factor for that series. These 10 congeners are prepared at different concentrations and run on the GC as outlined above in Section IV.D (note "final time 2" may have to be extended in order to see decachlorobiphenyl). Regression equations are calculated for each of the 10 congeners as described in Section IV.E.1.b. Samples are cleaned up as needed and run as described in Sections IV.A through IV.D. Sample peaks are summed for each PCB congener region. Sample data for each region is compared against the appropriate DCMA regional standards to determine individual congener concentrations.

Total PCB concentration in a given sample is determined by summing the individual regional/congener concentration.

V. Quality Control

Quality control data relating to PCBs are kept on the following matrix types: aqueous, solid, surface, air, and non-aqueous fluids. Quality control data relating to samples analyzed using this method are recorded under the category "Wastes" in our QC records. Results of the analyses of the EPA oils, surrogate data, and the quantitation standards are maintained. See the record categories "Environmental" and "Industrial Hygiene" for other PCB QC records.

A. The following data are recorded for each sample set:

1. The EPA QC oil's type, concentration and WP number, amount weighed, and dilution factor.
2. The date of analysis and run number.
3. The calculated true value of the QC sample and the observed value(s).
4. The percent recovery of the observed value as compared to the calculated true value. This is plotted for an estimate of instrument precision.

Currently, this data is entered into a LOTUS 123 spreadsheet which determines means, standard deviations, and plots results against these descriptive statistics.

B. The area counts of the aroclor standards are monitored as an estimate of detector sensitivity. Likewise the HBB peak is used to determine theoretical plate height as an indicator of degradation in chromatography.

Bow

Appendix 1. PCB program for HP 5880 gas chromatograph

```

LIST PRGM
PROGRAM:      (ANNOTATION OFF)
9      M=0
9      DIM C(100)
10     INPUT "WHICH SAMPLES DO YOU WANT INJECTED (FIRST, LAST)?", S1, S2
13     INPUT "PRIMARILY SINGLE(1) OR DOUBLE(2) INJECTION?", F
14     LET D1=0
15     IF F=1 THEN 450
16     LET D2=0
17     IF F=2 THEN 500
18     IF S1>S2 THEN 600
20     FOR I=S1 TO S2
40     WAIT
50     VALVE 5 ON
60     START AUTO SEQ I, I
70     GOSUB 100
73     FOR J=1 TO D1
75     IF I=C(J) THEN 82
76     NEXT J
77     FOR J=1 TO D2
78     IF I=C(J) THEN 90
79     NEXT J
80     IF F=1 THEN 90
82     WAIT
84     VALVE 5 ON
86     START AUTO SEQ I, I
88     GOSUB 100
90     NEXT I
92     IF M=1 THEN 650
95     VALVE 5 OFF
99     STOP
100    REM THIS SUBROUTINE GENERATES THE PEAK SUMMED TABLES
105    REPORT ANNOTATION OFF
110    FOR K=1 TO 3
120    DATA "1016/1232/1242/1248", 10, 15, "1254", 12.4, 17, "1260", 14.5, 23.5
130    READ N$, T1, T2
140    EXECUTE X, "REPORT TIME "&VAL$(T1)&" AREA SUM ON "
170    EXECUTE Y, "REPORT TIME "&VAL$(T2)&" AREA SUM OFF "
175    REPORT TIME 5 AREA SUM ON
180    EXECUTE W1, "REPORT TIME "&VAL$(T1-0.01)&" AREA SUM OFF "
190    EXECUTE Z1, "REPORT TIME "&VAL$(T2+0.01)&" AREA SUM ON "
195    REPORT TIME 17.59 AREA SUM OFF
220    PRINT "PEAKS SUMMED FROM RT"; T1; "TO"; T2; "FOR AROCLOR "; N$
230    LIST REPORT
240    EXECUTE X1, "DELETE REPORT TIME "&VAL$(T1)
250    EXECUTE Y1, "DELETE REPORT TIME "&VAL$(T2)
255    DELETE REPORT TIME 5
260    EXECUTE W2, "DELETE REPORT TIME "&VAL$(T1-0.01)
270    EXECUTE Z2, "DELETE REPORT TIME "&VAL$(T2+0.01)
275    DELETE REPORT TIME 17.59

```

```
300 NEXT K
310 REPORT ANNOTATION ON
315 RESTORE
320 RETURN
450 LET D1=0
460 INPUT "HOW MANY DO YOU WANT DOUBLE INJECTED?",D1
461 FOR N=1 TO 20
463 NEXT N
470 IF D1=0 THEN 16
475 FOR L=1 TO D1
480 INPUT "WHICH SAMPLE?",C(L)
485 NEXT L
490 GOTO 16
500 LET D2=0
510 INPUT "HOW MANY DO YOU WANT SINGLE INJECTED?",D2
520 IF D2=0 THEN 18
525 FOR L=1 TO D2
530 INPUT "WHICH SAMPLE?",C(L)
535 NEXT L
540 GOTO 18
600 S3=S2
610 S2=99
620 M=1
630 GOTO 20
650 S1=1
660 S2=S3
670 M=0
680 GOTO 20
```

Appendix 2. Determination of PCBs in Mixed Aroclor Samples

The attached figure includes three chromatograms: (A) a mixed aroclor waste sample containing aroclors 1242/1248 and 1260; (B) a 0.1 $\mu\text{g/mL}$ aroclor 1242 standard; (C) a 0.01 $\mu\text{g/mL}$ 1260 standard.

Some of the peaks from the 1242/1248 region that are not overlapped by 1260 peaks occur at retention times (RT): 7.73, 8.61, 9.01, 9.56, and 9.78 minutes. Similarly, non-overlapped peaks for the 1260 region occur at retention times: 18.58, 18.97, and 19.24 minutes. The area counts for these peaks are as follows:

<u>R.T.</u>	<u>Region</u>	<u>Area from standards</u>	<u>Area from sample</u>
7.73	1242	159.0	93.11
8.61	1242	302.8	261.83
9.01	1242	155.6	129.8
9.56	1242	408.13	325.8
9.78	1242	<u>204.2</u>	<u>165.8</u>
Sum:		1229.7	976.34
18.58	1260	43.63	74.76
18.97	1260	18.74	31.10
19.24	1260	<u>24.70</u>	<u>39.94</u>
Sum:		87.07	145.80

Calculation:

The concentration of each aroclor is determined from the ratio of peak areas in the sample to that of the standard. The 1260 contribution is therefore:

$$(0.01 \times 145.8)/87.07 = 0.0167 \mu/\text{mL}$$

and the 1242 contribution is:

$$(0.1 \times 976.34)/1229.7 = 0.0794 \mu/\text{mL}$$

The total concentration of PCBs in the sample extract is 0.096 μ/mL . This value is then substituted for "the observed PCB concentration in $\mu\text{g/mL}$ " in the equation for calculating ppm PCB in oil found in Section IV.E.1.g.

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A1-I
Table of Contents

HEHF Laboratory: Inorganics

Appendix Number	Lab Number	Method Name	Analytes
A1-I.10	EPA Method 5	Determination of Particulate Emissions from Stationary Sources	Particulates
A1-I.20	EPA Method 6	Determination of Sulfur Dioxide Emissions from Stationary Sources	SO ₂ (g)
A1-I.30	EPA Method 7C	Determination of Nitrogen Oxide Emissions from Stationary Sources-Alkaline-Permanganate/Colorimetric Method	NO _x (g)
A1-I.40	EPA Method 17	Determination of Particulate Emissions from Stationary Sources (In Stack Filtration Method)	Particulates
A1-I.50	EQN-1277-028	TGS-ANSA Method for the Determination of Nitrogen Dioxide in the Atmosphere	NO ₂
A1-I.60	EHS E-1	Extraction Procedure Toxicity Test-Metals	Metals Toxicity
A1-I.80	EHS M-3	Mercury in Soil	Hg
A1-I.90	EHS M-12	Metals in Waste Organic Matrices by Atomic Absorption Spectroscopy	Metals

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A1-I
Table of Contents

HEHF Laboratory: Inorganic

Appendix Number	Lab Number	Method Name	Analytes
A1-I.100	EHF M-1	Metals in H ₂ O-Atomic Absorption--Flame	Ag, Ba, Ca, Cr, Cu, Fe, Mg, Mn, and Zn
A1-I.110	EHF M-10	Metals in Water--Graphite Furnace AA	Ag, As, Be, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Ti and V
A1-I.120	EHF M-4	Total Mercury (Organic and Inorganic) in Water by Flameless AA	Hg
A1-I.130	EHF C-2	Hexavalent Chromium--Water and Air	Cr VI
A1-I.140	EHF C-3	Cyanide-Colorimetric Water and Air	Cn
A1-I.150	EHF A-7	Inorganic Anions in Water Using Ion Chromatography	F ⁻ , Cl ⁻ , PO ₄ ⁻³ , NO ₃ ⁻ , NO ₂ ⁻ , SO ₄ ⁻²
A1-I.160	EHF F-2	Fluoride--Specific Ion Electrode	F ⁻
A1-I.170	EHF F-8	Flash Point Determination	Flash Point
A1-I.180	EHF N-7	TGS-ANSA Method for the Determination of Nitrogen Dioxide in the Atmosphere	NO ₂
A1-I.190	EHF S-6	SO ₂ in Air and Stack Samples Using Barium Perchlorate Titration	SO ₂

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A1-I
Table of Contents

HEHF Laboratory: Inorganic

Appendix Number	Lab Number	Method Name	Analytes
A1-I.200	EHS N-1	Determination of NO _x in Stack Gas	NO _x
A1-I.210	EHS H	Hardness (EDTA)	Hardness
A1-I.220	EHS F	Filterable Residue (Total Dissolved Solids)	Dissolved Solids
A1-I.230	EHS C-11	Chemical Oxygen Demand (COD)--HACH Closed-Tube Method	0
A1-I.240	EHS B-4	Biochemical Oxygen Demand (BOD)- DO Probe	Dissolved Oxygen
A1-I.250	EHS L-1	Linear Alkylbenzene Sulfonate--Methylene Blue Substances (MBAS)	LAS-MBAS

3.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 3 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure the volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B_{ws} = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.

B_w = Water vapor in the gas stream, proportion by volume.

M_w = Molecular weight of water, 18.0 g/mole (18.0 lb/lb-mole).

P_a = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³)/(lb-mole) (°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_f = Final volume of impinger contents, ml.

V_i = Initial volume of impinger contents, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m,sc}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dcm (dcf).

$V_{w,sc}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

ρ_w = Density of water, 0.9983 g/ml (0.002391 lb/ml).

Y = Dry gas meter calibration factor.

3.3.2 Volume of water vapor collected, where:

$$V_{w,sc} = \frac{(V_f - V_i) B_{ws} R T_{std}}{P_{std} M_w}$$

$$= K_d (V_f - V_i)$$

Equation 4-5

$K_d = 0.001333 \text{ m}^3/\text{ml}$ for metric units
 $= 0.04707 \text{ ft}^3/\text{ml}$ for English units.

3.3.3 Gas volume.

$$V_{m,sc} = V_m \left(\frac{P_a}{P_{std}} \right) \left(\frac{T_{std}}{T_m} \right)$$

$$= K_d \frac{V_m P_a}{T_m}$$

Equation 4-6

where:

$K_d = 0.3888 \text{ °K/mm Hg}$ for metric units

$= 17.64 \text{ °R/in. Hg}$ for English units

3.3.4 Approximate moisture content.

$$B_{ws} = \frac{V_{w,sc}}{V_{m,sc} + V_{w,sc}} + B_w$$

$$= \frac{V_{w,sc}}{V_{m,sc} + V_{w,sc}} + (0.025)$$

Equation 4-7

4. Calibration

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); and Section 5.7 (barometer). The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the approximation method, use the procedures outlined in Section 5.1.1 of Method 5 to calibrate the metering system, and the procedure of Method 5, Section 5.7 to calibrate the barometer.

5. Bibliography

1. Air Pollution Engineering Manual (Second Edition). Danielson, J. A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N.C. Publication No. AP-40, 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, Calif. November, 1963.

3. Methods for Determination of Velocity, Volume Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif. Bulletin WP-50, 1968.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 120±14° C (248±25° F) or such other temperature as specified by an applicable subpart of the standards or approved by Administrator, U.S. Environmental Protection Agency, for a particular application. The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0561 (Citation 2 in Bibliography); commercial models of this train are also available. For changes from APTD-0561 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Bibliography). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

[Appendix A, Method 5]

Figure 5-1. Particulate-sampling train

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be $\leq 30^\circ$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for looking into sampling should be available, e.g., 0.32 to 1.27 cm ($\frac{1}{8}$ to $\frac{1}{2}$ in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm ($\frac{1}{16}$ in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

[2.1.1 amended by 52 FR 34639, September 14, 1987]

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0881 and utilizing the calibration curves of APTD-0876 (or calibrated according to the procedure outlined in APTD-0876) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F) quartz liners shall be used for temperatures between 480 and 900°C (900 and $1,650^\circ \text{F}$). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate

is 820°C ($1,508^\circ \text{F}$), and for quartz it is $1,800^\circ \text{C}$ ($2,732^\circ \text{F}$).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,¹ or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during

¹Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

[Appendix A, Method 5]

sampling. The Type S pilot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 **Differential Pressure Gauge.** Inclined manometer or equivalent device (two), as described in Section 2.3 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 **Filter Holder.** Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 **Filter Heating System.** Any heating system capable of maintaining a temperature around the filter holder during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 **Condenser.** The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm ($\frac{1}{2}$ in.) ID glass tube extending to about 1.3 cm ($\frac{1}{2}$ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's

law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20°C (68°F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

Note: If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 **Metering System.** Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pilot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APDT-0578 may be used provided that the specifications of this method are met.

2.1.9 **Barometer, Mercury, aneroid, or other barometer** capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 **Gas Density Determination Equipment.** Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pilot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement

with respect to the Type S pilot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pilot tube. (This alternative is subject to the approval of the Administrator.)

2.2 **Sample Recovery.** The following items are needed.

2.2.1 **Probe-Liner and Probe-Nozzle Brushes.** Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 **Wash Bottles—Two.** Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 **Glass Sample Storage Containers.** Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 **Petri Dishes.** For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 **Graduated Cylinder and/or Balance.** To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 **Plastic Storage Containers.** Airtight containers to store silica gel.

2.2.7 **Funnel and Rubber Policeman.** To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 **Funnel.** Glass or polyethylene, to aid in sample recovery.

2.3 **Analysis.** For analysis, the following equipment is needed.

2.3.1 **Glass Weighing Dishes.**

2.3.2 **Desiccator.**

2.3.3 **Analytical Balance.** To measure to within 0.1 mg.

2.3.4 **Balance.** To measure to within 0.5 g.

2.3.5 **Beakers.** 250 ml.

2.3.6 **Hygrometer.** To measure the relative humidity of the laboratory environment.

2.3.7 **Temperature Gauge.** To measure the temperature of the laboratory environment.

3. Reagents

3.1 **Sampling.** The reagents used in sampling are as follows:

[Appendix A, Method 5]

3.1.1 **Filters.** Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71 (Reapproved 1978) (incorporated by reference — see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3 , the filter material must be of a type that is unreactive to SO_2 or SO_3 . Citation 10 in Section 7 Bibliography, may be used to select the appropriate filter.

[§ 60.17 amended by 48 FR 3735, January 27, 1983]

3.1.2 **Silica Gel.** Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 **Water.** When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 **Crushed Ice.**

3.1.5 **Stopcock Grease.** Acetone-insoluble, bond-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 **Sample Recovery.** Acetone-reagent grade, <0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 **Analysis.** Two reagents are required for the analysis:

3.3.1 **Acetone.** Same as 3.2.

3.3.2 **Desiccant.** Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

Procedure

4.1 **Sampling.** The complexity of this method is such that, in order to obtain reliable results, testers should be trained and familiar with the test procedures.

4.2 **Test Preparation.** It is suggested that sampling equipment be maintained according to the procedures described in § 60.10.

[§ 60.10 amended by 50 FR 1165, January 9, 1985]

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Decalcinate the filters at $20 \pm 5.6^\circ\text{C}$ ($68 \pm 10^\circ\text{F}$) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, decalcinated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 **Preliminary Determinations.** Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling

time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 **Preparation of Collection Train.** During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

[Appendix A, Method 5]

Place crumpled ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plunging the nozzle and pulling a 300 mm Hg (15 in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

If an abrasion string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plunging the inlet to the filter holder (cyclone, if applicable) and pulling a 300 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 300 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve, completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applica-

ble) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of

true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120 ± 14° C (248 ± 25° F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pilot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pilot tube coefficient is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If C_p and M_s are outside the above stated ranges do not use the nomographs unless appropriate steps (see Citation 7 in Bibliography) are taken to compensate for the deviations.

[4.1.5 amended by 48 FR 39011, August 26, 1983]

[Appendix A, Method 5]

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
 BAROMETRIC PRESSURE _____
 ASSUMED MOISTURE, % _____
 PROBE LENGTH, in. Hg _____
 NOZZLE IDENTIFICATION NO. _____
 AVERAGE CALIBRATED NOZZLE DIAMETER, mm (in.) _____
 PROBE HEATER SETTING _____
 LEAK RATE, mJ/min. (cfm) _____
 PROBE LINER MATERIAL _____
 STATIC PRESSURE, mm Hg (in. Hg) _____
 FILTER NO. _____

[illegible]

When the stack is under significant negative pressure (height of impinger stem), be sure to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the port holes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjust-

ments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20° C (68° F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see Section 4.1.4.2). The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more

separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and

nomie from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in the identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in those cases, 12770 is water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid wastes to the container. Follow the acetone rinses with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until some remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed

manner at least six times since metal probes have small crevices in which particulate matter can be trapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of effluent grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

[4.2 Container No. 2 amended by 52 FR 34639, September 14, 1987]

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Moor, Section 2.1.7).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

[Appendix A, Method 5]

Plant _____
 Date _____
 Run No. _____
 Filter No. _____
 Amount liquid lost during transport _____
 Acetone blank volume, ml _____
 Acetone wash volume, ml _____
 Acetone blank concentration, mg/mg (equation 5-4) _____
 Acetone wash blank, mg (equation 5-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
Less acetone blank			
Weight of particulate matter			

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

* CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{1 \text{ g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

Alternatively, the sample may be oven dried at 105° C (225° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at 170° C (325° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analyzer sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents in a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field. "Acetone Wash" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Note.—At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be stirred occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

4.4 Quality Control Procedures. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional for the tester.

4.4.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 3.3, determine the ΔH_o for the metering system orifice. The ΔH_o is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 525°R and 29.92 in. Hg. The ΔH_o is calculated as follows:

[Appendix A, Method 5]

$$\Delta H_0 = 0.0319 \frac{T_a}{P_a} \frac{\theta}{Y V_a}$$

Eq. 5-9

Where:

 ΔH —Average pressure differential across the orifice meter, in. H₂O. T_a —Absolute average dry gas meter temperature, °R. P_a —Barometric pressure, in. Hg. θ —Total sampling time, min. Y —Dry gas meter calibration factor, dimensionless. V_a —Volume of gas sample as measured by dry gas meter, ccf.

$$0.0319 = (0.0567 \text{ in. Hg/}^\circ\text{R}) \times (0.78 \text{ cfm})^3$$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the ΔH_0 pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperature, and the barometric pressure. Calculate a dry gas meter calibration check value, Y_a , as follows:

$$Y_a = \frac{10}{V_a} \left[\frac{0.0319 T_a}{P_a} \right] \quad \text{Eq. 5-10}$$

Where:

 Y_a —Dry gas meter calibration check value, dimensionless.

10—10 minutes of run time.

Compare the Y_a value with the dry gas meter calibration factor Y to determine that:

$$0.97Y < Y_a < 1.03Y$$

If the Y_a value is not within this range, the volume metering system should be investigated before beginning the test.

4.4.2. Calibration Critical Orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a quality control check by following the procedure of Section 7.2.

[4.4.2 Amended by 52 FR 9658, March 26, 1987]

5. Calibration. Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The differences between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

[5.1 amended by 52 FR 34639, September 14, 1987]

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System.

[5.3 revised by 50 FR 1165, January 1985]

5.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5.5. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev). A spirometer of 400 liters (14 ft³) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the dry gas meter. Also note the barometric pressure, and the temperatures of the wet test meter, the inlet of the dry gas meter, and the outlet of the dry gas meter. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m³ (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5.6 and calculate Y , the dry gas meter calibration factor, at each orifice setting as shown on Figure 5.6. Allowable tolerances for individual Y and ΔH_0 values are given in Figure 5.6. Use the average of the Y values in the calculations in Section 6.

Figure 5.5 Equipment arrangement for metering system calibration.

[Appendix A, Method 5]

Date _____ Metering System Identification: _____
 Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H ₂ O	Spirometer (wet meter) gas volume V_w ft ³	Dry gas meter volume V_d ft ³	Spirometer (wet meter) t_w °F	Temperatures			Time 0 min
				Inlet t_i °F	Outlet t_o °F	Average t_m °F	

Calculations

ΔH in. H ₂ O	Y	ΔH
	$Y = \frac{V_w P_b (t_m + 460)}{V_d \left[P_b + \frac{\Delta H}{13.6} \right] (t_w + 460)}$	$\Delta H = \frac{0.0317 \Delta H}{P_b (t_o + 460)} \left[\frac{(t_w + 460) \theta^2}{V_w} \right]$
Average		

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.

ΔH = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H₂O; tolerance for individual values ± 0.20 from average.

Figure 5.6. Example data sheet for calibration of metering system (English units).

[Figure 5.6 revised by 52 FR 34639, September 14, 1987]

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m³/min (0.02 cfm); at the end of the run, take the difference of

the measured wet test meter and dry gas at orifice setting (based on the previous meter volumes; divided the difference by 10, field test), with the vacuum set at the maxi- to get the leak rate. The leak rate should mum value reached during the test series. not exceed 0.00057 m³/min (0.02 cfm).

8.3.2 Calibration After Use. After each tering system. Calculate the average value filled use, the calibration of the metering of the dry gas meter calibration factor. If system shall be checked by performing the value has changed by more than 5 per- three calibration runs at a single, intermedi- cent, recalibrate the meter over the full

[Appendix A, Method 5]

source of orifice settings, as previously detailed.

Alternative procedures, e.g., rechecking the orifice meter coefficient may be used, subject to the approval of the Administrator.

5.3.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field.

[5.4 revised by 50 FR 1165, January 9, 1985]

Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 3 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-4. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

Figure 5-4. Leak check of meter box.

[Appendix A, Method 5]

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature

- A. Cross-sectional area of nozzle, m^2 (ft²).
 B. Water vapor in the gas stream, proportion by volume.
 C. Acetone blank residue concentration, mg/mg.
 c. Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
 I. Percent of isokinetic sampling.
 L. Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.0057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.
 L. Individual leakage rate observed during the leak check conducted prior to the i^{th} component change ($i=1, 2, 3, \dots, n$), m³/min (cfm).
 L. Leakage rate observed during the post-test leak check, m³/min (cfm).
 n. Total amount of particulate matter collected, mg.
 M. Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
 m. Mass of residue of acetone after evaporation, mg.
 P. Barometric pressure at the sampling site, mm Hg (in. Hg).
 P. Absolute stack gas pressure, mm Hg (in. Hg).
 P. Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
 R. Ideal gas constant, 0.06236 mm Hg-m³/K g-mole (21.85 in. Hg-ft³/R-lb-mole).
 T. Absolute average dry gas meter temperature (see Figure 5-2), °K (°R).
 T. Absolute average stack gas temperature (see Figure 5-2), °K (°R).
 T. Standard absolute temperature, 293° K (528° R).
 V. Volume of acetone blank, ml.
 V. Volume of acetone used in wash, ml.
 V. Total volume of liquid collected in impingers and siliel gel (see Figure 5-3), ml.
 V. Volume of gas sample as measured by dry gas meter, dscm (dscf).
 V. Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V. Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v. Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W. Weight of residue in acetone wash, mg.

Y. Dry gas meter calibration factor.

ΔH. Average pressure differential across the orifice meter (see Figure 5-2), mm H₂O (in. H₂O).

ρ. Density of acetone, mg/ml (see label on bottle).

ρ. Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ. Total sampling time, min.

θ. Sampling time interval, from the beginning of a run until the first component change, min.

θ. Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ. Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6. Specific gravity of mercury.

60. Sec/min.

100. Conversion to percent.

(6.1 amended by 52 FR 34639, September 14, 1987)

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (30° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

$$V_{std} = V_m \left(\frac{T_{std}}{T_m} \right) \left[\frac{P_{std} + \frac{\Delta H}{13.6}}{P_{std}} \right]$$

$$= K_1 V_m Y \frac{P_{std} + (\Delta H/13.6)}{T_m}$$

Equation 5-1

where:

$K_1 = 0.1328$ °K/mm Hg for metric units

$= 17.64$ °R/in. Hg for English units

NOTE.—Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_p . If L_p or I exceeds L_p , Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 with the expression:

$$V_m = (L_p - L_p) \theta$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$V_m = \sum_{i=1}^n (L_p - L_p) \theta_i - (I_p - I_p) \theta_p$$

and substitute only for those leakage rates (I_p or I_p) which exceed L_p .
 6.4 Volume of water vapor.

Equation 5-2

$$V_w (std) = V_{te} \left(\frac{P_w}{P_{std}} \right) \left(\frac{RT_{std}}{P_{std}} \right) - A_2 V_{te}$$

where:
 $R_2 = 0.001333$ m³/ml for metric units
 $R_2 = 0.04707$ ft³/ml for English units.
 6.5 Moisture Content.

$$M_{wc} = \frac{V_w (std)}{V_m (std) + V_w (std)}$$

Equation 5-3

NOTE.—In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of M_{wc} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 1^\circ$ C ($\pm 2^\circ$ F).

6.6 Acetone Blank Concentration.

$$C_b = \frac{m_b}{V_{ab}}$$

Equation 5-4

6.7 Acetone Wash Blank.

$$W_b = C_b V_{wb}$$

Equation 5-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3).

NOTE: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$C_p = (0.001 \text{ g/mg}) (m_p / V_m)$$

Equation 5-6

[Appendix A, Method 5]

6.10 Conversion Factors:

From	To	Multiply by
wt	m ³	0.02832
g/m ³	g/m ³	15.42
g/m ³	lb/m ³	2.205 × 10 ⁻⁴
g/m ³	g/m ³	38.51
g	mg	0.001

[6.10 table amended by 52 FR 34639, September 14, 1987]

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I =$$

$$100 \frac{T_1(K) V_w + V_m Y_1 / T_m \times P_{atm} + \Delta H / 13.61}{60 \times P_1 \Delta t}$$

Equation 6-7

where:

$K_1 = 0.003484 \text{ mm Hg} \cdot \text{m}^3/\text{ml} \cdot ^\circ\text{K}$ for metric units,
 $= 0.002869 \text{ in. Hg} \cdot \text{ft}^3/\text{ml} \cdot ^\circ\text{R}$ for English units.

6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_1 V_{m(100)} P_{atm} 100}{T_{m(100)} \Delta t \lambda_a P_1 60 (1 - B_{m1})}$$

$$= K_1 \frac{T_1 V_{m(100)}}{T_{m(100)} \Delta t \lambda_a \theta (1 - B_{m1})}$$

Equation 6-8

where:

$K_1 = 4.320$ for metric units
 $= 0.09480$ for English units.

6.12 Acceptable Results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable. If the particulate results are low in comparison to the standard, and I is over 110 percent or less than 90 percent, the Administrator may accept the results. Citation 4 in the bibliography section can be used to make acceptability judgments. If I is judged to be unacceptable, reject the particulate results and repeat the test.

[6.12 revised by 50 FR 1165, January 9, 1985]

6.13 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate. If needed, using data obtained in this method and the equations in Sections 6.2 and 6.3 of Method 2,

[6.13 added by 52 FR 34639, September 14, 1987]

7. Alternative Procedures

[7. added by 48 FR 39011, August 26, 1983]

7.1 Dry Gas Meter as a Calibration Standard. A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 6.3, provided that it is calibrated initially and recalibrated periodically as follows:

7.1.1 Standard Dry Gas Meter Calibration.

7.1.1.1 The dry gas meter to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity, e.g., 3 liters/rev (0.1 ft³/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev) and capable of measuring volume to within ± 1.0 percent;

wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

7.1.1.2 Set up the components as shown in Figure 5.7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the dry gas meter should be minimized (no greater than 100 mm H₂O (4 in. H₂O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

7.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

Figure 5.7, Equipment arrangement for dry-gas meter calibration.

[Appendix A, Method 5]

DATE: _____

DRY GAS METER IDENTIFICATION: _____

BAROMETRIC PRESSURE (P_b): _____ in. Hg

APPROXIMATE FLOW RATE (Q) cfm	SPIROMETER (WET METER) GAS VOLUME (V _w) ft ³	DRY GAS METER VOLUME (V _{dg}) ft ³	TEMPERATURES				DRY GAS METER PRESSURE (Δp) in. H ₂ O	TIME (t) min.	FLOW RATE (Q) cfm	METER METER COEFFICIENT (Y _m)	AVERAGE METER COEFFICIENT (Y _{av})
			SPIROMETER (WET METER) (t _w) °F	DRY GAS METER							
				INLET (t _i) °F	OUTLET (t _o) °F	AVERAGE (t _a) °F					
0.00											
0.00											
0.00											
1.00											
1.20											

$$Q = 17.55 \cdot \frac{V_w}{\theta} \cdot \frac{P_b}{(t_w + 460)}$$

$$Y_m = \frac{V_d}{V_w} \cdot \frac{(t_w + 460)}{(t_a + 460)} \cdot \frac{P_b}{(P_b + \frac{\Delta P}{12.8})}$$

Figure 5.8. Example data sheet for calibration of a standard dry gas meter for method 5 sampling equipment (English units).

7.1.1.4 Calculate flow rate, Q, for each run using the wet test meter gas volume, V_w, and the run time, θ. Calculate the dry gas meter coefficient, Y_m, for each run. These calculations are as follows:

$$Q = K_1 \cdot \frac{P_w}{t_w + t_m} \cdot \frac{V_w}{\theta}$$

$$Y_m = \frac{V_d}{V_w} \cdot \frac{(t_w + t_m)}{(t_a + t_m)} \cdot \frac{P_w}{(P_w + \frac{\Delta P}{12.8})}$$

Where:

K₁ = 0.3858 for international system of units (SI); 17.54 for English units.

V_w = Wet test meter volume, liters (ft³).

V_d = Dry gas meter volume, liters (ft³).

t_w = Average dry gas meter temperature, °C (°F).

t_m = 273° C for SI units; 460° F for English units.

t_a = Average wet test meter temperature, °C (°F).

P_w = Barometric pressure, mm Hg (in. Hg).

ΔP = Dry gas meter inlet differential pressure, mm H₂O (in. H₂O).

θ = Run time, min.

7.1.1.5 Compare the three Y_m values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.98 and 1.08. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If the specifications are met, average the three Y_m values at each flow rate resulting in five average meter coefficients, Y_a.

7.1.1.6 Prepare a curve of meter coefficient, Y_a, versus flow rate, Q, for the dry gas meter. This curve shall be used as a reference when the meter is used to calibrate other dry gas meters and to determine whether recalibration is required.

7.1.2 Standard Dry Gas Meter Recalibration.

7.1.2.1 Recalibrate the standard dry gas meter against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard dry gas meter is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

7.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates (suggested rates are 14 and 28 liters/min (0.5 and 1.0 cfm)). Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within ±1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

7.2 Critical Orifices As Calibration

Standards. Critical orifices may be used as calibration standards in place of the wet test

[Appendix A, Method 5]

meter specified in Section 5.3, provided that they are selected, calibrated, and used as follows:

[7.2 added by 52 FR 9658, March 26, 1987]

7.2.1 Section of Critical Orifices.

7.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, i.e., a critical vacuum

can be obtained, as described in Section 7.2.2.3. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range.

A minimum of three critical orifices will be needed to calibrate a Method 5 dry gas meter (DGM); the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown below give the following approximate flow rates:

Gauge/cm	Flow rate (liters/min)	Gauge/cm	Flow rate (liters/min)
12/7.6	32.96	14/2.5	19.84
12/10.2	30.02	14/5.1	17.27
12/2.5	25.77	14/7.6	16.14
12/5.1	22.99	15/2.5	14.10
12/7.6	22.37	15/7.6	11.61
12/10.2	20.67	15/10.2	10.40

7.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13- by 20-mm sleeve type, into a 1/4-inch Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9.

Figure 5-9. Critical orifice adaptation to Method 5 metering system.

7.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in Section 2.1.8 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

7.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used; i.e., there should be no connections to the inlet of the orifice.

7.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero;

i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

7.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See Section 5.6 for the procedure: make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

7.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in Section 5.3. Make sure that the wet test meter meets the requirements stated in Section 7.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

7.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5-10.

[Appendix A, Method 5]

Figure 5-10. Apparatus setup.

7.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

7.2.2.2.2 Leak check the system as in Section 7.2.2.1.1. The leakage rate shall be zero.

7.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the approximate operating vacuum is follows: Operate the pump, fully open the coarse control valve and adjust the bypass valve to a vacuum reading corresponding to half of atmospheric pressure. Observe meter box critical manometer reading. If slowly increase the vacuum reading until a stable reading is obtained on the meter box critical manometer. Record the critical vacuum for each orifice.

Orifices that do not reach a critical value shall not be used.

7.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section

2.1.9. Record the barometric pressure, P_{bar} , in mm Hg (in. Hg).

7.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of 0.00283 m³ (0.1 ft³) or in increments of complete revolutions of the DGM. As a guideline, the

times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5 percent in K' . Record the information listed in Figure 5-11.

[7.2.2.2.5 corrected by 52 FR 22898, June 10, 1987]

7.2.2.2.6 Calculate K' using Equation 5-9.

where:

$$K' = \frac{K_1 V_m Y (P_{bar} + \Delta H / 13.6) \sqrt{T_{amb}}}{P_{amb} T_{amb} \Theta} \quad \text{Eq. 5-9}$$

$$\frac{(m^3 \cdot K)^{1/2}}{(mm. Hg) (min)} \left[\frac{(ft^3 \cdot K)^{1/2}}{(in. Hg) (min)} \right]$$

percent from the average.

[7.2.2.2.6 corrected by 52 FR 22898, June 10, 1987]

7.2.3 Using the Critical Orifices as Calibration Standards.

K' = Critical orifice coefficient.

T_{amb} = Absolute ambient temperature, $^{\circ}K$ ($^{\circ}R$).

Average the K' values. The individual K' values should not differ by more than ± 0.5

[Appendix A, Method 5]

7.2.3.1 Record the barometric pressure.

Date _____ Train ID _____ DGM cal. factor _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m ³ (ft ³)		
Initial reading	m ³ (ft ³)		
Difference, V _{meas}	m ³ (ft ³)		
Inlet/Outlet			
temperatures:			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. Temperature, T _{meas}	°C (°F)		
Time, Θ	min/sec	/	/
Orifice man. rdg., ΔH, H ₂ O	mm (in.)		
Bar. pressure, P _{amb}	mm (in.) Hg		
Ambient temperature, T _{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
K' factor			
Average			

Figure 5-11. Data sheet for determining K' factor.

7.2.3.2 Calibrate the metering system according to the procedure outlined in Sections 7.2.2.1 to 7.2.2.5. Record the information listed in Figure 5.12.

7.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{std}(d) = K' V_{meas} \frac{P_{amb} + (\Delta H/13.6)}{T_{meas}} \quad \text{Eq. 5-10}$$

$$V_{std}(d) = K' \frac{P_{amb} \Theta}{T_{meas}} \quad \text{Eq. 5-11}$$

$$Y = \frac{V_{std}(d)}{V_{meas}} \quad \text{Eq. 5-12}$$

where:

V_{std(d)} = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dm³ (scf).

K' = 0.3868 °K/mm Hg for metric units = 17.64 °R/in. Hg for English units.

120:0549 corrected by 52 FR 22888, June 16, 1987.

7.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates

should not differ by more than ±2 percent from the average.

7.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to Section 7.2.2.1.

Date _____ Train ID _____ Critical orifice ID _____ Critical orifice K' factor _____

Dry gas meter		Run No.	
		1	2
Final reading	m ³ (ft ³)		
Initial reading	m ³ (ft ³)		
Difference, V _{meas}	m ³ (ft ³)		
Inlet/Outlet			
temperatures:			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. Temperature, T _{meas}	°C (°F)		
Time, Θ	min/sec	/	/
Orifice man. rdg., ΔH, H ₂ O	mm (in.)		
Bar. pressure, P _{amb}	mm (in.) Hg		
Ambient temperature, T _{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
V _{meas}	m ³ (ft ³)		
V _{std}	m ³ (ft ³)		
DGM cal. factor, Y			

Figure 5-12. Data sheet for determining DGM Y factor.

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[12. added by 52 FR 9658, March 26, 1987]

EXMINATION OF PARTICULATE IN THE ASPHALT PROCESSING INDUSTRY

ided and corrected by 52 nber 14, 1987] id principle.

ty. This method applies to 3 of particulate emissions ing industry process satu- ills, and other sources as guilations.

Particulate matter is with- uted mechanically from the source and collected on a glass filter fiber maintained at a temperature of 47±10°C (108±18°F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

2. Apparatus.

2.1 Sampling Train. The sampling train configuration is the same as shown in Figure 5-1 of Method 5. The sampling train consists of the following components:

2.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Holder, Condenser, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3 to 2.1.5, and 2.1.7 to 2.1.10, respectively.

2.1.2 Probe Liner. Same as in Method 5, Section 2.1.2, with the note that at high stack gas temperatures (greater than 250°C

[Appendix A, Method 5A]

10.0 REFERENCE METHOD*

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The sulfur dioxide mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium-thionite titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.1 milligrams (wet) of SO₂/m³ (2.12 × 10⁻⁶ lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 20,000 mg/m³ of SO₂ can be collected efficiently in two midsize impingers, each containing 15 milliliters of 3 percent barium peroxide, at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 25,300 mg/m³.

Possible interferences are free ammonia, water-soluble oxides, and sulfuric acid. The oxides and sulfuric acid are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO₂ analysis. When samples are being taken from a gas stream with high concentrations of very fine visible fumes (such as in tests to control diesel), a high-efficiency glass fiber filter must be used in place of the glass wool plug (U.S. the one in the probe) to remove the carbon particulate.

Free ammonia interferences by reacting with SO₂ to form particulate sulfate and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and nothing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, U.S. Environmental Protection Agency, are required.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 6-1, and component parts are discussed below. The train has the option of substituting sampling equipment described in Method 5 in place of the midsize impinger equipment of Method 6. However, the Method 6 train must be modified to include a heated filter between the probe and isopropanol bubbler, and the operation of the sampling train and sample analysis must be at the flow rates and collection volumes defined in Method 6. The train also has the option of determining SO₂ simultaneously with particulate matter and moisture determinations by (1) collecting the water in a Method 6 impinger system with 3 percent barium peroxide solution, or (2) by replacing the Method 6 water impinger system with a Method 6 isopropanol-filter-peroxide system. The analysis for SO₂ must be consistent with the procedure in Method 5.

2.1.1 Probe. Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6-mm inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated outside) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers. One midsize bubbler, with medium-course glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover. The 20-ml midsize impingers. The bubbler and midsize impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

At the option of the tester, a midsize impinger may be used in place of the midsize bubbler.

Other collection absorbents and flow rates may be used, but are subject to the approval of the Administrator. Also, collection efficiency must be shown to be at least 90 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO₂.

2.1.3 Glass Wool. Borosilicate or quartz.

2.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

2.1.5 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1° C (2° F).

2.1.6 Drying Tube. Tube packed with 6- to 10-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 3 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

2.1.7 Valve. Needle valve, to regulate sample gas flow rate.

2.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small leak between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min.

2.1.10 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 3 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 0.5° C (1° F).

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation difference between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.12 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for leak check of the sampling train.

2.2 Sample Recovery.

2.2.1 Wash Bottle. Polyethylene or glass, 200 ml, two.

2.2.2 Storage Bottle. Polyethylene, 200 ml, to store impinger samples (one per sample).

2.3 Analysis.

2.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one per sample), and 25-ml sizes.

2.3.2 Volumetric Flask. 100-ml size (one per sample) and 150-ml size.

2.3.3 Burets. 5- and 20-ml sizes.

2.3.4 Erlenmeyer Flasks. 250 ml-size (one for each sample, blank, and standard).

2.3.5 Dropping Bottle. 15-ml size, to add indicator.

2.3.6 Graduated Cylinder. 100-ml size.

2.3.7 Spectrophotometer. To measure absorbance at 285 nm maximum.

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Solutions.

3.1.1 Water. Deionized, distilled to conform to ASTM specification D1193-74, Type 1. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol. 99 percent. Mix 50 ml of isopropanol with 50 ml of deionized, distilled water. Check each lot of isopropanol for peroxide impurities as follows: transfer 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 285 nm maximum on a spectrophotometer. If absorbance exceeds 0.1, repeat alcohol for use.

Peroxide may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (20 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent. Dissolve 10.0 grams KI in deionized, distilled water and dilute to 100 ml. Prepare when needed.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 20 Percent. Mix 20 ml of isopropanol with 80 ml of deionized, distilled water.

3.3 Analysis.

3.3.1 Water. Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 Percent.

3.3.3 Thionin Indicator. 1-(4-aminophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium Peroxide Solution, 0.0100 N. Dissolve 1.26 g of barium peroxide trihydrate [Ba(C₂O₄)₂·3H₂O] in 200 ml distilled water and dilute to 1 liter with isopropanol. Alternatively, 1.26 g of BaC₂O₄·2H₂O may be used instead of the peroxide. Standardize as in Section 5.4.

3.3.5 Sulfuric Acid Standard, 0.0100 N. Prepare or standardize to 0.0025 N and then 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

4. Procedure

4.1 Sampling.

4.1.1 Preparation of collection train. Measure 15 ml of 30 percent isopropanol into the midsize bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midsize impingers. Leave the final midsize impinger dry. Assemble the train as shown in Figure 6-1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-check procedure. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

With the probe disconnected, place a vacuum gauge at the inlet to the bubbler and pull a vacuum of 250 mm (10 in.) Hg; pinch or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end to prevent back flow of the impinger fluid.

Other leak check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency. The procedure used in Method 3 is not suitable for diaphragm pumps.

4.1.3 Sample collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings of dry gas meter, temperatures at dry gas meter and at impinger outlet and rate meter at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 2° C (36° F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final reading. Conduct a leak check as in Section 4.1.2 (This leak check is mandatory.) If a leak is found, void the test run. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

Clean ambient air can be provided by passing air through a charcoal filter or through an extra midsize impinger with 15 ml of 3 percent H₂O₂. The tester may opt to simply use ambient air, without purification.

4.2 Sample Recovery. Disconnect the impingers after pouring. Discharge the contents of the midsize bubbler into a leak-free polyethylene bottle for shipment. Rinse the three midsize impingers and the connecting tubes with deionized distilled water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample Analysis. Note level of liquid in container, and record whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or the methods, subject to the approval of the Administrator, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 50 ml of 100 percent isopropanol and two to four drops of thionin indicator, and titrate to a pink endpoint using 0.0100 N barium peroxide. Repeat and average the titration volume. Run a blank with each series of samples. Rapid-catch titrations must agree within 1 percent or 0.2 ml, whichever is larger.

(Note.—Protect the 0.0100 N barium peroxide solution from evaporation at all times.)

5. Calibration

5.1 Metering System.

5.1.1 Initial Calibration. Before its initial use in the field, first leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows: place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm (10 in.) Hg; pinch or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

Next, calibrate the metering system (at the sampling flow rate specified by the method) as follows: convert an appropriately sized wet test meter (e.g., 1 liter per revolution) to the inlet of the drying tube. Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 3 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three, or more, revolutions of the dry gas meter may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 3 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 3 percent, recalculate the metering system as in Section 5.1.1, and for the calculations, use the calibration factor (initial or recalculated) that yields the lower gas volume for each test run.

5.3 Thermometers. Calibrate against mercury-in-glass thermometers.

5.4 Rotameter. The rotameter need not be calibrated but should be cleaned and maintained according to the manufacturer's instruction.

5.5 Barometer. Calibrate against a mercury barometer.

5.6 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature

C_{SO_2} = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dm³ (lb/dm³).

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (30.00 in. Hg).

T_m = Average dry gas meter absolute temperature, °K (°F).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_s = Volume of sample aliquot titrated, ml.

$V_{(std)}$ = Dry gas volume as measured by the dry gas meter, dm³ (cu ft).

$V_{(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dm³ (cu ft).

V_{std} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{bl} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.00 = Equivalent weight of sulfur dioxide.

6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar}}{P_{std}} \right) = K_1 Y \frac{V_m P_{bar}}{T_m}$$

Equation 6-1

where:

$K_1 = 0.0008 \text{ } ^\circ\text{K}/\text{mm Hg}$ for metric units.

$= 17.04 \text{ } ^\circ\text{R}/\text{in. Hg}$ for English units.

6.3 Sulfur dioxide concentration.

$$C_{SO_2} = K_2 \frac{(V_t - V_{bl}) N \left(\frac{V_{std}}{V_s} \right)}{V_{std}}$$

Equation 6-2

where:

$K_2 = 32.00 \text{ mg/m}^3$ for metric units.

$= 7.524 \times 10^{-3} \text{ lb/m}^3$ for English units.

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Figure 6-1. SO₂ sampling train.

SURGE TANK

In Method 8 of Appendix A, Sections 2.1, 2.1.6, 2.1.7, 2.1.8, 2.1.11, 2.1.12, 2.3.2, 2.3.4, 4.1.2, 4.1.3, and 5.1.1 are amended as follows:

1. In Section 2.1, the word "periox-ide" in the fourth line of the second paragraph is corrected to read "perox-ide."

2. In Section 2.1.6, the word "sillic" in the third line is corrected to read "silica."

3. In Section 2.1.7, the word "value", which appears twice is corrected to read "valve."

4. In Section 2.1.8, the word "disph-ragm" is corrected to read "dia-phragm" and the word "surge" is inserted between the words "small" and "tank."

5. In Section 2.1.11, the word "amer-old" is corrected to read "aneroid."

6. In Section 2.1.12, the phrase "and Rotameter." is inserted after the phrase "Vacuum Gauge" and the phrase "and 0-40 cc/min rotameter" is inserted between the words "gauge" and ", to."

7. In Section 2.3.2, the phrase "and 100-ml size" is corrected to read "and 1000-ml size."

8. In Section 3.3.4, the word "sopro-panol" in the fourth line is corrected to read "isopropanol."

9. In Section 4.1.2, delete the last sentence of the last paragraph. Also delete the second paragraph and replace it with the following paragraph:

Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

Note: Carefully release the probe inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

10. In Section 4.1.3, the sentence "If a leak is found, void the test run" on the sixteenth line is corrected to read "If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage."

11. In Section 5.1.1, the word "or" on the sixth line is corrected to read "of."

ard solution (1 ml- 10 µg NO₂) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO₂, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO₂.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used. Calculate the spectrophotometer calibration factor K as follows:

$$K_c = \frac{N}{M_1} \frac{A_1}{A_1^2} = \frac{1}{1} = 1 \quad (\text{Eq. 7.1.})$$

Where:

M₁ = Mass of NO₂ in standard 1, µg.

A₁ = Absorbance of NO₂ standard 1.

N = Total number of calibration standards.

For the set of calibration standards specified here, Equation 7-1 simplifies to the following:

$$K_c = 80 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad (\text{Eq. 7-2})$$

[5.1 Note corrected by 52 FR 34639, September 14, 1987]

6. Calculations.

Same as Method 7, Sections 6.1, 6.2, and 6.4 with the addition of the following:

6.1 Total µg NO₂ Per Sample:

$$m = 5K_c AF \quad (\text{Eq. 7-3})$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

6.2 Relative Error (RE) for Quality Assurance Audits.

$$RE = \frac{C_d - C_a}{C_a} \times 100 \quad (\text{Eq. 7-4})$$

Where:

C_d = Determined audit concentration.

C_a = Actual audit concentration.

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METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES—ALKALINE-PERMANGANATE/COLORIMETRIC METHOD

[Method 7C amended and corrected by 52 FR 34639, September 14, 1987]

1. Applicability, principle, interferences, precision, bias, and stability.

1.1 **Applicability.** The method is applicable to the determination of NO_x emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations. The lower detectable limit is 13 mg NO_x/m³, as NO₂ (7 ppm NO₂) when sampling at 500 cc/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_x emissions quantitatively up to 1,782 mg NO_x/m³, as NO₂ (932 ppm NO₂).

1.2 **Principle.** An integrated gas sample is extracted from the stack and collected in alkaline-potassium permanganate solution; NO_x (NO+NO₂) emissions are oxidized to NO₂- and NO₂-. The NO₂- is reduced to

NO₂- with cadmium, and the NO₂- is analyzed colorimetrically.

1.3 **Interferences.** Possible interferences are SO₂ and NH₃. High concentrations of SO₂ could interfere because SO₂ consumes MnO₄- (as does NO₂) and, therefore, could reduce the NO_x collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1-percent sulfur coal with no control of SO₂ emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO₂ will reduce the MnO₄- concentration by only 5 percent if all the SO₂ is consumed in the first impinger.

NH₃ is slowly oxidized to NO₂- by the absorbing solution. At 100 ppm NH₃ in the gas stream, an interference of 6 ppm NO₂ (11 mg NO₂/m³) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH₃ injection to control NO_x emissions unless means are taken to correct the results. An equation has been developed to allow quantitation of the interference and is discussed in Citation 5 of the bibliography.

1.4 **Precision and Bias.** The method does not exhibit any bias relative to Method 7. The within-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO₂, respectively.

1.5 **Stability.** Collected samples are stable for at least 4 weeks.

2. Apparatus.

2.1 **Sampling and Sample Recovery.** The Sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated.

Figure 7C-1. NO_x sampling train

[Appendix A, Method 7C]

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. (Note: Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.)

2.1.3 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower until they become available commercially.)

Figure 7C-2. Restricted orifice impinger

2.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, Sections 2.1.3, 2.1.4, 2.1.6, 2.1.7, 2.1.8, 2.1.11, and 2.1.12, respectively.

2.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate between 400 and 500 cc/

min. For rotameters, a range of 0 to 1 liter/min is recommended.

2.1.5 Volume Meter. Dry gas meter capable of measuring the sample volume, under the sampling conditions of 400 to 500 cc/min for 60 minutes within an accuracy of 2 percent.

[Appendix A, Method 7C]

2.1.6 Filter. To remove NO₂ from ambient air, prepared by adding 20 g of a 5-angstrom molecular sieve to a cylindrical tube, e.g., a polyethylene drying tube.

2.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

2.1.8 Funnel and Stirring Rods. For sample recovery.

2.2 Sample Preparation and Analysis.

2.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

2.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

2.2.3 Filtering Flask. 500-ml capacity with side arm.

2.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

2.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

2.2.6 Stirring Rods.

2.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

2.2.8 Watch Glasses. To cover 600- and 1,000-ml beakers.

2.2.9 Graduated Cylinders. 50- and 250-ml capacities.

2.2.10 Pipettes. Class A

2.2.11 pH Meter. To measure pH from 0.5 to 12.0

2.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalogue No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 40201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm from the top of plug, and have a glass blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

2.2.13 Glass Funnel. 75-mm ID at the top.

2.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm. One-cm cells are adequate.

2.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C.

2.2.16 Culture Tubes. 20- by 150-mm, Kimax No. 45048.

2.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.

2.2.18 CO₂ Measurement Equipment. Same as in Method 3.

3. Reagents

Unless otherwise indicated, all reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling.

3.1.1 Water. Deionized distilled to conform to ASTM specification D 1193-74, Type 3 (incorporated by reference—see § 60.17).

3.1.2 Potassium Permanganate, 4.0 percent (w/w). Sodium Hydroxide, 2.0 percent (w/w). Dissolve 40.0 g of KMnO₄ and 20.0 g of NaOH in 940 ml of water.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Sulfuric Acid. Concentrated H₂SO₄.

3.2.3 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [(COOH)₂·2H₂O] in water, and dilute to 500 ml. Do not heat the solution.

3.2.4 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

3.2.5 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water and dilute to 100 ml.

3.2.6 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 Percent. Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Solution is best accomplished by using a magnetic stirrer.

3.2.7 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 980 ml of water, and adjust the pH to 11.7 to 12.0 with 0.5 N NaOH.

3.2.8 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500-ml volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

3.2.9 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

$$\mu\text{g NO}_2^-/\text{ml} = \text{g of NaNO}_2 \times \frac{\text{purity, \%}}{100} \times 10^3 \times \frac{46.01}{69.01}$$

This solution is stable for at least 6 months under laboratory conditions.

3.2.13 KNO₃ Standard Solution. Dry KNO₃ at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of

3.2.10 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA, showing more than one absorption peak over this range, is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

3.2.11 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalogue No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H₂ is liberated during preparation. Prepare in an exhaust hood away from any flame.

3.2.12 NaNO₂ Standard Solution. Nominal Concentration, 1000 μg NO₂⁻/ml. Desiccate NaNO₂ overnight. Accurately weigh 1.4 to 1.6 g of NaNO₂ (assay of 97 percent NaNO₂ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO₂⁻ concentration from the following relationship:

[3.2.12 corrected by 52 FR 34639, September 14, 1987]

KNO₃ to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO₂⁻ concentration from the following relationship:

$$\mu\text{g NO}_2^-/\text{ml} = \text{g of KNO}_3 \times 10^3 \times \frac{62.01}{101.10}$$

This solution is stable for 2 months without preservative under laboratory conditions.

3.2.14 Spiking Solution. Pipette 7 ml of the KNO₃ standard into a 100-ml volumetric flask, and dilute to volume.

3.2.15 Blank Solution. Dissolve 2.4 g of KMnO₄ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO₄/NaOH solution to 100 ml.

3.2.16 Quality Assurance Audit Samples. Same as in Method 7, Section 3.3.9. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7C.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train. Add 200 ml of KMnO₄/NaOH solution (3.1.2) to each of three impingers, and assemble the train as shown in Figure 7C-1.

Adjust probe heater to a temperature sufficient to prevent water condensation.

4.1.2 Leak-Check Procedure. A leak-check prior to the sampling run should be carried out; a leak-check after the sampling run is mandatory. Carry out the leak-check(s) according to Method 6, Section 4.1.2.

4.1.3 Check of Rotameter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter (2.1.6). Start the pump, and adjust the rotameter to read between 400 and 500 cc/min. After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter (DGM), and the sampling time. Collect enough volume to measure accurately the flow rate, and calculate the flow rate. This average flow rate must be less than 500 cc/min for the sample to be valid; therefore, it is recommended that the

[Appendix A, Method 7C]

flow rate be checked as above prior to each test.

4.1.4 Sample Collection. Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations, e.g., Section 60.46(c) of 40 CFR Part 60. Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 cc/min. **CAUTION: HIGHER FLOW RATES WILL PRODUCE LOW RESULTS.** Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point. [Note.—When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2 . For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point)]. Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct a leak-check as in Section 4.1.2. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

4.1.5 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times—near the start, midway, and before the end of a run and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

4.2 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings that are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

4.3 Sample Preparation for Analysis. Prepare a cadmium reduction column as follows: Fill the burette (2.2.12) with water. Add freshly prepared cadmium slowly with tapping until no further settling occurs. The height of the cadmium column should be 39 cm. When not in use, store the column under rinse solution (3.2.7). [Note.—The column should not contain any bands of cadmium fines. This may occur if regenerated column is used and will greatly reduce the column lifetime.]

Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume

lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

Take a 100-ml aliquot of the sample and blank (unexposed $\text{KMnO}_4/\text{NaOH}$) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50°C . Keep the temperature below 60°C . Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the KMnO_4 solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to 11.7 to 12.0 with 10 N NaOH . Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (250-ml may be required), and dilute to volume. The samples are now ready for NO_3^- analysis. [Note.—Both the sample and blank should go through this procedure. Additionally, two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the

sample suspected to have the highest NO_3^- concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see 6.2.1) is below 95 percent, prepare a new column, and repeat the cadmium reduction].

4.4 Sample Analysis. Pipette 10 ml sample into a culture tube. [Note.—Some test tubes give a high blank NO_3^- value but culture tubes do not.] Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $\text{KMnO}_4/\text{NaOH}$ solution (3.1.2). Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read $\mu\text{g NO}_3^-/\text{ml}$ from the calibration curve. If the absorbance is greater than that of the highest calibration standard, pipette less than 10 ml of sample and enough water to make the total sample volume 10 ml, and repeat the analysis. Determine the NO_3^- concentration using the calibration curve obtained in Section 5.3.

4.5 Audit Analysis. This is the same as in Method 7, Section 4.4.

5. Calibration

5.1 Dry Gas Metering System (DGM).

5.1.1 Initial Calibration. Same as in Method 6, Section 5.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 4 in the bibliography be consulted.

5.1.2 Post-Test Calibration Check. Same as in Method 6, Section 5.1.2.

5.2 Thermometers for DGM and Barometer. Same as in Method 6, Sections 5.2 and 5.4, respectively.

5.3 Calibration Curve for Spectrophotometer. Dilute 5.0 ml of the NaNO_3 standard solution to 200 ml with water. This solution nominally contains $25 \mu\text{g NO}_3^-/\text{ml}$. Use this solution to prepare calibration standards to cover the range of 0.25 to $3.00 \mu\text{g NO}_3^-/\text{ml}$. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

Run standards and a water blank as instructed in Section 4.4. Plot the net absorbance vs $\mu\text{gNO}_3^-/\text{ml}$. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/ $\mu\text{g NO}_3^-/\text{ml}$. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Sample volume, dry basis, corrected to standard conditions.

[Appendix A, Method 7C]

$$V_{\text{std}} = V_{\text{XY}} \frac{T_{\text{std}}}{T_{\text{m}}} \frac{P_{\text{std}}}{P_{\text{m}}} - K_1 \frac{V_{\text{P}}}{T_{\text{m}}} \quad (\text{Eq. 7C-1})$$

Where:

V_{std} —Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

V_{m} —Dry gas volume as measured by the dry gas meter, dcm.

Y —Dry gas meter calibration factor.

X —Correction factor for CO_2 collection.

P_{std} —Standard absolute pressure, 760 mm Hg.

T_{m} —Average dry gas meter absolute temperature, °K.

T_{std} —Standard absolute temperature, 293 °K.

$K_1 = 0.3858$ °K/mm Hg.

6.2 Total $\mu\text{g NO}_x$ Per Sample.

6.2.1 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$= \frac{100}{100 - \% \text{CO}_2 (v/v)}$$

P_{m} —Barometric pressure, mm Hg.

$$E = \frac{(x - y) 200}{s \times 1.0 \times \frac{46.01}{62.01}} = \frac{269.6 (x - y)}{s} \quad (\text{Eq. 7C-2})$$

Where:

E —Column efficiency, unitless.

x —Analysis of spiked sample, $\mu\text{g NO}_x/\text{ml}$.

y —Analysis of unspiked sample, $\mu\text{g NO}_x/\text{ml}$.

200—Final volume of sample and blank after passing through the column, ml.

s —Concentration of spiking solution, $\mu\text{g NO}_x/\text{ml}$.

1.0—Volume of spiking solution added, ml.

46.01— $\mu\text{g NO}_x/\mu\text{mole}$.

62.01— $\mu\text{g NO}_x/\mu\text{mole}$.

6.2.2 Total $\mu\text{g NO}_x$.

$$m = \frac{(S-B)}{E} \times 200 \times \frac{500}{50} \times \frac{1000}{100} = \frac{(3 \times 10^7 (S-B))}{E} \quad (\text{Eq. 7C-3})$$

Where:

m —Mass of NO_x as NO_x in sample, μg .

S —Analysis of sample, $\mu\text{g NO}_x/\text{ml}$.

B —Analysis of blank, $\mu\text{g NO}_x/\text{ml}$.

500—Total volume of prepared sample, ml.

50—Aliquot of prepared sample processed through cadmium column, ml.

100—Aliquot of $\text{KMnO}_4/\text{NaOH}$ solution, ml.

1000—Total volume of $\text{KMnO}_4/\text{NaOH}$ solution ml.

6.3 Sample Concentration.

$$C = K_2 \frac{m}{V_{\text{std}}}$$

Where:

C —Concentration of NO_x as NO_x , dry basis, mg/dscm.

$K_2 = 10^{-3}$ mg/ μg .

6.4 Conversion Factors.

1.0 ppm $\text{NO} = 1.247$ mg NO/m^3 at STP.

1.0 ppm $\text{NO}_2 = 1.912$ mg NO_2/m^3 at STP.

1 ft³ = 2.832×10^{-2} m³.

1000 mg = 1g

[6.4 amended by 52 FR 34639, September 14, 1987]

7. Quality control.

Quality control procedures are specified in Sections 4.1.3 (flow rate accuracy); 4.3 (cadmium column efficiency); 4.4 (calibration curve accuracy); and 4.5 (audit analysis accuracy).

8. Bibliography.

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_x Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Journal of the Air Pollution Control Association. 32:1210-1215, 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite

with Cadmium. Anal. Chem. 52:1955-57, 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. August 1977. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-027b. August 1977.

5. Margeson, J.H., et al. An Integrated Method for Determining NO_x Emissions at Nitric Acid Plants. Manuscript submitted to Analytical Chemistry. April 1984.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES—ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD

[Method 7D amended by 52 FR 34639, September 14, 1987]

[Appendix A, Method 7D]

3. Margeson, J.H., J.E. Knoll, and P.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

METHOD 17—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES (IN-STACK FILTRATION METHOD)

[Method 17 corrected by 52 FR 34639, September 14, 1987]

Introduction

Particulate matter is not an absolute quantity; rather, it is a function of temperature and pressure. Therefore, to prevent variability in particulate matter emission regulations and/or-associated test methods, the temperature and pressure at which particulate matter is to be measured must be carefully defined. Of the two variables (i.e., temperature and pressure), temperature has the greater effect upon the amount of particulate matter in an effluent gas stream; in most stationary source categories, the effect

of pressure appears to be negligible.

In method 5, 250° F is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standards, particulate matter is defined with respect to temperature. In order to maintain a collection temperature of 250° F, Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where particulate matter concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and heating systems, and sample at stack temperature.

This method describes an in-stack sampling system and sampling procedures for use in such cases. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator.

1. Principle and Applicability.

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The particulate mass

is determined gravimetrically after removal of uncombined water.

1.3 Applicability. This method applies to the determination of particulate emissions from stationary sources for determining compliance with new source performance standards, only when specifically provided for in an applicable subpart of the standards. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see Section 4.1.2).

2. Apparatus.

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17-1. Construction details for many, but not all, of the train components are given in APTD-0581 (Citation 2 in Section 7); for changes from the APTD-0581 document and for allowable modifications to Figure 17-1, consult with the Administrator.

[Appendix A, Method 17]

Figure 17-1. Particulate-Sampling Train, Equipped with In-Stack Filter.

[Appendix A, Method 17]

The operating and maintenance procedures for many of the sampling train components are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass, with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used subject to the approval of the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/4 to 1/2 in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (5/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1.

2.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass, or stainless steel; if a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

2.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

2.1.4 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator; the pitot tube be attached to the probe extension to provide constant monitoring of the stack gas velocity (see Figure 17-1). The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane during sampling (see Method 2, Figure 2-6b). It is recommended: (1) that the pitot tube have a known baseline coefficient, determined as outlined in Section 4 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17-1). Note that the 1.9 cm (0.75 in) free-space between the nozzle and pitot tube shown in Figure 17-1, is based on a 1.3 cm (0.5 in) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (0.75 in) with the largest sized nozzle in place.

Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17-1 (or the equivalent of these requirements, e.g., Figure 2-7 of Method 2)

may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

2.1.5 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.6 Condenser. It is recommended that the impinger system described in Method 5 be used to determine the moisture content of the stack gas. Alternatively, any system that allows measurement of both the water condensed and the moisture leaving the condenser, each to within 1 ml or 1 g, may be used. The moisture leaving the condenser can be measured either by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

Flexible tubing may be used between the probe extension and condenser. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.7 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 17-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.8 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.9 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as

described in Method 3.

The temperature sensor shall be attached to either the pitot tube or to the probe extension, in a fixed configuration. If the temperature sensor is attached in the field; the sensor shall be placed in an interference-free arrangement with respect to the Type S pitot tube openings (as shown in Figure 17-1 or in Figure 2-7 of Method 2). Alternatively, the temperature sensor need not be attached to either the probe extension or pitot tube during sampling, provided that a difference of not more than 1 percent in the average velocity measurement is introduced. This alternative is subject to the approval of the Administrator.

2.2 Sample Recovery.

2.2.1 Probe Nozzle Brush. Nylon bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 mg.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. Reagents.

3.1 Sampling.

[Appendix A, Method 17]

3.1.1 Filters. The in-stack filters shall be glass mats or thimble fiber filters, without organic binders, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency tests shall be conducted in accordance with ASTM Standard Method D2986-71 (Reapproved 1978) (incorporated by reference—see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Crushed Ice.

3.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone, reagent grade, 0.001 percent residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with low blank values (0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis.

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. Procedure.

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedure described in APTD-0676, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper size on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at $20 \pm 5.6^\circ \text{C}$ ($68 \pm 10^\circ \text{F}$) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively

(unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17-2. Calculate the estimated cross-section blockage, as shown in Figure 17-2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Citation 10 in Section 7). Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particular sample run.

Figure 17-2. Projected-area model of cross-section blockage (approximate average for a sample traverse) caused by an in-stack filter holder-probe extension assembly.

[Appendix A, Method 17]

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.3 of Method 2).

Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval if specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

If impingers are used to condense stack gas moisture, prepare them as follows: place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and

weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 17-1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

4.1.4 Leak Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg); note that a lower vacuum may be used, provided that it is not exceeded during the test. Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m³/min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse direction of by-pass valve. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be con-

ducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate - Train Operation. During the sampling run, maintain a sampling rate such that sampling is within 10 percent of true isokinetic, unless otherwise specified by the Administrator.

For each run, record the data required on the example data sheet shown in Figure 17-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 17-3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

[Appendix A, Method 17]

PLANT _____	BAROMETRIC PRESSURE _____
LOCATION _____	ASSUMED MOISTURE, % _____
OPERATOR _____	PROBE EXTENSION LENGTH, in (ft.) _____
DATE _____	NOZZLE IDENTIFICATION NO. _____
RUN NO. _____	AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____
SAMPLE BOX NO. _____	FILTER NO. _____
METER BOX NO. _____	LEAK RATE, m ³ /min, (cfm) _____
METER ΔH _g _____	STATIC PRESSURE, mm Hg (in. Hg) _____
C FACTOR _____	
PITOT TUBE COEFFICIENT, C _p _____	

[illegible]

Figure 17-3. Particulate field data.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment to the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 ± 0.02 , and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4 . APTD-0876 details the procedure for using the nomographs. If C, and M, are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Citation 7 in Section 7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain a temperature of less than 20°C (68°F) at the condenser outlet; this will prevent excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter holder assembly be used rather than attempting to change the filter itself. Before a new filter holder is installed, conduct a leak check, as outlined in Section 4.1.4.2. The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator. Note that when two or more trains are used, a separate analysis of the collected particulate from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the particulate catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Section 3.1 of Method 2; the lines must pass this leak-

check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Section 6.11) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank and follow Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until acetone rinses shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease (if applicable), clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove viable particulate. Make final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. If silica gel is used in the condenser system for moisture content determination, note the color of the gel to determine if it has been completely spent; make a notation of its condition. Transfer the silica gel back to its original container and seal. A funnel may make it easier to pour the silica gel without spilling, and a rubber policeman may be used as an aid in removing the silica gel. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 under "Analysis."

Condenser Water. Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the liquid volume to within ± 1 ml by using a graduated cylinder or, if a balance is available, determine the liquid weight to within ± 0.5 g. Record the total volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight.

4.3 Analysis. Record the data required on the example sheet shown in Figure 17-4. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at the average stack temperature or

105° C (220° F), whichever is less, for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at the average stack temperature or 105° C (220° F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

105° C (220° F), whichever is less, for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at the average stack temperature or 105° C (220° F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

105° C (220° F), whichever is less, for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at the average stack temperature or 105° C (220° F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Plant _____

Date _____

Run No. _____

Filter No. _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone blank concentration, mg/mg (equation 17-4) _____

Acetone wash blank, mg (equation 17-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
Less acetone blank			
Weight of particulate matter			

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

* CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{1 \text{ g/ml}} = \text{VOLUME WATER, ml}$$

Figure 17-4. Analytical data.

[Appendix A, Method 17]

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Note.—At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

8. Calibration. Maintain a laboratory log of all calibrations.

8.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest

0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

8.2 Pitot Tube. If the pitot tube is placed in an interference-free arrangement with respect to the other probe assembly components, its baseline (isolated tube) coefficient shall be determined as outlined in Section 4 of Method 2. If the probe assembly is not interference-free, the pitot tube assembly coefficient shall be determined by calibration, using methods subject to the approval of the Administrator.

8.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values.

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00087 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00087 m³/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the

previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a pin between the wet test meter and the line of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

Note.—If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.5 Leak Check of Metering System. Shown in Figure 17-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 17-5). Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system by adding 10 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

Figure 17-5. Leak check of meter box.

[Appendix A, Method 17]

5.6 Barometer. Calibrate against a mercury barometer.

6. Calculations. Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature.

[6.1 corrected by 52 FR 34639, September 14, 1987; 52 FR 42061, November 2, 1987]

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/mg .

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, $g/dscm$ ($g/dscf$).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.0057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the " i " component change ($i=1, 2, 3 \dots n$), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

m_s = Total amount of particulate matter collected, mg .

M_w = Molecular weight of water, 18.0 g/g -mole (18.0 lb/lb -mole).

m_a = Mass of residue of acetone after evaporation, mg .

P_{at} = Barometric pressure at the sampling site, mm Hg ($in.$ Hg).

P_s = Absolute stack gas pressure, mm Hg ($in.$ Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 $in.$ Hg).

R = Ideal gas constant, 0.08206 mm Hg- m^3/K - g -mole (21.85 $in.$ Hg- ft^3/R - lb -mole).

T_a = Absolute average dry gas meter temperature (see Figure 17-3), $^{\circ}K$ ($^{\circ}R$).

T_s = Absolute average stack gas temperature (see Figure 17-3), $^{\circ}K$ ($^{\circ}R$).

T_{std} = Standard absolute temperature, 293 $^{\circ}K$ (528 $^{\circ}R$).

V_a = Volume of acetone blank, ml .

V_{aw} = Volume of acetone used in wash, ml .

V_{ls} = Total volume of liquid collected in impingers and silica gel (see Figure 17-4), ml .

V_m = Volume of gas sample as measured by dry gas meter, dcm ($dscf$).

V_{mstd} = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, $dscm$ ($dscf$).

V_{ws} = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 17, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg .

Y = Dry gas meter calibration coefficient.

ΔH = Average pressure differential across the orifice meter (see Figure 17-3), mm H₂O ($in.$ H₂O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min .

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min .

θ_i = Sampling time interval, between two successive component changes, begin-

ning with the interval between the first and second changes, min .

θ_n = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min .

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

6.3 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 17-3).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 $^{\circ}$ C, 760 mm Hg or 68 $^{\circ}$ F, 29.92 $in.$ Hg) by using Equation 17-1.

$$V_{m(std)} = V_m \left(\frac{T_{std}}{T_m} \right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right]$$

$$= K_1 V_m \frac{P_{bar} + (\Delta H/13.6)}{P_{std}}$$

Equation 17-1

where:

$K_1 = 0.3858^{\circ}K/mm$ Hg for metric units;
17.84 $^{\circ}R/in.$ Hg for English units.

Note.—Equation 17-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a . If L_p or L_i exceeds L_a , Equation 17-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 17-1 with the expression:

$$[V_m - (L_p - L_a)\theta]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 17-1 by the expression:

$$[V_m - (L_i - L_a)\theta_i - \sum_{i=2}^n (L_i - L_a)\theta_i - (L_p - L_a)\theta_p]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a .

6.4 Volume of water vapor.

$$V_{ws(std)} = V_{lc} \left(\frac{P_w}{P_{std}} \right) \left(\frac{RT_{std}}{P_{std}} \right) = K_2 V_{lc}$$

Equation 17-2

where:

$K_2 = 0.001333$ m^3/ml for metric units; 0.04707 ft^3/ml for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{ws(std)}}{V_{m(std)} + V_{ws(std)}}$$

Equation 17-3

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a}$$

Equation 17-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a$$

Equation 17-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 17-4).

Note.—Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_s = (0.001 \text{ g/mg}) (m_s/V_{mstd})$$

Equation 17-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation from Raw Data.

$$I = \frac{100 T_s [K_3 V_{lc} + (V_m/T_m) (P_{bar} + \Delta H/13.6)]}{60 v_s P_s A_n}$$

Equation 17-7

where:

$K_3 = 0.003454$ mm Hg- m^3/ml - $^{\circ}K$ for metric units; 0.002889 $in.$ Hg- ft^3/ml - $^{\circ}R$ for English units.

6.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60 (1-B_{ws})}$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1-B_{ws})}$$

Equation 17-8

where:

$K_4 = 4.320$ for metric units; 0.09450 for English units.

6.12 Acceptable Results. If 90 percent 010110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 in Section 7 to make judgments. Otherwise, reject the results and repeat the test.

7. Bibliography.

[Appendix A, Method 17]

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10. Vollaro, R. F., Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, N.C. November, 1976.

METHOD 18 — MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

[Method 18 added by 48 FR 48335, October 18, 1983; amended by 49 FR 22606, May 30, 1984; 52 FR 5106, February 19, 1987]

Introduction. [This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.]

1. Applicability and Principle

1.1 Applicability. This method applies to the analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as

those found in building air and fugitive emission sources.

This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.2 Principle. The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles.

[1.2 revised by 52 FR 5106, February 19, 1987]

The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

2. Range and Sensitivity

2.1 Range. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

3. Precision and Accuracy

Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Duplicate analyses are within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

4. Interferences

Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

The analytical system is demonstrated to be essentially free from contaminants by pe-

riodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately, is best dealt with by thorough purging of the GC sample loop between samples.

To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

[4. amended by 52 FR 5106, February 19, 1987]

5. Presurvey and Presurvey Sampling

Perform a presurvey for each source to be tested. Refer to Figure 18-1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

[5. revised by 52 FR 5106, February 19, 1987]

5.1 Apparatus. This apparatus list also applies to Sections 6 and 7.

[5.1 revised by 52 FR 5106, February 19, 1987]

5.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

5.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

5.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

5.1.4 Flowmeters. To measure flow rates.

[5.1.4 revised by 52 FR 5106, February 19, 1987]

5.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

5.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

5.1.7 Syringes. 0.5 ml, 1.0- and 10-microliter sizes, calibrated, maximum accuracy (gas tight), for preparing calibration standards. Other appropriate sizes can be used.

[5.1.7 revised by 52 FR 5106, February 19, 1987]

[Appendix A, Method 18]

TGS-ANSA METHOD FOR THE
DETERMINATION OF NITROGEN
DIOXIDE IN THE ATMOSPHERE

EPA Designated Equivalent Method
No. EQN-1277-028

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

December 1977

T ~~Guaiacol~~ Guaiacol.

TGS-ANSA METHOD FOR THE DETERMINATION
OF NITROGEN DIOXIDE IN THE ATMOSPHERE

EPA Designated Equivalent Method No. EQN-1277-028

1. Principle and Applicability

1.1 Ambient nitrogen dioxide (NO_2) is collected by bubbling air through a solution of triethanolamine, o-methoxyphenol, and sodium metabisulfite.^(1,2) The concentration of nitrite ion (NO_2^-) produced during sampling is determined colorimetrically by reacting the nitrite ion with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid ammonium salt and measuring the absorbance of the highly colored azo dye at 550 nm.

1.2 The method is applicable to 24-hour integrated sampling of NO_2 in ambient air. Collected samples are transferred to a laboratory for manual analysis.

1.3 Agencies desiring to use this method in a network operation may find it necessary to develop and use additional operation and quality assurance procedures not provided in the method description. Information regarding quality assurance procedures can be found in reference 3.

2. Range and Lower Detectable Limit

2.1 The nominal range of the method is 15 to 750 $\mu\text{g NO}_2/\text{m}^3$ (0.008 to 0.4 ppm).⁽²⁾ The range of the analysis is 0.025 to 4.0 $\mu\text{g NO}_2^-/\text{ml}$, following Beer's law throughout this range (0 to 2.0 absorbance units).

Under the specified conditions of 50 ml of absorbing reagent, a sampling rate of $200 \text{ cm}^3/\text{min}$ for 24 hours, and a sampling efficiency of 0.93, the range of the method is therefore 5 to $750 \text{ } \mu\text{g NO}_2/\text{m}^3$ (0.003 to 0.4 ppm).

2.2 Based on results from a collaborative study, the lower detectable limit of the method is estimated to be $15 \text{ } \mu\text{g NO}_2/\text{m}^3$ (0.008 ppm).⁽⁴⁾

3. Interferences

3.1 At a NO_2 concentration of $100 \text{ } \mu\text{g}/\text{m}^3$ the following pollutants, at the levels indicated, do not interfere: ammonia, $205 \text{ } \mu\text{g}/\text{m}^3$ (0.29 ppm); carbon monoxide, $154,000 \text{ } \mu\text{g}/\text{m}^3$ (134 ppm); formaldehyde, $750 \text{ } \mu\text{g}/\text{m}^3$ (0.61 ppm); nitric oxide, $734 \text{ } \mu\text{g}/\text{m}^3$ (0.60 ppm); phenol, $150 \text{ } \mu\text{g}/\text{m}^3$ (0.04 ppm); ozone, $400 \text{ } \mu\text{g}/\text{m}^3$ (0.20 ppm); and sulfur dioxide, $439 \text{ } \mu\text{g}/\text{m}^3$ (0.17 ppm).⁽¹⁾

4. Precision, Accuracy, and Stability

4.1 Based on results from a collaborative study, the within laboratory standard deviation is $7 \text{ } \mu\text{g}/\text{m}^3$ (0.004 ppm) and the between laboratory standard deviation is $12 \text{ } \mu\text{g}/\text{m}^3$ (0.006 ppm) over the range of 50 to $300 \text{ } \mu\text{g NO}_2/\text{m}^3$ (0.027 to 0.16 ppm).⁽⁴⁾ Based on results from the Subpart C consistent relationship test (see Appendix), the within laboratory standard deviation is $9 \text{ } \mu\text{g}/\text{m}^3$ (0.005 ppm) over the range of 120 to $540 \text{ } \mu\text{g NO}_2/\text{m}^3$ (0.062 to 0.29 ppm).

4.2 Based on results from a collaborative study, the method has an average bias of -5% over the range of 50 to $300 \text{ } \mu\text{g NO}_2/\text{m}^3$ (0.027 to

0.16 ppm).⁽⁴⁾ Based on results from the Subpart C consistent relationship test (see Appendix), the method has an average bias of +2% over the range of 120 to 540 $\mu\text{g NO}_2/\text{m}^3$ (0.062 to 0.29 ppm).

4.3 Collected samples are stable for at least 3 weeks at room temperature. Stored samples should be tightly sealed to prevent absorption of NO_2 from the atmosphere.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling system is shown in Figure 1.

5.1.1 Sample Inlet. Teflon[®] or glass tube with an inverted Teflon[®] or glass funnel at the sampling point to prevent entrance of precipitation.

5.1.2 Absorber. Polypropylene tube, 164 mm long x 32 mm diameter, equipped with a polypropylene two-port closure (see Figure 1). (Rubber stoppers cause high and variable blank values and should not be used.) The closure must be fitted with an 8 mm O.D., 6 mm I.D. glass tube approximately 152 mm long having the end drawn out to form an orifice with an I.D. of 0.3-0.6 mm. This tube must be positioned to allow a clearance of 6 mm from the orifice to the bottom of the absorber. The closure and ports must be free of leaks.

5.1.3 Moisture Trap. Polypropylene tube similar to absorber. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool or silica gel to trap moisture to protect the flow control device. The trap must be repacked with fresh glass wool or silica gel before the start of each sampling period.

5.1.4 Membrane Filter. Of 0.8 to 2.0 micron porosity and 3 cm diameter. Be sure the filter does not leak. The filter must be replaced after collecting 10 samples.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180 and 220 cm^3/min . A convenient flow control device is a 27 gauge hypodermic needle,⁽⁵⁾ 10 mm (3/8 inch) long, used as a critical orifice. (Most 27 gauge needles will give flow rates in this range.)

5.1.6 Air Pump. Capable of maintaining a vacuum of at least 0.6 atmosphere (450 torr) across the flow control device. [This value is based on the critical pressure differential, 0.53 atmosphere (400 torr)⁽⁵⁾, plus a safety factor to allow for variations in atmospheric pressure and minor variations in pump performance.]

5.1.7 Flowmeter. Properly calibrated flowmeter for measuring air flow rates in the range of 150-250 cm^3/min . The use of a mass flowmeter is particularly convenient since no corrections are required when used under temperature and pressure conditions that differ from the conditions under which it is calibrated (see 10.1).

5.1.8 Flow Measurement Standard. Precision wet test meter (1 liter/revolution), bubble flowmeter, or other reliable standard.

5.2 Analysis

5.2.1 Volumetric Flasks. 100, 200, 250, 1,000-ml.

5.2.2 Pipets. 1, 2, 5, 10, 15, 20, 50-ml volumetric; 1, 3-ml, graduated in 1/10-ml intervals.

5.2.3 Test Tubes. Approximately 150 mm long x 20 mm diameter.

5.2.4 Spectrophotometer. Capable of measuring absorbance at 550 nm; equipped with 1 cm optical path length cells.

6. Reagents All reagents should conform to ACS specifications for reagent grade materials unless otherwise specified.

6.1 Sampling

6.1.1 Distilled Water. Must be reagent water as defined by ASTM procedure 1193-66 part 6.3 (Consumption of potassium permanganate test). (6)

6.1.2 Triethanolamine.

6.1.3 o-Methoxyphenol. Also known by its trivial name, guaiacol. Melting point, 27-28°C. CAUTION: Technical grade material will not meet this specification and should not be used.

6.1.4 Sodium Metabisulfite.

6.1.5 Absorbing Reagent: Dissolve 20 g of triethanolamine, 3.5 g of o-methoxyphenol, and 0.250 g of sodium metabisulfite consecutively in 500 ml of distilled water. Dilute to 1000 ml with distilled water. Mix thoroughly. The solution should be colorless. This solution is stable for 3 weeks if protected from light.

6.2 Analysis

6.2.1 Sulfanilamide, melting point 165-167°C.

6.2.2 8-Anilino-1-naphthalenesulfonic Acid Ammonium Salt (ANSA). Molecular weight = 316.38. The ANSA must have a molar absorptivity (ϵ) of 19,000 to 19,300 liter/mole-cm as given by:

$$\epsilon = \frac{A}{b \times c} \quad (1)$$

where: A = Absorbance measured at a wavelength of 264 nm

b = Cell length, cm

c = Concentration, mole/liter on a dry basis, in water at
pH 7.0 $\pm$ 0.2

Note: ANSA usually has a moisture content of 2 to 3%.

Note: Eastman Chemical Co. ANSA, minimum analysis 98%, has been found to meet the above specifications. (a)

6.2.3 Hydrogen Peroxide, 30%.

6.2.4 Methanol, absolute.

6.2.5 Hydrochloric Acid, concentrated.

6.2.6 Sulfanilamide Solution: Add 2.0 g of sulfanilamide to a 100-ml volumetric flask containing approximately 50 ml of distilled water. Then slowly add 33 ml of concentrated HCl and dilute to 100 ml with distilled water. Mix thoroughly. This solution can be used for 4 weeks when stored under normal laboratory conditions.

6.2.7 ANSA Solution: Dissolve 0.1 g of ANSA in 50 ml of absolute methanol. Dilute to 100 ml with absolute methanol in a volumetric flask. Mix thoroughly. Keep stoppered, when not in use, to minimize evaporative losses. This solution can be used for 3 weeks when stored under normal laboratory conditions. The solution will develop some color under these conditions, but this color does not affect subsequent analyses. (If this color formation is objectionable to the analyst, the solution can be stored in the dark to minimize color formation.) Exposure to elevated temperature should be avoided. Solutions exposed to temperatures of 30°C or higher for 8 hours or more should be discarded.

6.2.8 Hydrogen Peroxide Solution: Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution may be used for one month, if refrigerated and protected from light.

^aMention of commercial products does not constitute endorsement of the product by the U. S. Government.

6.3 Calibration

6.3.1 Sodium Nitrite, assay of 97% NaNO_2 or greater.

6.3.2 Sodium Nitrite Stock Solution (500 $\mu\text{g NO}_2^-/\text{ml}$):

Dissolve an accurately weighed (to nearest 0.1 mg) amount of desiccated sodium nitrite in distilled water and dilute to 1,000 ml such that a solution containing 500 $\mu\text{g NO}_2^-/\text{ml}$ is obtained. The amount of NaNO_2 to use is calculated as follows:

$$G = \frac{1.500}{A} \times 50 \quad (2)$$

where: G = Amount of NaNO_2 , grams

1.500 = Gravimetric conversion factor

A = Assay, percent (should be 97 or greater)

This stock solution can be stored for 6 weeks, if refrigerated.

6.3.3 Sodium Nitrite Working Standard (10 $\mu\text{g NO}_2^-/\text{ml}$):

Pipet 5 ml of the stock solution into a 250-ml volumetric flask and dilute to volume with absorbing reagent. Prepare fresh daily.

7. Calibration

7.1 Flowmeter. Calibrate the flowmeter against a calibrated flow measurement standard, such as a wet test meter, bubble flowmeter, or other reliable volume measurement standard. Calibrate in units of standard cm^3/min (i.e., corrected to 25°C and 760 torr).

7.2 Absorber. Calibrate the polypropylene absorber (see 5.1.2) by pipeting 50 ml of water or absorbing reagent into the absorber. Scribe

the level of the meniscus with a sharp object, mark over the area with a felt-tip marking pen, and rub off the excess.

7.3 Spectrophotometer

7.3.1 Prepare calibration standards by dilution of the sodium nitrite working standard (see 6.3.3) as indicated below. Use absorbing reagent for all dilutions.

	<u>Volume of working standard, ml</u>	<u>Final volume, ml</u>	<u>Concentration $\mu\text{g NO}_2^-/\text{ml}$</u>
	0.0	100	0.0
	1.0	100	0.1
	2.0	100	0.2
	5.0	100	0.5
	10.0	100	1.0
	15.0	100	1.5
	20.0	100	2.0
(Optional)	25.0	100	2.5
(Optional)	30.0	100	3.0
(Optional)	40.0	100	4.0

7.3.2 In accordance with the analytical procedure given in 8.2, measure and record the absorbance for each calibration standard (0.1, 0.2, 0.5, 1.0, 1.5, and 2.0 $\mu\text{g NO}_2^-/\text{ml}$).

7.3.3 Plot absorbance (y-axis) versus the corresponding concentration in $\mu\text{g NO}_2^-/\text{ml}$ (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve. A straight line with a slope of 0.50 ± 0.02 absorbance units/ $\mu\text{g NO}_2^-/\text{ml}$ and a y-intercept of approximately 0.01 absorbance units should be obtained. The absorbance is linear up to a concentration of 4.0 $\mu\text{g NO}_2^-/\text{ml}$. Therefore, if samples exceed the absorbance of the highest calibration standard and the above absorbance is within the range of the spectrophotometer, the calibration curve can be extended by including the higher concentration standards. If a higher absorbance range is not available, samples must be diluted with unexposed absorbing reagent until the absorbance is within the range of the highest standard.

8. Procedure

8.1 Sample Collection

8.1.1 Assemble the sampling apparatus (Figure 1) at the sampling site. Components upstream from the absorber may be connected, where required, with Teflon[®] tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with Tygon[®], Teflon[®], or polypropylene.

8.1.2 Add exactly 50 ml of absorbing reagent to the calibrated absorber.

8.1.3 Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F_i . If the flow rate before sampling is not between 180 and 220 cm³/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range.

8.1.4 Sample for 24 hours. Record the exact sampling time in minutes as t_s .

8.1.5 Measure the flow rate after the sampling period and record as F_f .

8.1.6 Seal the collected samples and transport to the laboratory for analysis.

8.2 Analysis

8.2.1 Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorber. Mix thoroughly.

8.2.2 Pipet 5 ml of the collected sample into a test tube. Pipet in 0.5 ml of hydrogen peroxide solution and mix vigorously for approximately 15 seconds. Add 2.7 ml of sulfanilamide solution and mix

vigorously for about 30 seconds. Then pipet 3 ml of the ANSA solution and mix vigorously for about 30 seconds. CAUTION: The ANSA must be added within 6 minutes after adding the sulfanilamide solution. Longer time intervals will result in lower absorbance values.

8.2.3 Prepare a blank in the same manner using 5 ml of unexposed absorbing reagent.

8.2.4 Measure and record the absorbance of each sample and the blank at 550 nm against distilled water. The absorbance measurement can be made anytime from 1 to 40 minutes after addition of the ANSA. The absorbance of the blank should be approximately the same as the y-intercept in the calibration curve (see 7.3.3).

8.2.5 Determine $\mu\text{g NO}_2^-/\text{ml}$ from the calibration curve (see 7.3.3).

8.2.6 When using a spectrophotometer with an absorbance range of 0 to 1, samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot of the collected sample with unexposed absorbing reagent.

8.2.7 A randomly selected 5-10% of the samples should be reanalyzed as part of an internal quality assurance program.

8.2.8 After use, the spectrophotometer cells must be rinsed thoroughly with distilled water and acetone, and dried; otherwise a film will build up on the cell walls.

9. Sampling Efficiency The overall average efficiency is 93% from 20 to 750 $\mu\text{g NO}_2^-/\text{m}^3$ (0.01 to 0.4 ppm).⁽¹⁾

10. Calculations

10.1 Air Volume. Calculate the volume of air sampled as follows:

$$V = \frac{F_i + F_f}{2} \times t_s \times 10^{-6} \quad (3)$$

where: V = Volume of air sample, m^3

F_i = Air flow rate before sampling, cm^3/min

F_f = Air flow rate after sampling, cm^3/min

t_s = Sampling time, min

10^{-6} = Conversion of cm^3 to m^3

If the temperature and pressure conditions at the time of the initial and final air flow rate measurements are substantially different from the conditions under which the flowmeter was calibrated, appropriate corrections to the flow rate measurements may be made to improve the accuracy of the resultant NO_2 concentration measurement. The mathematical form of these corrections depends on the type of flowmeter used; consult an appropriate reference for guidance.

10.2 NO_2^- Concentration in Analyzed Sample. Determine $\mu g NO_2^-/ml$ graphically from the calibration curve or compute from the slope and intercept values (see 7.3.3).

10.3 NO_2 Concentration in Air Sample. Calculate as μg of NO_2 per standard cubic meter of air as follows:

$$\mu g NO_2/m^3 = \frac{\mu g NO_2^-/ml \times 50}{V \times 0.93} \times D \quad (4)$$

where: $\mu\text{g NO}_2/\text{ml}$ = NO_2 concentration in analyzed sample

50 = Volume of absorbing reagent used in sampling, ml

V = Volume of air sample, m^3

0.93 = Sampling efficiency

D = Dilution factor (D = 1 for no dilution; D = 2 for 1:1 dilution; etc.)

10.4 The NO_2 concentration may be calculated as ppm using:

$$\text{ppm NO}_2 = (\mu\text{g NO}_2/\text{m}^3) \times 5.32 \times 10^{-4} \quad (5)$$

11. References

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2. Fuerst, R. G. and Margeson, J. H. "An Evaluation of the TGS-ANSA Procedure for Determination of Nitrogen Dioxide in Ambient Air." EPA Report No. 650/4-74-047, November 1974.
3. "Quality Assurance Handbook for Air Pollution Measurement Systems." EPA Publication No. EPA-600/9-76-005, January 1976.
4. Constant, P. C., Jr. et al. "A Collaborative Test of the TGS-ANSA Method for Determination of Nitrogen Dioxide in Ambient Air." EPA Contract No. 68-02-1363. EPA Report No. 650/4-74-046, September 1974.
5. Lodge, J. P., Jr., et al. "The Use of Hypodermic Needles as Critical Orifices in Air Sampling." J.A.P.C.A., 16, 197-200 (1966).
6. ASTM Standards (Water; Atmospheric Analysis), Part 23. October 1969. (p. 225).

Figure 1. Sampling system.

APPENDIX

LA 4000 PROTECTION
AGENCY

AMERICAN AIRLINES SYSTEM, INC.
NEW YORK, N. Y.

המחלקה הכלכלית והמסרתי
המחלקה הכלכלית והמסרתי

1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 26

(1) 7571-1277-026, "Sodium Azide Method for the Determination of Nitrogen Dioxide in the Atmosphere."

(2) HQN-1277-027, "Sodium Arsenite Method for the Determination of Nitrogen Dioxide in the Atmosphere—Technique II Automated Analysis System."

(3) IQX-1277-023. "TGIS-ANCA Method for the Determination of Nitrogen Dioxide in the Atmosphere."

All three methods are applicable to 24-hour integrated measurements of NO_x in ambient air. Collected samples are transferred from the sampling site to a laboratory for analysis. The first two methods are very similar, and have identical sampling procedures. In the second method, an automated analysis procedure replaces the manual analysis procedure specified in the first method.

With both sodium arsenite methods, nitric oxide is a positive interferent and carbon dioxide is a negative interferent. Because these interferents exhibit compensating effects, the resulting error is small for most monitoring situations and does not necessitate applying a correction to NO_x measurements obtained with the method. However, use of these arsenite methods in areas of high and varying concentrations of these potential interferents (such as near roadways or other highway traffic density locations) is not recommended.

Each of these methods was tested, and information was compiled, by EPA under 152.7 of 40 CFR Part 55 (40 FR 7019, 11 FR 52694). The pertinent information will be kept on file by Department E at the address shown below and will be available for inspection to the extent consistent with 40 CFR Part 2 (EPA's regulations implementing the Freedom of Information Act).

As designated equivalent methods, each of these methods is acceptable for use by States and other control agencies for purposes of § 51.17a of 40 CFR Part 51—Requirements for Preparation, Adoption, and Submittal of Implementation Plans (36 FR 22698) as amended December 1, 1976 (41 FR 52692). For these purposes, measurements made by any of these methods must be carried out in strict accordance with the procedures and specifications provided in the complete and detailed method description. However, users of any of these methods should be aware that promulgation of a short term (1 to 3 hour) standard for NO_x is likely under the 1977 amendments to the Clean Air Act, and that none of these 24-hour methods would be applicable to such a short term standard.

Copies of the method description for each of these methods, or further information, may be obtained from any of the EPA Regional Offices or from the Environmental Monitoring and

Support Laboratory, Department
(MD-70), U.S. Environmental
Protection Agency, Research Triangle
Park, N.C. 27711.

Manual methods such as 161 often used in a network of sites associated with a "central" laboratory. Such networks may entail a number of different technicians and laboratory varieties of sampling and analysis, and various modes of collecting or shipping samples to the laboratory. It is EPA's observation that under such conditions, the accuracy and precision of the method is degraded markedly. Frequent sources of error include improperly calibrated flow measurement devices, air in sampling apparatus, medium clogging of air flow control, leakage of absorbing solution sample during transport or exposure to impure reagents or water, and improperly calibrated spectrophotometers. Agencies desiring to use one method in a network operation should develop and use additional quality and quality assurance procedures provided in the method description to ensure accurate measurement. Routine network operation can be further information regarding quality assurance can be found in EPA publication number EPA-600/4-77-010 "Quality Assurance Handbook for Air Pollution Measurement Systems" obtainable from the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Federal Environmental Protection Agency, P.O. Box 1219, Triangle Park, N.C. 27711.

Dated: December 6, 1977.

STEPHEN J. CHAI
Acting Assistant Administrator
for Research and Development

(FBI Doc. 77-35003 Filed 12-10-77)

SUBPART C CONSISTENT RELATIONSHIP TEST SUMMARY

In June of 1977, the TGS-ANSA method for the determination of nitrogen dioxide in the atmosphere was tested and information was compiled by EPA under §53.7 of 40 CFR Part 53 (40 FR 7049, 41 FR 52694). The test procedures given in Subpart C of Part 53 were used to determine if the candidate method has a consistent relationship to a reference method when both methods measure pollutant concentrations in a real atmosphere. The tests were conducted in the Continuous Air Monitoring Program station located at 427 N. New Jersey Avenue in Washington, D. C.

Two designated reference method analyzers were used during the course of the tests: (1) RFNA-0677-021, Monitor Labs Model 8440E Nitrogen Oxides Analyzer; (2) RFNA-0777-022, Bendix Model 8101-C Oxides of Nitrogen Analyzer. The reference method analyzers were calibrated according to the manufacturers' instruction manuals using a NBS NO₂ Standard Reference Material (SRM 1629) as the reference standard. The candidate method was calibrated according to the procedure specified in the method description.

In order to generate a conclusive set of consistent relationship data and to obtain an estimate of the precision of the candidate method, 15 samples were obtained each test day for 8 days for a total of 32 samples. Following collection, the samples were transported to RTP, I.C. for analysis. From the time of collection to the time of analysis, the samples were kept at a temperature of 20° to 25°C.

Data from the two reference method analyzers were reduced by taking 5-minute averages throughout the 24-hour sampling period. The 15-minute averages for each analyzer were used to calculate a 24-hour average.

The difference (discrepancy) between the candidate method measurement and the average of the two reference method measurements was calculated and compared to the maximum discrepancy specifications given in Table -1 of Subpart C of Part 53. The candidate method met all requirements for a consistent relationship. Accordingly, on December 6, 1977, EPA designated the TGS-ANSA method as an equivalent method for the measurement of nitrogen dioxide in the atmosphere.

The Subpart C consistent relationship test data is tabulated below along with a statistical evaluation of the test results.

CANDIDATE DISCREPANCY COMPARISON

Sample Number	Date	16.4.4.4		Monitor Labs		Reference		Difference (Candidate-Reference)	Max. Discrepancy/Specification (ppm)	Pass/Fail	Conc. Range
		NO ₂ (ppm)	NO ₂ (ppm)	NO ₂ (ppm)	NO ₂ (ppm)	Analyzer Avg. (ppm)	Reference (ppm)				
A ₁	6/15-16	.0627	.071	.067	.069	.069	-.006	.020	Pass	Low	
B ₁₀		.0727					+.004		Pass		
C ₁		.0681					-.001		Pass		
D ₁₀		.0664	.071	.067	.069	.069	-.003	.020	Pass	Low	
A ₂	6/16-17	.3163	.295	.283	.289	.289	+.027	.030	Pass	High	
B ₉		.3060					+.017		Pass		
C ₂		.3110					+.022		Pass		
D ₉		.3070	.295	.283	.289	.289	+.018	.030	Pass	High	
A ₃	6/18-19	.1258	.125	.115	.120	.120	+.006	.020	Pass	Medium	
B ₁₂		.1262					+.006		Pass		
Q		.1328					+.013		Pass		
D ₃		.1252	.125	.115	.120	.120	+.005	.020	Pass	Medium	
A ₅	6/19-20	.0565	.059	.066	.063	.063	-.007	.020	Pass	Low	
B ₁₃		.0591					-.004		Pass		
C ₅		.0591					-.004		Pass		
D ₁₃		.0537	.059	.066	.063	.063	-.009	.020	Pass	Low	

CANDIDATE - REFERENCE COMPARISON

Sample Number	Date	TGS-ANSA NO ₂ (ppm)	Bendix NO ₂ (ppm)	Monitor Labs NO ₂ (ppm)	Reference Analyzer Avg. (ppm)	Difference (Candidate- Reference)	Max. Discrepancy Specification (ppm)	Pass/ Fail	Conc. Range
A ₄	6/20-21	.2765	.274	.271	.272	+.005	.030	Pass	High
B ₁₁		.2603				-.012		Pass	
C ₄		.2655				-.007		Pass	
D ₁₁	6/20-21	.2778	.274	.271	.272	+.006	.030	Pass	High
A ₆	6/21-22	.1175	.121	.119	.120	-.003	.020	Pass	Medium
Z		.1193				-.001		Pass	
C ₆		.1305				+.011		Pass	
D ₁₂	6/21-22	.1192	.121	.119	.120	-.001	.020	Pass	Medium
A ₇	6/22-23	.0558	.062	.062	.062	-.006	.020	Pass	Low
B ₁₅		.0584				-.004		Pass	
C ₇		.0613				-.001		Pass	
D ₁₅	6/22-23	.0586	.062	.062	.062	-.003	.020	Pass	Low
A ₈	6/23-24	.1201	.127	.124	.126	-.006	.020	Pass	Medium
B ₁₄		.1256				.000		Pass	
C ₈		.1309				+.005		Pass	
D ₁₄	6/23-24	.1249	.127	.124	.126	-.001	.020	Pass	Medium

Statistical Evaluation of Subpart C Consistent Relationship

Test Results (TGS-ANSA Method)

In statistically comparing the TGS-ANSA candidate method to the reference method, the following definitions apply:

Bias refers to the average size of deviations of the candidate method from the reference method average. The average differences are calculated on a day-to-day basis and reported as bias (B) in the table below.

Precision refers to the size of deviations from the candidate method average obtained by repeated application of the sampling and analytical procedure. This is expressed as the standard deviation (S) of the within-day candidate samples.

Date	TGS-ANSA Avg. (ppm)	Reference Method Avg. (ppm)	B (ppm)	S (ppm)
1/14-16	.0675	.069	-.0015	.0041
1/18-20	.3101	.289	.0211	.0047
1/21-23	.1275	.120	.0075	.0036
1/24-26	.0571	.063	-.0059	.0026
1/28-30	.2700	.272	-.0020	.0085
1/31-2	.1216	.120	.0016	.0060
1/23-25	.0585	.062	-.0035	.0022
1/26-28	.1254	.126	-.0006	.0044
Avg:			.0021 Pooled:	.0049 with 24 d.f.

The following probability statement incorporates both bias and precision in evaluating the candidate:

$$\text{PROBABILITY } [-.02 \text{ ppm} < \text{CANDIDATE} - \text{REFERENCE} < .02 \text{ ppm}] \geq 1 - \frac{(B^2 + S^2)}{(.02)^2}$$

where $(B^2 + S^2)$ is the mean square error (MSE) of the candidate.

Based on the data, the following statement applies:

GS-ANSA. The probability of the candidate being within ± 0.02 ppm of the reference is greater than .93. Another way of stating this is that if 100 analyses were made, 7 of these would be expected to differ by chance alone by more than ± 0.02 ppm from the reference.

Method No. EHS E-1

Title: Extraction Procedure Toxicity Test - Metals

Date Issued: Before 2-83 Approved by: MK Hamilton *MK*

Written by: MK Hamilton

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____ Date: _____

Date: _____

EP TOXICITY EXTRACTION PROCEDURE--METALS

REFERENCES

1. Test Methods for Evaluating Solid Waste: Physical and Chemical Methods., Method 1310 & appropriate 7000 series methods, USEPA SW-846 3rd Edition, 1986.
2. Hazardous Waste Testing Manual, Millipore Corp., pp. 108+.
3. April 21, 1982 Memorandum from J. Knudson, Washington State Department of Ecology, on the use of buffer for EP-Toxicity Test.

PRINCIPLES

Solid samples are extracted in a pH 5 acetic acid buffer to determine the characteristic of EP toxicity due to the eight heavy metals arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.

LIMITATIONS

This procedure does not recover the analytes of interest quantitatively, it is a simulation of the leaching process that might occur in a landfill. All analyte recovery studies(i.e. spikes) should be performed after the extraction process.

DEFINITIONS

1. EP Toxic Metals: These metals are arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver. For liquid samples EP-TOX concentration equals total metals concentration; for solids it is the concentration of the extract resulting from the EP toxicity extraction procedure.
2. Total Metals: The metals concentration determined using a mineral acid digestion without filtration or centrifugation of the digestate.
3. Laboratory Control Sample (LCS): A sample containing known quantities of the analytes of interest (preferably certified) in the matrix of interest, prepared using the appropriate preparation method. The LCS is used to monitor the analyte recovery value of the sample preparation method employed.
4. Preparation Blank: An aliquot of the analytical solvent (DI water, acetic acid buffer, etc.) prepared by the appropriate sample preparation method. The preparation blank is used to monitor for contamination introduced by the sample preparation method.
5. Matrix Spike: A sample to which known quantities of analyte have been added before sample preparation. The matrix spike is used to monitor analyte recovery for a particular matrix/preparation method combination.

6. Post Preparation Spike: A sample to which known quantities of analyte have been added after sample preparation. The post preparation spike is used to monitor analyte loss due to a particular matrix/interference independent of the sample preparation method.
7. Duplicate: A second identical preparation of a sample or spike. Duplicates are used to monitor method precision.
8. Method of Standard Additions (MSA): The use of multiple additions of analyte to equal portions of sample to create a calibration curve and determine concentration. MSA is used to compensate for altered sensitivity created by certain matrix effects, especially in the analysis of organic matrices.

EQUIPMENT

1. Nucleopore filtration chamber and stand
2. NBS rotating extractor
3. Polyethylene bottles compatible with extractor
4. Prefilters and filter membranes (Nucleopore P80, P100, and P300)
5. Wide mouth funnel
6. Graduated cylinders
7. pH meter
8. 50 ml buret
9. Forceps. rubber policeman
10. Nitrogen tank, regulator, tubing, fittings

REAGENTS & STANDARDS

A. REAGENTS (STOCK)

1. Milli-Q Plus deionized water
2. Glacial acetic acid
3. Sodium acetate
4. Sodium hydroxide
5. Materials for metal standards as listed in EHS M-1, M-4 & M-10

B. REAGENTS (PREPARED)

1. 0.1 M Sodium acetate buffer: Dissolve 13.6 g sodium acetate and 5.75 ml glacial acetic acid in Milli-Q deionized water and dilute to 1 liter using Milli-Q water. This solution can be stored for up to six months.
2. 5.0 N Sodium hydroxide solution: Dissolve 200 g sodium hydroxide in deionized water. This solution can be stored for up to one year.
3. 0.5 N Acetic acid dilute 28.74 ml of glacial acetic acid to 1 liter with deionized water. this solution can be stored for up to one year.

C. Standards

1. 1000 mg/L stock metal standards - See EHS M-1, M-4 & M-10

PROCEDURE

- A. Initial filtration is often required to separate solid phase from liquid phase portions of the sample. Initial filtration is performed as follows:

1. Place 3 filters onto the teflon support screen in increasing pore size using forceps (P80, P100, P300).
2. Assemble the filtration system. Place the chamber over the filter pad carefully and tighten the 3 bolts. Place a funnel in the opening at the top of the chamber and a suitable filtrate collector underneath the filtration assembly.
3. Transfer a portion of the sample via the funnel into the filtration assembly. Secure the lid on the chamber and attach the nitrogen supply. Close the gas supply and pressure release valves. Turn on the nitrogen regulator and adjust so that a small amount of pressure is indicated (~10 psi). Slowly open the gas supply valve. Liquid should begin to flow. Increase the pressure slowly (maximum pressure 75 psi) until all of the liquid has been expelled and gas breaks through.
4. Close the nitrogen tank valve and dial the pressure down to zero. Open the pressure release valve and vent the filtration assembly. Remove the three bolts and take the chamber off the filter pad.
5. Remove the filter pad from the filtration assembly. Remove solid from the filter pad and weigh an aliquot into an extraction vessel. Discard the filter pad.
6. Clean all apparatus immediately to prevent corrosion.

B. Sample Extraction

1. Transfer 12.5 g of solid to a 500 mL polyethylene bottle.
2. Add 200 mL 0.1 M acetate/acetic acid buffer to the bottle.
3. Adjust the pH with 0.5 N acetic acid or 5.0 N sodium hydroxide to 5.0 ± 0.2 units.
4. Start the extractor and repeat step B.3 every hour or until the pH change is less than 0.5 units.
5. Run the extractor overnight and check the pH in the morning. If the pH is 5.0 ± 0.2 units after 24 hours, stop the extraction. If the pH is not within this range adjust and extract for 4 more hours.

C. Second Filtration

1. Following the procedure for the first filtration, transfer all of the liquid from the extraction to the filtration apparatus.
2. Filter the extract, collecting it in a 250 mL volumetric flask.
3. Dilute to volume with acetate buffer solution.
4. Transfer the extract to a polyethylene bottle (optional).

D. ANALYSIS

1. Analyze the final extract for the eight metals using flame, graphite furnace or cold vapor atomic absorption spectroscopy (AAS).
 - a. Analyze for mercury by cold vapor AAS as described in EHS M-4, using 2.0 mL of sample.
 - b. Analyze for arsenic and selenium by graphite furnace AAS as described in EHS M-10, using the following standards:

0. 0.005, 0.01, 0.03, 0.05, 0.10 mg/L As & Se
 - c. Analyze for barium, cadmium, chromium, lead and silver by flame AAS as described in EHS M-1, using the following standards:

0, 0.04, 0.10, 0.20, 0.60, 1.0, 2.0 mg/L Cd, Cr & Ag
0, 0.2, 0.5, 1.0, 3.0, 5.0, 10.0 mg/L Pb
0, 0.2, 0.5, 1.0, 3.0, 5.0, 10.0 mg/L Ba (1000 mg/L K added to all Ba samples and standards)

2. If the extract is cloudy or otherwise presents problems for direct analysis, digest the extract as described in EHS M-11 and then proceed with the AAS analysis as described above.
3. Report all EP-TOX concentrations as mg/L metal in the final extract.

QUALITY CONTROL

The quality control measures required to assure that the sample preparation procedures presented here are adequate are discussed below. Other quality control measures associated with the atomic absorption spectroscopic analysis of samples are presented in those methods.

LABORATORY CONTROL SAMPLE: A Laboratory control sample should be prepared by spiking a volume of the extraction solution with known quantities of all analytes of interest in the concentration ranges of interest. The use of spiking solutions that are reference materials is preferred.

PREPARATION BLANK: A volume of extraction solution should be analyzed with each batch of samples as a preparation blank.

POST PREPARATION SPIKE AND POST PREPARATION DUPLICATE SPIKE: Two identical post preparation spikes should be prepared with each batch of samples.

M. J. P.

Method No. EHS M-3

Title: Mercury in Soil

Date Issued: Before 11-82 Approved by: MK Hamilton *[Signature]*

Written by: MK Hamilton

Supersedes Method No. _____.

[illegible]

Replaced by Method No. _____

Date: _____

MERCURY IN SOILS

Reference

Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry, March 1971, Method GC-2 (Reference - Hatch and Ott, Anal. Chem., 40, 2085 (1968)).

Principles

Mercury is extracted from soil by the addition of nitric acid and hydrogen peroxide. The peroxide prevents the mercury from being reduced to the elemental state and lost by volatilization. The amount of mercury extracted is determined by the flameless atomic absorption technique described in EHS Procedure M-4.

Limitations

Oxidizing conditions must be maintained during the extraction to prevent loss of mercury. This method is suitable for the analysis of mercury pesticide residues in most soils. If the soil is a potentially hazardous waste, see EP Toxicity Procedure (EHS E-1).

Equipment

1. 250 mL glass-stoppered erlenmyer flasks
2. 100 mL glass-stoppered graduated cylinders
3. Atomic absorption spectrophotometer and recorder
4. Absorption cell and reduction apparatus shown in EHS Procedure M-4

Reagents (stock)

1. Mercuric chloride - HgCl_2
2. Stannous chloride - $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
3. Conc. nitric acid - HNO_3
4. 30% hydrogen peroxide - H_2O_2
5. Potassium permanganate - KMnO_4
6. Tributyl phosphate - TBP
7. Conc. hydrochloric acid - HCl
8. Magnesium perchlorate - $\text{Mg}(\text{ClO}_4)_2$

Reagents (Prepared) - See EHS Procedure M-4.

Standards - See EHS Procedure M-4.

Procedure

1. Rinse all glassware with 1:1 HNO₃, and deionized H₂O before using.
2. Weigh out 5.0 g soil samples and place in 250 mL glass-stoppered erlenmeyers.
3. Prepare standards by adding 0.5, 1.0, 3.0, and 5.0 mL of 0.1 µg/mL Hg standard to 5.0 g portions of a representative soil sample.
4. Add 25 mL conc. HNO₃ and one mL 30% H₂O₂ to each sample and standard. Stopper the flasks and allow to stand overnight.
5. Add an additional one mL 30% H₂O₂ to each solution.
6. Transfer samples (including soil) to 100 mL glass-stoppered cylinders and dilute to volume with deionized H₂O.
7. Allow the soil to settle and transfer a 50 mL aliquot (less if the soil is known to be contaminated) to a mercury reduction flask and add deionized H₂O to give a total volume of 75 mL.
8. Analyze according to EHS Procedure M-4 beginning with Procedure Step 7.

Calculations

1. Plot absorbance vs. µg Hg added to the spiked soil. Use the absorbance of the unspiked soil as 0 µg Hg added.
2. Back extrapolate the calibration curve to 0 absorbance to determine the amount of Hg present in the original soil.
3. Use this calibration curve to determine the amount of Hg present in the remaining soil samples.
4. Determine the soil Hg concentration as follows:

$$\text{soil ppm Hg} = \frac{A \times B}{C \times D}$$

A = µg Hg found

B = 100 mL initial volume

C = aliquot used in determination (usually 50 mL)

D = 5.0 g sample weight

(Note: Average Hg level in untreated soil = 0.07 ppm. Reference Elvaldo Kothny, Trace Elements in the Environment, ACS, 1973, p. 60.)

Revised 11/82 MK Hamito

METALS IN WASTE-ORGANIC MATRICES
BY ATOMIC ABSORPTION SPECTROSCOPY

REFERENCES

1. Test Methods for Evaluating Solid Waste: Physical and Chemical Methods, Methods 3040, 3050, and 7000, Section 8.7, and 7060, SW-846 3rd Edition, 1986, USEPA.

PRINCIPLES

The metals cadmium, chromium, and lead are determined in organic liquid matrices by dissolution in methyl isobutyl ketone (MIBK) or xylene followed by flame atomic absorption analysis. Matrix effects make the use of the method of standard additions mandatory. This method is also applicable to barium, silver, and other metal species.

Arsenic is determined in organic matrices using a sub-boiling nitric acid/hydrogen peroxide digestion for sample preparation, followed by analysis by graphite furnace atomic absorption spectroscopy. Digestion of samples is necessary to provide an aqueous matrix for graphite furnace atomic absorption analysis.

LIMITATIONS

This method does not apply to solid organic matrices or to organic materials which are water miscible. This method may not be adequate for organic liquids with high suspended solids content if determination of total metal content is desired. Due to the instability of diluted samples and organometallic standards, samples should be run as soon after dilution as possible.

The acid digestion method for arsenic may not completely destroy the organic matrix of many samples. A possible consequence of incomplete matrix destruction is incomplete recovery of analyte. The use of method control samples, preparation blanks, matrix spikes, duplicates, and post-preparation spikes is necessary to assure the applicability of this procedure to a given sample matrix.

DEFINITIONS

1. EP Toxic Metals: The heavy metals arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. For liquid samples equal to total metals concentrations; for solids the concentration determined using the EP toxicity extraction procedure.
2. Laboratory Control Sample (LCS): A sample containing known quantities of the analytes of interest (preferably certified) in the matrix of interest, prepared using the appropriate preparation method. The LCS is used to monitor the analyte recovery value of the sample preparation method employed.

3. Preparation Blank: An aliquot of the analytical solvent (DI water, MIBK, Etc.) prepared by the appropriate sample preparation method. The preparation blank is used to monitor for contamination introduced by the sample preparation method.
4. Matrix Spike: A sample to which known quantities of analyte have been added before sample preparation. The matrix spike is used to monitor analyte recovery for a particular matrix/preparation method combination.
5. Post Preparation Spike: A sample to which known quantities of analyte have been added after sample preparation. The post preparation spike is used to monitor analyte loss due to a particular matrix/interference independent of the sample preparation method.
6. Duplicate: A second identical preparation of a sample or spike. Duplicates are used to monitor method precision.
7. Instrument calibration verification/continuing calibration verification sample (ICV/CCV): A sample, prepared from standard reference materials, used to verify the initial accuracy and the continuing accuracy of the calibration. The ICV/CCV should have a concentration near the center of the calibration range.
8. Instrument calibration blank/continuing calibration blank (ICB/CCB): A blank used to verify the initial and continuing accuracy of the calibration.
9. Method detection limit (MDL): The minimum concentration of analyte that can be measured and reported with 99% confidence that its concentration can be reported as greater than zero. The MDL is determined from analysis of a sample in a given matrix processed using the appropriate preparation procedure.
10. Instrument detection limit (IDL): The concentration equivalent to $\pm$ signal, due to the analyte, which is equal to three times the standard deviation of a series of at least seven replicates of the reagent blank signal at the analyte wavelength.

EQUIPMENT

A. Flame metals analysis

1. Atomic absorption spectrophotometer, equipped with deuterium arc background correction
2. Hollow cathode lamps (HCLs) for the elements of interest
3. Volumetric flasks and pipets
4. Disposable volumetric pipets

5. 13 x 125 mm test tubes with threaded tops and teflon lined caps
6. Test tube racks
7. Analytical balance with 0.1 mg sensitivity

B. Graphite Furnace Analysis

1. Atomic absorption spectrophotometer, equipped with deuterium arc background correction, graphite furnace and autosampler
2. Electrodeless discharge lamp (EDL) for arsenic, and EDL power supply (other lamps as needed)
3. 100 mL Griffin beakers
4. Ribbed watch glasses
5. Hot plate
6. Centrifuge and centrifuge tubes
7. Volumetric flasks with stoppers, volumetric pipets
8. Analytical balance with 0.1 mg sensitivity

REAGENTS

A. Flame Metals Analysis--Stock

1. Methyl isobutyl ketone (MIBK)
2. Xylene
3. Organometallic standards (see Standards for details)

B. Graphite Furnace Analysis--Stock

1. Concentrated, distilled nitric acid
2. Milli-Q finished deionized water
3. Hydrogen peroxide 30%
4. Nickel metal--Class 2 Suspect Human Carcinogen
5. Arsenic Trioxide--Class 1 Human Carcinogen

C. Reagents (Prepared)--Graphite Furnace Analysis

1. 0.5% (V/V) nitric acid: Transfer approximately 1800 mL Milli-Q finished deionized water to a 2000 mL volumetric flask. Transfer 10.0 mL concentrated re-distilled nitric acid to the flask and fill to the mark with Milli-Q finished deionized water. Transfer the solution to an acid rinsed polyethylene container.
2. 1000 mg/L nickel solution: Prepared as indicated in EHS M-10.

STANDARDS

A. Flame Metals Analysis

1. Organometallic standards, 5000 mg/Kg (available from the Conostan Division, Conoco Specialty Products Inc., Ponca City OK).
2. Organometallic Reference Materials (available from the National Institute of Standards and Technology).
3. Standard Addition Solution: Weigh approximately 0.100 g of 5000 mg/Kg lead standard, 0.050 g of 5000 mg/Kg chromium standard and 0.020 g of 5000 mg/Kg cadmium standard to a 100 mL volumetric flask. Record the weights added for each standard. Fill the flask to the mark with solvent (MIBK or xylene), stopper, and shake to dissolve the standards. Calculate and record the standard concentrations of each metal in the solution using the formula shown below:

$$SW (g) \times 5000 (\mu g/g) / 100 (mL) = \text{Std. Conc. (mg/L)}$$

Where: SW = Standard Weight.

Approximate Conc. = 5 mg/L Pb, 2.5 mg/L Cr, 1 mg/L Cd

B. Graphite Furnace Analysis

1. Arsenic stock solution 1000 mg/L: Prepared as indicated in EHS M-10.
2. NIST SRM 3103 Arsenic Solution 10 g/L
3. Arsenic intermediate solution 10.0 mg/L: Transfer 1.0 mL 1000 mg/L arsenic stock solution to a 100 mL volumetric flask and dilute to the mark with 0.5% (v/v) nitric acid. Transfer to an acid rinsed polyethylene bottle. This solution should be replaced monthly.
4. Prepare standards by transferring the following amounts of arsenic intermediate solution to 100 mL volumetric flasks and diluting to the mark with 0.5% (v/v) nitric acid.

<u>Standard Concentration mg/L</u>	<u>μL As Intermediate Added</u>
0.100	1000
0.050	500
0.030	300
0.010	100
0.005	50

Use the 0.5% (v/v) nitric acid as the calibration blank. Transfer the standard solutions to acid rinsed, labeled polyethylene bottles. Standards should be prepared daily.

5. ICV/CCV stock solution: Transfer 100 μL NIST SRM 3103 (As 10 g/L) to a 100 mL volumetric and dilute to the mark with 0.5% (v/v) nitric acid. Transfer this solution to an acid rinsed, labeled polyethylene bottle. This solution is 10.0 mg/L. Prepare this solution monthly.
6. ICV/CCV solution: Transfer 100 μL ICV/CCV stock solution to a 25 mL volumetric flask and dilute to the mark with 5% (v/v) nitric acid. This solution is 0.040 mg/L As. Prepare this solution daily.

PROCEDURE

A. Flame Metals Analysis--Pb, Cd, Cr

1. Weigh between 1.0 and 5.0 grams of sample into a 25 mL volumetric flask.
2. Dilute to the mark with MIBK. If the sample is insoluble in MIBK, use xylene. Samples insoluble in both MIBK or xylene are not amenable to analysis by this method.
3. Label 4 test tubes with the sample number and +0, +1, +2, and +3.
4. Transfer a 5 mL aliquot from the sample flask to each of the 4 test tubes placed in the test tube rack. Transfer the remaining sample to a labeled test tube. Cap the test tube and save the sample.
5. Add 1.0 mL standard addition solution to the tube labeled +1, 2.0 mL to the tube labeled +2, and 3.0 mL to the tube labeled +3.
6. Bring the total volume added to each tube to 10 mL with solvent (5.0 mL for the +0 tube, 4.0 mL for the +1 tube, 3.0 mL for the +2 tube and 2.0 mL for the +3 tube).

7. Cap the test tubes and shake vigorously. The samples are ready for analysis.
8. Set up the atomic absorption spectrophotometer according to the manufacturer's instructions for flame operation with organic solvents for the analyte of interest. The use of background correction is mandatory for wavelengths below 300 nm.
9. Analyze the samples using the following steps:
 - a. Aspirate solvent and zero the instrument.
 - b. Take duplicate absorbance measurements of each sample and sample addition. Aspirate solvent continuously between sample readings.
 - c. Check the absorbances of the four sample solutions. If the concentration/ absorbance relationship deviates significantly from linear behavior or the absorbance of the +2 standard addition is not at least twice that of the +0 standard addition, repeat the standard addition analysis with a smaller initial sample aliquot or with a dilute sample.
10. Clean the sample introduction system of the AA spectrophotometer and remove and clean the sample drain trap. Discard the solvent portion of the waste generated and the sample solutions in the "Waste Solvent" container.

B. Graphite Furnace Analysis

1. Transfer a 5.00 mL aliquot of sample to a 100 mL Griffin beaker.
2. Slowly add 5 mL of 50 % nitric acid to the sample and cover with a ribbed watch glass. Heat the sample so that it refluxes without boiling. Reflux for one hour or until the digestate volume is ~5 mL, whichever is shorter.
3. Very slowly add 5 mL concentrated, redistilled nitric acid to the sample. Continue heating the sample so that it refluxes without boiling until the digestate volume is ~5 mL. Allow the sample to cool.
4. Repeat step 3 until oxidation is complete. For matrices containing organic compounds this may take many iterations. Oxidation is considered complete when addition of acid ceases to generate brownish red fumes and the sample ceases to change in appearance.

5. After step 4 has been completed and the sample has cooled, carefully add 2 mL 30% hydrogen peroxide. Return the covered sample to the hot plate. Watch the sample carefully as vigorous effervescence may cause it to overflow. Heat until the effervescence subsides and cool the sample.
6. Continue to add hydrogen peroxide in 2 mL aliquots with warming until effervescence is minimal or until the general sample appearance does not change. Add a maximum of 10 mL of hydrogen peroxide.
7. Continue to reflux sample until the volume has been reduced to ~5 mL. Transfer the sample to a 25 mL volumetric flask and dilute to volume with Milli-Q/deionized water. The sample should be centrifuged if particulate residue is present and organic residue floating at the top of the sample should be withdrawn with a pasteur pipet. The sample is ready for analysis.
8. Set up the graphite furnace atomic absorption instrument for the analysis of arsenic according to the manufacturer's instructions. Conditions for a Perkin Elmer 2380/HGA-400 are listed below:

Wave length: 193.7 nm

Slit width: 0.7 nm

Peak height mode

Integration time: 5 sec

Background correction: on

Dry: Temp: 160 C Ramp: 5 sec Hold: 30 sec

Ash: Temp: 1050 C Ramp: 5 sec Hold: 25 sec

Atomize: Temp: 2500 C Ramp: 0 sec Hold: 5 sec

Clean: Temp: 2600 C Ramp: 1 sec Hold: 3 sec

Cool: Temp: 30 C Ramp: 1 sec Hold: 5 sec

Sample volume: 20 μ L

Matrix modifier: Nickel Nitrate, 1000 mg/L, 20 μ L

Tube type: Pyrolytically coated L'vov platform type with platforms.

9. Make replicate analyses of all standards and samples.

CALCULATIONS

A. Flame Metals Analysis

1. Calculate the μ g analyte added for each standard addition:

$$\mu\text{g added} = \text{CONC STD ADD } (\mu\text{g/mL}) \times \text{ADD VOL (mL)}$$

2. Prepare a calibration curve plotting standard addition concentration (in μ g) in the horizontal (x) axis versus absorbance (peak height) in the vertical (y) axis using curvilinear regression.

3. Sample aliquot concentration (in μg) is the absolute value of x at point where the calibration curve intercepts the horizontal (x) axis. (See Appendix 1.)
4. Calculate the sample concentration in mg/Kg :

$$\text{CONC}(\text{mg/Kg}) = \text{ALIQ. CONC}(\mu\text{g})/\text{AW}(\text{g})$$

$$\text{AW}(\text{g}) = \text{Aliquot Weight} = \text{SW}(\text{g}) \times \text{AV}(\text{mL})/\text{DV}(\text{mL})$$

SW = Sample Weight, AV = Aliquot Volume, DV = Dilution Volume

B. Graphite Furnace Analysis

1. Generate a calibration curve and regression equation by plotting standard concentration in the horizontal (x) axis versus peak height in the vertical (y) axis and using curvilinear regression.
2. From the calibration curve determine sample analytical concentrations, AC ($\mu\text{g/mL}$) using the regression equation generated in Step 1.
3. Using dilution factors, sample weights, and dilution volumes, calculate the original sample concentrations (mg/Kg).

$$\text{C}(\text{mg/Kg}) = \text{AC}(\mu\text{g/mL}) \times \text{DF} \times \text{DV}(\text{mL}) / \text{SW}(\text{g})$$

Where DF = Dilution factor, DV = Dilution volume (mL), and SW = Sample weight (g).

QUALITY CONTROL

A. Flame Metals Analysis

1. Solvents must be free from impurities. Solvents containing impurities may be suitable for use after distillation.
2. Standard reference materials should be analyzed with each batch of samples.
3. Duplicates should be analyzed in each batch of samples
4. NIST Standard reference materials diluted to the concentrations of analysis should be analyzed with each batch of samples to verify instrument performance and method accuracy.

B. Graphite Furnace Analysis

1. An ICV/CCV and a ICB/CCB must be analyzed after the initial calibration and after every fifth sample to verify the continuing accuracy of the calibration.
2. A method control sample and preparation blank must be prepared and analyzed with each sample batch.
3. For 10% of all samples, or at least once per batch of samples, a matrix spike and duplicate matrix spike shall be prepared and analyzed.
4. A post preparation spike and duplicate post preparation spike must be analyzed in cases where matrix spike recovery and/or matrix spike duplication error are not satisfactory.

M. Z. Z. Z.

Figure 1. Standard Addition Plot.

METALS IN H₂O - ATOMIC ABSORPTION - FLAME
Ag, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Zn

References

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., 1985, pp. 151-160, 162-164.
2. Analytical Methods for Atomic Absorption Analyses, Perkin-Elmer, 1971.

Principles

When a solution containing metals is aspirated into a flame, some of the atoms will be dissociated from their chemical bonds and placed in an unexcited unionized ground state. If a beam of light from a source lamp whose cathode is composed of the element of interest is directed into the flame, the ground state atoms of that element will absorb light at a characteristic wavelength. The amount of light absorbed can be measured and is directly proportional to the concentration of the element in the sample.

Limitations

It is important to use the proper flame conditions to ensure maximum dissociation of the element of interest in order to obtain adequate sensitivity. In some cases, sensitivity will be decreased by the presence of interfering substances (phosphate interference of Ca and Mg) or by an excess degree of ionization of the desired element. These interferences can often be overcome by the addition of a cation that undergoes the undesired reaction more readily than the element of interest (La added in Ca and Mg determination). When extremely diluted solutions are encountered, it may be possible to increase the sensitivity of the analysis by using graphite furnace techniques (EHS M-10).

Equipment

1. Atomic absorption spectrophotometer and recorder
2. Hollow cathode lamps for metals of interest
3. 100 mL volumetric flasks
4. 250 mL volumetric flasks
5. 1-liter beakers

Reagents (stock)

1. Nitric acid, conc. 70% HNO₃ - redistilled
2. Hydrochloric acid, conc. 37-38% HCl
3. Barium chloride, BaCl₂

4. Potassium chloride, KCl
5. Calcium carbonate, CaCO_3
6. Copper powder 99.99+%
7. Iron oxide, 99.99+% - Fe_2O_3
8. Zinc powder, 99.99+%
9. Manganese dioxide, MnO_2
10. Silver nitrate, AgNO_3
11. Potassium dichromate, primary standard $\text{K}_2\text{Cr}_2\text{O}_7$
12. Magnesium metal
13. Lanthanum nitrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
14. Hydrogen peroxide, H_2O_2

Reagents (Prepared)

1. Lanthanum solution (20,000 $\mu\text{g/mL}$ La) - dissolve 62.3 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in dilute HNO_3 and dilute to 1 liter with deionized water. Prepare annually.
2. Potassium solution (20,000 $\mu\text{g/mL}$ K) dissolve 38.13g KCl in deionized water and dilute to 1 Liter. Store in polyethylene. Prepare annually.

Standards

A. Stock Solutions (prepare every 6 months)

1. Barium stock solution - dissolve 1.516g oven dried BaCl_2 in deionized H_2O , add 10 mL conc. HNO_3 and dilute to 1 Liter with deionized H_2O . 1 mL = 1000 μg Ba. Prepare every 6 months.
2. Calcium stock solution - dissolve 2.4972 oven dried CaCO_3 in a minimum volume of HCl and dilute to 1 liter with deionized H_2O . 1 mL = 1000 μg Ca. Prepare every 6 months.
3. Chromium stock solution - dissolve 2.828 g oven dried $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water to give a final volume of 1 liter. 1 mL = 1000 μg Cr. Prepare every 6 months.
4. Copper stock solution - dissolve 1.000 g Cu powder in a minimum volume of 1:1 HNO_3 . Add an additional 10 mL of conc. HNO_3 and dilute to 1 liter with deionized H_2O . 1 mL = 1000 μg Cu. Prepare every 6 months.

5. Iron stock solution - dissolve 1.430 g oven dried Fe_2O_3 in 50 mL of 1:1 HCl and dilute to 1 liter with deionized H_2O . 1 mL = 1000 μg Fe. Prepare every 6 months.
6. Magnesium stock solution - dissolve 1.000 g Mg metal in 1:1 HCl, add an additional 10 mL conc. HCl and dilute to 1 liter with deionized water. 1 mL = 1000 μg Mg. Prepare every 6 months.
7. Manganese stock solution - dissolve 1.5823 g MnO_2 in a minimum volume of 1:1 HCl. Add H_2O_2 as needed to complete dissolution. Add an additional 10 mL of conc. HCl and dilute to 1 liter with deionized water. 1 mL = 1000 μg Mn. Prepare every 6 months.
8. Silver stock solution - dissolve 1.575 g oven dried AgNO_3 in deionized water, add 10 mL conc. HNO_3 and dilute to 1 liter with deionized water. Store away from light in a brown glass bottle. 1 mL = 1000 μg Ag. Prepare every 6 months.
9. Zinc stock solution - dissolve 1.000 g Zn powder in a minimum volume of 1:1 HCl. Add an additional 10 mL of conc. HCl and dilute to 1 liter with deionized H_2O . 1 mL = 1000 μg Zn. Prepare every 6 months.

B. Working Standards

1. Composite Cu, Fe, Mn, Zn standards - pipet 1.0 mL Cu stock, 0.5 mL Fe stock, 0.1 mL Mn stock, and 3.0 mL Zn stock into a 100 mL volumetric flask, add 1 mL conc. HNO_3 and dilute to volume with deionized water.

1 mL = 10 μg Cu
 1 mL = 5 μg Fe
 1 mL = 1 μg Mn
 1 mL = 30 μg Zn

Prepare working standards by pipeting the following amounts of the composite standard into 100 mL volumetric flasks, adding 0.5 mL conc. HNO_3 , and diluting to volume with deionized water. Prepare fresh weekly.

<u>mL Composite Standard</u>	<u>Conc. $\mu\text{g/mL}$</u>			
	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Zn</u>
0	0	0	0	0
1.0	0.1	0.05	0.01	0.3
2.0	0.2	0.1	0.02	0.6
5.0	0.5	0.25	0.05	1.5
8.0	0.8	0.4	0.08	2.4
10.0	1.0	0.5	0.10	3.0

2. Ba standards - Pipet 1.0 mL Ba stock into a 100 mL volumetric flask and dilute to volume with deionized water. 1 mL = 10 μ g Ba. Prepare working standards by pipetting 0, 1.0, 3.0, 5.0, 8.0, and 10.0 mL of the above standard into 100 mL volumetric flasks. Add 5 mL 20,000 μ g/mL K solution to each and 1 mL conc. HNO_3 . Dilute to volume with deionized water. This gives standards containing 0, 0.1, 0.3, 0.5, 0.8, and 1.0 μ g Ba/mL. Prepare monthly.

3. Composite Ag and Cr standards - pipet 1.0 mL Ag stock and 1.0 mL Cr stock into a 100 mL volumetric flask, add 1 mL conc. HNO_3 , and dilute to volume with deionized water.

1 mL = 10 μ g Ag

1 mL = 10 μ g Cr

Prepare working standards by pipeting the following amounts of the composite standard into 100 mL volumetric flasks, adding 0.5 mL conc. HNO_3 , and diluting to volume with deionized water. Prepare fresh weekly.

mL Composite Standard	Conc. (μ g/mL)	
	Cr	Ag
0	0	0
0.1	0.01	0.01
0.3	0.03	0.03
0.5	0.05	0.05
1.0	0.1	0.1

4. Composite Ca and Mg standards - pipet 1.0 mL Mg stock and 10.0 mL Ca stock into a 100 mL volumetric flask, add 1 mL conc. HNO_3 , and dilute to volume with deionized water.

1 mL = 10 μ g Mg

1 mL = 100 μ g Ca

Prepare working standards by pipeting the following amounts of the composite standard into 100 mL volumetric flasks, adding 5 mL of 20,000 μ g/mL La and 0.5 mL conc. HNO_3 , and diluting to volume with deionized water. Prepare fresh monthly.

mL Composite Standard	Conc. (μ g/mL)	
	Ca	Mg
0	0	0
1.0	1	0.1
3.0	3	0.3
5.0	5	0.5
8.0	8	0.8
10.0	10	1.0

Procedure

- A. Sample Collection - collect in glass or polyethylene bottles that have been rinsed with 1:1 HNO_3 and deionized H_2O .

B. Analysis

1. Preliminary preservative treatment - as soon as the water sample is collected, add 5 mL redistilled conc. HNO_3 per liter of sample. Stable up to 6 months.
2. Direct determination of Ag, Cu, Cr, Fe, Mn, Zn - directly aspirate the acidified sample along with the appropriate standards, using the following instrument conditions:

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Slit (nm)</u>	<u>Fuel Mixture</u>	<u>Flame</u>
Ag	328.1	0.7	Air-acetylene	Lean, blue*
Cu	324.7	0.7	Air-acetylene	Lean, blue
Cr	357.9	0.7	Air-acetylene	Rich, yellow**
Fe	248.3	0.2	Air-acetylene+	Lean, blue
Mn	279.5	0.2	Air-acetylene+	Lean, blue*
Zn	213.8	0.7	Air-acetylene+	Lean, blue

* Use 30x scale expansion.

** Use 3-slot burner head and 30x scale expansion.

+ Use deuterium background correction.

3. Determination of Ba

- a. Pipet 2.5 mL 20,000 $\mu\text{g/mL}$ K solution into a dry 50 mL volumetric flask and dilute to volume with sample.
- b. Aspirate the sample and standards using the following instrument conditions:

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Slit (nm)</u>	<u>Fuel Mixture</u>	<u>Flame</u>
Ba	553.6 (276.8 vis.)	0.4	N_2O -acetylene	10mm red zone*

*Use 30x scale expansion

4. Determination of Ca and Mg

- a. Prepare a dilution of the sample by pipeting 1.0 mL of the acidified sample prepared in Procedure B.1 into a 25 mL volumetric flask. Add 1.25 mL of 20,000 $\mu\text{g/mL}$ La solution, 0.25 mL conc. HNO_3 and dilute to volume with deionized H_2O . (Low samples may require less than a 1:25 dilution.) Run every 5th sample in duplicate.

- b. Aspirate the samples and standards using the following instrument conditions:

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Slit (nm)</u>	<u>Fuel Mixture</u>	<u>Flame</u>
Ca	422.7	1.4	Air-acetylene	Lean, blue
Mg	285.2	0.7	air-acetylene+	Lean, blue

+Use deuterium background correction.

Calculations

1. Ag, Cu, Cr, Fe, Mn, Zn

Using the standard values, plot $\mu\text{g/mL}$ metal vs. absorbance. Determine the sample concentration from the calibration curves. Report directly as mg/L in the samples.

2. Ba

Using the standard values, plot $\mu\text{g/mL}$ Ba versus absorbance. Determine the dilution concentration of each sample from the calibration curve. Determine the initial sample concentration as follows:

$$\begin{aligned}\text{mg/L Ba} &= C \times A \\ C &= \mu\text{g/mL measured in dilution} \\ A &= 50/47.5 = \text{normal dilution factor}\end{aligned}$$

3. Ca and Mg

Using the standard values, plot $\mu\text{g/mL}$ metal vs. absorbance. Determine the sample dilution concentration from the calibration curves. Determine the initial sample concentration as follows:

$$\begin{aligned}\text{mg/L Ca or Mg} &= C \times A \\ C &= \mu\text{g/mL measured in dilution} \\ A &= \text{dilution factor (normally 25)}\end{aligned}$$

Quality control all samples - prepare new calibration curve every time values vary by more than 10%. If precision data are out of control, rerun 20% of the samples. If still out of control, evaluate method to find source of error and rerun entire sample set if sample volume permits.

<u>Metal</u>	<u>Accuracy % Recovery</u>	<u>Precision ±mg/L</u>	<u>Range (mg/L)</u>
Ag	98.9	0.001	0.01-0.1
Fe	106.9	0.010	0.02-1.0
Mn	99.3	0.002	0.01-0.5
Cu	109.3	0.037	0.01-0.45
Zn	105.1	0.006	0.01-1.0
Ba	94.3	0.014	0.05-1.0
Cr	102.1	0.003	0.08-0.4
Ca	97.0	0.15	0.5-10
Mg	110.0	0.14	0.05-1.0

Method No. EHS M-10

Title: Metals in Water - Graphite Furnace A.A.
Ag, As, Ba, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Ti, & V
Be 190 MKH

Date Issued: Before 3-83 Approved by: MK Hamilton MKH

Written by: MK Hamilton/D. Palke

Supersedes Method No. _____

Date	Reviewed By	Date	Revised By
		3-14-83	MK Hamilton
		9-23-85	MK Hamilton
		1-11-90	MK Hamilton

Replaced by Method No. _____ Date: _____

METALS IN WATER - GRAPHITE FURNACE A. A.
Aq. As. Be. Cd. Cr. Co. Cu. Fe. Mn. Mo. Ni. Pb. Se. Sn. Ti. V

References

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, 1983, Section 200.
2. Analytical Methods for Furnace Atomic Absorption Spectroscopy, Perkin Elmer, Corporation, 1980.
3. Standard Methods for the Evaluation of Water and Wastewater, 17th. Ed., 1989, Sections 3000 & 3113.
4. USEPA Test Methods for Evaluating Solid Waste, SW-846, 3rd. Ed., 1986, 7000 Series methods.

Principles

In furnace atomic absorption spectroscopy, a sample is thermally atomized into unionized, unexcited atoms in their ground states without the use of a flame. A light beam from a hollow cathode lamp, which is composed of the element to be determined, is directed through the atomization area and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the furnace. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed is a measure of the concentration of that metal in the sample.

Limitations

Background absorption of light from the source beam due to volatilized or atomized matrix material is the major source of interference in furnace atomic absorption. This problem can be alleviated in a number of ways. The addition of a matrix modifier to the sample which increases the volatility of the matrix or decreases the volatility of the analyte allows for separation of the components and achievement of more accurate results. Reduction of the sample size or use of a deuterium background corrector will also help to reduce background absorption. (For samples with complex matrices, the method of standard additions may be needed to completely overcome matrix problems.) The use of proper drying, ashing, and atomizing parameters is also necessary for good results.

Equipment

1. Atomic absorption spectrophotometer
2. Hollow cathode or electrodeless discharge lamps for metals of interest
3. Strip chart recorder & printer
4. HGA 400 graphite furnace plus autosampler
5. Pyrolytically coated graphite tubes, with and without platform

6. Deuterium background corrector
7. EDL power source
8. Various volumetric flasks and pipets

Reagents (Stock)

1. Hydrogen peroxide, 30% H_2O_2
2. Nitric acid, conc. HNO_3 , redistilled
3. Ammonium phosphate, dibasic, $(NH_4)_2HPO_4$
4. Lanthanum nitrate, $LA(NO_3)_3 \cdot 6H_2O$
5. Nickel powder--CLASS 2 SUSPECT HUMAN CARCINOGEN
6. Cadmium metal--CLASS 2 SUSPECT HUMAN CARCINOGEN
7. Potassium dichromate, $K_2Cr_2O_7$
8. Copper powder
9. Lead nitrate, $Pb(NO_3)_2$
10. Silver nitrate, $AgNO_3$
11. Arsenic trioxide, As_2O_3 --CLASS 1 SUSPECT HUMAN CARCINOGEN
12. Sodium hydroxide, $NaOH$
13. Selenium metal
14. Beryllium metal--CLASS 2 SUSPECT HUMAN CARCINOGEN
15. Manganese dioxide, MnO_2
16. Iron oxide, Fe_2O_3
17. Hydrochloric acid, conc. HCl
18. Cobalt metal
19. Ammonium molybdate-- $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
20. Titanium dioxide-- TiO_2
21. Vanadyl sulfate-- $VOSO_4 \cdot 2H_2O$
22. Potassium antimony tartrate-- $K(SbO)C_4H_4O_6 \cdot 1/2 H_2O$
23. Tin metal

24. Ammonium hydroxide-- NH_4OH
25. Ammonium sulfate $(\text{NH}_4)_2 \text{SO}_4$
26. Sulfuric acid, conc. H_2SO_4

Reagents (Prepared)

1. 40% $(\text{NH}_4)_2\text{HPO}_4$ dissolve 40 g $(\text{NH}_4)_2\text{HPO}_4$ in 100 mL volumetric flask and dilute to volume with deionized water. Prepare annually.
2. Lanthanum solution (50,000 $\mu\text{g/mL}$ La)--dissolve 77.9 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in dilute HNO_3 and dilute to 500 mL with deionized water. Prepare annually.
3. Ti dissolving solution--Dissolve 80g $(\text{NH}_4)_2\text{SO}_4$ in 200 mL conc. H_2SO_4 . Prepare annually.

Standards

A. Stock Solutions--Prepare every 6 months

1. Antimony stock solution--Dissolve 0.6855g $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2 \text{H}_2\text{O}$ in deionized water and dilute to 250 mL. DO NOT add acid. 1 mL = 1000 $\mu\text{g/Sb}$.
2. Arsenic stock solution Dissolve 0.3302 g arsenic trioxide, As_2O_3 , in 25 mL deionized water containing 1 g NaOH and dilute to 250 mL with deionized water. 1 mL--1000 $\mu\text{g As}$.
3. Beryllium stock solution--Dissolve 0.250 g Be metal in 15 mL 1:1 HCl, add an additional 2.5 mL conc. HCl and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Be}$.
4. Cadmium stock solution--Dissolve 0.250 g cadmium metal in a minimum volume of 1:1 HNO_3 . Add an additional 2.5 mL conc. HNO_3 and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Cd}$.
5. Chromium stock solution--Dissolve 0.707 g oven dried $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water to give a final volume of 250 mL. 1 mL = 1000 $\mu\text{g Cr}$.
6. Cobalt stock solution--Dissolve 0.250 g cobalt metal in a minimum volume of 1:1 HNO_3 . Add an additional 2.5 mL conc. HNO_3 and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Co}$.
7. Copper stock solution--Dissolve 0.250 g copper powder in a minimum volume of 1:1 HNO_3 . Add an additional 2.5 mL conc. HNO_3 and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Cu}$.
8. Iron stock solution--dissolve 0.3575 g oven dried Fe_2O_3 in 15 mL of 1:1 HCl and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Fe}$.
9. Lead stock solution--Dissolve 0.3995 g oven dried $\text{Pb}(\text{NO}_3)_2$ in 1:1 HNO_3 and dilute to 250 mL with deionized water. 1 mL = 1000 $\mu\text{g Pb}$.

10. Manganese stock solution--Dissolve 0.3956 g MnO_2 in a minimum volume of 1:1 HCl . Add H_2O_2 as needed to complete dissolution. Add an additional 2.5 mL of conc. HCl and dilute to 250 mL with deionized water. 1 mL = 1000 μg Mn.
11. Molybdenum stock solution--Dissolve 0.433 g dried $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in 1% NH_4OH and dilute to 250 mL with deionized water. 1 mL = 1000 μg Mo.
12. Ni solution (1 mL = 1000 μg Ni)--Dissolve 0.250 g Ni powder in a minimum volume of 1:1 HNO_3 . Add an additional 2.5 mL conc. HNO_3 and dilute to 250 mL with deionized water.
13. Selenium stock solution--Dissolve 0.250 g selenium metal in 2 mL conc. HNO_3 . Warm until reaction is complete. Cautiously evaporate just to dryness and dilute to 250 mL with deionized water. 1 mL = 1000 μg Se.
14. Silver stock solution--Dissolve 0.3938 g oven dried AgNO_3 in deionized water. Add 2.5 mL conc. HNO_3 and dilute to 250 mL with deionized water. Store away from light in a brown glass bottle. 1 mL = 1000 μg Ag.
15. Tin stock solution--Dissolve 0.250 g Sn metal in 15 mL conc. HCl (not dilute). Dilute to 250 mL with deionized water, adding more HCl if necessary to keep tin in solution. 1 mL = 1000 μg Sn.
16. Titanium stock solution--Dissolve 0.417 g TiO_2 in 25 mL of $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ dissolving solution and dilute to 250 mL with deionized water. 1 mL = 1000 μg Ti.
17. Vanadium stock solution--Dissolve 0.9768 g $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ in deionized water and dilute to 250 mL. 1 mL = 1000 μg V.

B. Working Standards

Note: Prepare all intermediate and working standards using Milli-Q deionized water.

1. Ag, As, Cd, Cr, Pb, Sb, and Se working standards

- a. Intermediate Cd & Ag--pipet 1.0 mL Cd stock and 2.0 mL Ag stock into a 10 mL volumetric flask and dilute to volume with deionized water. 1 mL = 100 μg Cd & 200 μg Ag. Prepare monthly.

b. Composite Ag, As, Cd, Cr, Pb, Sb and Se standard

Pipet 0.5 mL Cr stock, 1.0 mL each of the As, Pb, Sb, and Se stock solutions and 1.0 mL of the Cd/Ag intermediate solution into a 1000 mL volumetric flask, add 5 mL conc. HNO_3 , and dilute to volume with deionized water. Prepare weekly.

1 mL = 1 μg As, Pb, Sb, Se

- = 0.5 μg Cr
- = 0.2 μg Ag
- = 0.1 μg Cd

- c. Prepare working standards by pipetting the following amounts of the composite standard into 100 mL volumetric flasks adding 0.5 mL redistilled conc. HNO_3 and diluting to volume with Milli-Q deionized water. Prepare weekly.

<u>mL Composite Standard</u>	<u>Conc. $\mu\text{g/mL}$</u>				
	<u>Ag</u>	<u>As. Pb. Se. Sb</u>	<u>Cd</u>	<u>Cr</u>	
0	0	0	0	0	
0.5	0.001	0.005	0.0005	0.0025	
1.0	0.002	0.01	0.001	0.005	
3.0	0.006	0.03	0.003	0.015	
5.0	0.010	0.05	0.005	0.025	
10.0	0.020	0.10	0.010	0.050	

2. Be, Co, Cu, Fe, Ni, Mn, Mo, and Sn Working Standards

- a. Intermediate Be--pipet 1.0 mL Be stock into a 10 mL volumetric flask and dilute to volume with deionized water. 1 mL = 100 μg Be. Prepare monthly.
- b. Composite Be, Co, Cu, Fe, Ni, Mn, Mo and Sn standard--Pipet 1.0 mL each Cu, Fe and Mn stocks, 2.0 mL each Mo, Co and Ni stocks, 10.0 mL Sn stock and 1.0 mL Be intermediate into a 1000 mL volumetric flask, add 5 mL conc. HNO_3 and dilute to volume with deionized water. Prepare weekly.

1 mL = 0.1 μg Be
 = 1 μg Cu, Mn
 = 2 μg Co, Ni, Mo
 = 3 μg Fe
 = 10 μg Sn

- c. Prepare working standards by pipetting the following amounts of the composite standard into 100 mL volumetric flasks, adding 0.5 mL redistilled conc. HNO_3 and diluting to volume with deionized water. Prepare weekly.

<u>mL Composite Standard</u>	<u>Conc. $\mu\text{g/mL}$</u>			
	<u>Be</u>	<u>Cu. Fe. Mn</u>	<u>Sn</u>	<u>Co. Mo. Ni</u>
0	0	0	0	0
0.5	0.0005	0.005	0.05	0.01
1.0	0.001	0.01	0.10	0.02
3.0	0.003	0.03	0.30	0.06
5.0	0.005	0.05	0.50	0.10
10.0	0.010	0.10	1.00	0.20

3. Ti and V Working Standards

- a. Composite Ti and V standard--pipet 2.0 mL stock Ti and V into a 1000 mL volumetric flask, add 5 mL conc. HNO_3 and dilute to volume with deionized water. Prepare weekly.
 1 mL = 2 μg Ti, V

- b. Prepare working standards by pipetting the following amounts of the composite standard into 100 mL volumetric flasks, adding 0.5 mL redistilled conc. HNO_3 and diluting to volume with deionized water. Prepare weekly.

<u>mL Composite Std.</u>	<u>$\mu\text{g/mL Ti \& V}$</u>
0	0
0.5	0.01
2.0	0.04
5.0	0.10
10.0	0.20
15.0	0.30
25.0	0.50

Procedures

A. Sample Collection

1. Collect samples in glass or polyethylene bottles that have been rinsed with 1:1 HNO_3 and deionized water.
2. As soon as the water sample is collected, add 5 mL redistilled conc. HNO_3 per liter of sample as preservative. Stable up to 6 months.

B. Determination of Ag, Be, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V

1. Preparation

- a. Ag, Co, Cu, Be, Fe, Mn, Mo, Ni, Sb, Ti, and V--no treatment needed.
- b. Cd--add 0.2 mL of 40% $(\text{NH}_4)_2\text{HPO}_4$ solution to every 10.0 mL of sample and standard.
- c. Pb--add 1.0 mL of La solution (50,000 g/mL La) to every 10.0 mL of sample and standard.
- d. Cr--add 0.1 mL 30% H_2O_2 to every 10.0 mL of sample and standard.
- e. Sn--normally run without treatment. For improved sensitivity a matrix modifier of 10 μL of 2% $(\text{NH}_4)_3\text{PO}_4$ and 0.5% $\text{Mg}(\text{NO}_3)_2$ is recommended but has not been tried by EHS.

2. Analysis

Set up the PE 2380 AA furnace and autosampler as per Lab Operating Procedure L-8.8. Program HGA 400 Graphite Furnace with the correct program for determination of the desired element as shown on the attached "Entry Sheets."

C. Determination of As and Se

1. Preparation

As and Se--add 0.2 mL of 30% H₂O₂ to every 10.0 mL of sample and standard.

2. Analysis

Set up the PE 2380 AA, furnace and autosampler as per Lab Operating Procedure L-8.8. Include programming of the autosampler to inject into the graphite tube, before injecting the sample or standard, an aliquot of Ni solution (1 mL = 1000 µg Ni) equal in size to the sample aliquot (20 µL).

Program HGA 400 Graphite Furnace with the correct program for determination of the desired element as shown on the attached "Entry Sheets".

Calculations - All Metals

Using the standard values, plot µg/mL metal vs. absorbance. Determine the sample concentration from the calibration curves. Report directly as mg/L in the sample.

W. Hamilton

Element: Ag Matrix: WaterTube Type: CoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	120	400	950	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	25	20	5	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:Samples and standards 0.5% HNO₃

3/83 MKH

Element: As Matrix: WaterTube Type: CoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	120	1050	2500					
RAMP TIME* (s)	1	5	0					
HOLD TIME (s)	30	25	4					
REC								
READ								
BASELINE								
MINI FLOW								
ml/min								
STOP FLOW			X					

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Requires matrix modifier. Use equal aliquots of 1000 ppm Ni standard along with As samples and standards. Inject Ni standard first, then As samples or standard. Samples and standards are 0.5% HNO₃. Add 0.2 mL 30% H₂O₂ to every 10.0 mL of sample or standard. Waste water and other such waters may require preliminary sample digestion.

Element: Be Matrix: WaterTube Type: coated w/platformSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	200	900	2500	2600	30			
RAMP TIME* (s)	5	5	0	1	5			
HOLD TIME (s)	25	20	4	3	5			
REC			X					
READ			X					
BASELINE								
MINI FLOW								
ml/min								
STOP FLOW			X					

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Not yet optimized

PERKIN-ELMER

Element: Cd Matrix: WaterTube Type: CoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	120	550	1050	2700				
RAMP TIME* (s)	1	15	0	1				
HOLD TIME (s)	30	15	6	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Prepare .8% $(\text{NH}_4)_2\text{HPO}_4$ samples and standard. Dissolve 40 g $(\text{NH}_4)_2\text{HPO}_4$ in 100 mL volumetric flask. Add 0.2 mL of this to every 10.0 mL sample or standard. Samples and standards should be 0.5% HNO_3 before dilution with phosphate.

3/83 MKH

Element: Cr Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1050	2400	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	25	25	5	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Samples and standards are 0.5% HNO_3 . Add 0.1 mL 30% H_2O_2 to every 10.0 mL sample or standard.

3/83 MKH

Element: Co Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	900	2300	2700				
RAMP TIME* (s)	1	5	0	1				
HOLD TIME (s)	25	25	6	3				
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Not optimized

Element: Cu Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1000	2450	2700				
RAMP TIME* (s)	1	1	0	1				
HOLD TIME (s)	20	10	10	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Samples and standards are 0.5% HNO_3 .

3/83 MKH

Element: Fe Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1050	2150	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	25	20	5	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Samples and standards are 0.5% HNO_3 .

3/83 MKH

Element: Mn Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1000	2100	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	25	20	5	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Samples and standards are 0.5% HNO_3 .

3/83 MEH

Element: Mo Matrix: WaterTube Type: CoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	120	1400	2500	2700				
RAMP TIME* (s)	1	5	0	1				
HOLD TIME (s)	25	25	10	3				
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Not totally optimized for char step

Element: Ni Matrix: WaterTube Type: CoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	120	1000	2400	2700				
RAMP TIME* (s)	1	5	0	1				
HOLD TIME (s)	25	20	6	3				
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Element: Pb Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	550	1400	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	20	20	5	3				
REC								
READ								
BASELINE								
MINI FLOW			NE					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Requires matrix modifier. Dissolve 77.9 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 500 mL deionized H_2O . Add 1.0 mL of this solution to every 10.0 mL of sample and standard. Sample and standards should be 0.5% HNO_3 before dilution with La solution.

3/83 MKH

Element: Sb Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	900	2000	2700				
RAMP TIME* (s)	1	5	0	1				
HOLD TIME (s)	25	25	10	3				
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Element: Se Matrix: WaterTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1000	2000	2700				
RAMP TIME* (s)	1	10	0	1				
HOLD TIME (s)	30	20	5	3				
REC								
READ								
BASELINE								
MINI FLOW								
ml/min								
STOP FLOW			NE					

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Requires matrix modifier. Use equal aliquots of 1000 ppm Ni standard along with Se samples and standards. Inject Ni standard first, then Se samples and standards. Samples and standards are 0.5% HNO_3 . Add 0.2 mL 30% H_2O_2 to every 10.0 mL of sample and standard. Waste water and other such waters may require preliminary digestion.

3/8 MKH

Element: Sn Matrix: Water (1% HNO₃)Tube Type: UncoatedSample Aliquot: 20 µLKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	110	600	2200	2500				
RAMP TIME* (s)	10	10	0	1				
HOLD TIME (s)	30	15	5	5				
REC			X					
READ			X					
BASELINE								
MINI FLOW								
ml/min								
STOP FLOW			X					

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Above program not optimized - for improved sensitivity may also add 10 µL of 2% (NH₄)₃PO₄ & 0.5% Mg (NO₃)₂ as matrix modifier (have not tried this).

Element: Ti Matrix: H₂OTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1100	2700					
RAMP TIME* (s)	1	8	0					
HOLD TIME (s)	25	25	10					
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES: Not optimized

Element: V Matrix: H₂OTube Type: CoatedSample Aliquot: 20 μ LKeyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP ($^{\circ}$ C)	120	1200	2600	2700				
RAMP TIME* (s)	1	8	0	1				
HOLD TIME (s)	25	25	10	3				
REC								
READ								
BASELINE								
MINI FLOW			X					
ml/min			50					
STOP FLOW								

* When RAMP TIME is zero (Max. Power Heating), Temperature Control requires calibration.

NOTES:

Method No. EHS M-4

Title: TOTAL MERCURY (ORGANIC AND INORGANIC) IN WATER BY FLAMELESS AA

Date Issued: . Before 3/83

Approved by: M K Hamilton *MKH*

Written by: M K Hamilton

Supersedes Method No. EHS M-2

[illegible]

Replaced by Method No. _____

Date: _____

TOTAL MERCURY (ORGANIC AND INORGANIC) IN WATER BY FLAMELESS AA

References

1. Analysis for Mercury in Water, a Preliminary Study of Methods, John A. Winter and Harold A. Clements, Environmental Monitoring Series EPA-R4-72-003, September, 1972.
2. Standard Method for the Examination of Water and Wastewater, 16th Edition, 1985, pp. 171-173.

Principles

For organic mercurial compounds to respond to the flameless atomic absorption (AA) technique, they must first be broken down and converted to mercuric ions. This may be accomplished by oxidizing the compounds with potassium permanganate followed by potassium persulfate. Heating is also necessary to insure the oxidation of any methyl mercuric chloride that may be present. Once the oxidation is complete, the mercury may be determined by flameless AA. Mercury, in an acidic media, is reduced to the elemental state by the addition of stannous chloride. The mercury vapor is then passed through a cell positioned in the light path of the AA. The resulting absorbance is measured and used to determine the amount of mercury present.

Limitations

This method is applicable for surface waters, saline waters, waste-waters, effluents and domestic sewage. Copper and sulfide in concentrations above 20 mg/L may interfere. High chloride concentrations (sea waters, brines, etc.) require the use of additional permanganate. Excess hydroxylamine hydrochloride and purging of the air space in the reagent flask are also required to remove the free chlorine formed as this will absorb at the 253.7 nm mercury wavelength. Some volatile organic materials may also absorb at the mercury wavelength. Such interferences may be eliminated by analyzing the sample as usual and again without the reducing reagents. The difference in the two values will be the true mercury value.

Equipment

1. Atomic absorption spectrophotometer with deuterium background corrector and mercury hollow cathode lamp.
2. Absorption cell, reduction flasks and apparatus as shown in Fig. 1.
3. Covered water bath capable of maintaining a temperature of 90-95° C.
4. 300 mL stoppered BOD bottles.

Figure 1

EHS M-4-2

Reagents (stock)

1. Mercuric chloride - HgCl_2
2. Sulfuric acid, conc. H_2SO_4
3. Nitric acid, conc. - HNO_3
4. Potassium permanganate - KMnO_4
5. Potassium persulfate - $\text{K}_2\text{S}_2\text{O}_8$
6. Stannous chloride - $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
7. Sodium chloride - NaCl
8. Hydrochloric acid, conc. - HCl
9. Hydroxylamine hydrochloride - $\text{NH}_2\text{OH} \cdot \text{HCl}$
10. Magnesium perchlorate - $\text{Mg}(\text{ClO}_4)_2$

Reagents (prepared)

1. KMnO_4 - 5% w/v solution - dissolve 25g KMnO_4 in deionized water and dilute to 500 mL. Prepare every 6 months.
2. $\text{K}_2\text{S}_2\text{O}_8$ - 5% w/v solution - dissolve 12.5g $\text{K}_2\text{S}_2\text{O}_8$ in deionized water and dilute to 250 mL. Prepare every 6 months.
3. NaCl - hydroxylamine hydrochloride - dissolve 30g NaCl and 25g hydroxylamine hydrochloride in deionized water and dilute to 250 mL. Prepare every 6 months.
4. SnCl_2 - 20% w/v in 10% HCl - add 25 mL conc. HCl to about 150 mL deionized water and mix. Add 50g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, mix well and dilute to 250 mL with deionized water. (Solution will be milky). Prepare every 6 months.

Standards

1. Stock Hg solution - 1000 $\mu\text{g/mL}$ - dissolve 1.3535g HgCl_2 in deionized water, add 1 g $\text{K}_2\text{S}_2\text{O}_8$ and dilute to one Liter with deionized water. Prepare every 6 months. Discard in inorganic heavy metal and carcinogen waste container.
2. Intermediate Hg standard - 10 $\mu\text{g/mL}$ - pipet 1.0 mL stock Hg solution into a 100 mL volumetric flask, add 1 mL conc. HNO_3 and dilute to volume with deionized water. Prepare monthly.
3. Working Hg standard - 0.1 $\mu\text{g/mL}$ - pipet 1.0 mL intermediate Hg standard into a 100 mL volumetric flask, add 1 mL conc. HNO_3 and dilute to volume with deionized water. Prepare daily.

Procedure

A. Sample Collection - collect in glass bottles that have been rinsed with 1:1 HNO_3 and deionized water.

B. Analysis

1. Preserve all samples by adding 1 g $\text{K}_2\text{S}_2\text{O}_8/\text{L}$ or by acidifying to pH2 or less with HNO_3 immediately after collection. Samples stable for 2 weeks if refrigerated.
2. Rinse all glassware with 1:1 HNO_3 , and deionized water prior to use.
3. Check $\text{Mg}(\text{ClO}_4)_2$ drying tube and refill if caked or wet.
4. Fill covered water bath and heat to 90-95°C.
5. Prepare standards by pipetting 0, 0.5, 1.0, 3.0, and 5.0 mL of 0.1 $\mu\text{g}/\text{mL}$ Hg standard into a series of BOD flasks. Add enough deionized water to each to give a total volume of 75 mL. Prepare duplicates of all standards.
6. Transfer a 75 mL aliquot of sample or a smaller amount diluted to 75 mL with deionized water to another BOD flask. Run every 10th sample in duplicate. Spike one sample with 1.0 mL of 0.1 $\mu\text{g}/\text{mL}$ Hg standard.
7. Add 5 mL conc. H_2SO_4 and 2.5 mL conc. HNO_3 to each flask.
8. Add 15 mL KMnO_4 solution to each sample and standard and allow to stand until the purple color persists for at least 15 minutes. Add more KMnO_4 if necessary.
9. Add 8 mL persulfate solution to each flask, stopper, and heat for two hours in the water bath at 90-95°C. Record bath temperature on analyst worksheet.
10. Cool the flask and add 6 mL sodium chloride-hydroxylamine hydrochloride solution to each. Swirl until the KMnO_4 color is completely removed giving a colorless solution with no black precipitate.
11. Set up the spectrophotometer and measure the absorbance of each solution as follows:
 - a. Mount the absorption cell on top of the atomic absorption burner. Use the following instrument parameters (P.E. 306).
wavelength - 253.7 nm
Slit - 4 (7A°)
mode - absorbance with background correction

- b. Connect the reduction apparatus, minus reduction flask, to the cell. Adjust vacuum to give an air flow of 0.5 Lpm (10 on rotameter).
 - c.. Place 3 mL SnCl_2 reducing solution in funnel reservoir.
 - d. Transfer sample or standard to reduction flask under reservoir. Add SnCl_2 and immediately connect flask to reduction apparatus, thus sweeping Hg into absorption cell.
 - e. Record absorbance at peak and disconnect flask.
12. Repeat steps c - e for remaining samples and standards making all measurements in the same reduction flask. Run entire standard curve at the beginning and at the end of the analysis.

Calculations

Plot average absorbance vs μg Hg present in standards. Use this calibration curve to determine μg Hg present in the sample aliquots.

$$\mu\text{g/L Hg} = \frac{\mu\text{g found} \times 1000}{\text{mL sample}}$$

Accuracy: 93.4% recovery

Precision: 0.0006 mg/L

Method No. EHS C-2-1

Title: Hexavalent Chromium - Water and Air

Date Issued: 2-73

Approved by: MK Hamilton *MH*

Written by: MK Hamilton

Supersedes Method No. _____

Date	Reviewed By	Date	Revised By
<u>6/80</u>	<u>MK Hamilton</u>	<u>10-1-85</u>	<u>MK Hamilton</u>
<u>10-27-82</u>	<u>MKA</u>		
<u>1/11/90</u>	<u>QAT</u>		

Replaced by Method No. _____

Date: _____

HEXAVALENT CHROMIUM - WATER AND AIR

References

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., 1985, pp. 201-204.
2. NIOSH Manual of Analytical Methods, 3rd Ed., Method 7600, 1984.

Principle

Hexavalent chromium reacts with diphenylcarbazide in acidic solutions to produce a reddish-purple color with maximum absorbance at 540 nm.

Limitations

This method is intended for use with potable water samples or personal air samples collected from an occupational environment. Mercury, iron, copper, molybdenum, nickel, and vanadium interfere with the color development but not in the concentrations normally found in these types of samples. Water samples should be analyzed within 24 hours of collection. For waste samples or other water samples that may have high concentrations of interfering metals, refer to Reference 1 for pretreatment procedures.

Equipment

1. Spectrophotometer for use at 540 nm with 1.0 cm sipper cell.
2. 50 mL graduated cylinders with ground glass stoppers.
3. 50 mL side arm test tubes.
4. 37 mm Buchner funnel.
5. Personal sampling pumps.
6. Styrene cassettes.
7. PVC filters and cellulose backup pads.
8. Screw cap vials.
9. pH meter.
10. 100 mL beakers.
11. Hotplate
12. Water glasses

Reagents (stock)

1. Acetone.
2. 1, 5-diphenylcarbazide

3. Sulfuric acid, conc. H_2SO_4 .
4. Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
5. Sodium hydroxide, NaOH
6. Sodium carbonate, Na_2CO_3
7. High purity nitrogen

Reagents (prepared):

A. Water Analysis

1. Dilute H_2SO_4 solution (0.2N) - slowly add 2.8 mL conc. H_2SO_4 to deionized H_2O and dilute to 500 mL. Prepare annually.
2. Diphenylcarbohydrazide reagent - dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Reagent stable for one month if stored in brown bottle and refrigerated. (Discard if solution becomes discolored.)

B. Air Analysis

1. 0.25 M H_2SO_4 - add 14 mL conc. H_2SO_4 to about 500 mL deionized H_2O and dilute to 1 liter with deionized H_2O . Prepare every 6 months.
2. 6N H_2SO_4 - slowly add 84 mL of conc. H_2SO_4 to deionized H_2O , cool and dilute to 500 mL. Prepare annually.
3. Diphenylcarbazide reagent - dissolve 0.25g 1,5-diphenylcarbazide in 50 mL acetone plus 50 mL deionized H_2O . Store in amber bottle in refrigerator. Prepare monthly.
4. Filter extract solution - Dissolve 5g NaOH plus 7.5g Na_2CO_3 in deionized H_2O and dilute to 250 mL. Prepare every 6 months.

Standards

1. Stock chromium solution - dissolve 2.828g dried anhydrous $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized H_2O and dilute to one liter. 1.0 mL = 1000 μg Cr^{+6} . Prepare every 6 months.
2. Intermediate chromium solution - dilute 5.0 mL of stock chromium solution (1000 $\mu\text{g}/\text{mL}$) to 100 mL with deionized H_2O . 1.0 mL = 50 μg Cr^{+6} . Prepare monthly.
3. Standard chromium solution - dilute 2.0 mL of intermediate chromium solution (50 $\mu\text{g}/\text{mL}$) to 100 mL with deionized H_2O . 1.0 mL = 1.0 μg Cr^{+6} . Prepare daily.

Procedure

A. Sample Collection

1. Water - collect the sample in a glass or plastic container that has been precleaned with HNO_3 , and deionized H_2O . Refrigerate and analyze within 24 hr.
2. Air - using a personal sampling pump precalibrated at 1-2 Lpm, pull air through a 37 mm cassette containing a PVC (5μ) filter with cellulose backup pad. Sample for at least 30 min. Within 1 hr transfer the filter and backup pad to a clean screw cap vial. Analyze within 2 weeks.

B. Water Analysis

1. Using 50 mL graduated cylinders with ground glass stoppers and the standard Cr^{+6} solution ($1\mu\text{g/mL}$), prepare standards containing 0, 0.5, 1.0, 2.0, 3.0, 4.0, and $5.0\mu\text{g Cr}^{+6}$ in 40 mL deionized H_2O .
2. Transfer a 40 mL aliquot of sample to a graduated cylinder. (Filter or centrifuge samples if necessary to remove turbidity.)
3. Use 0.2 N H_2SO_4 to adjust the pH of each sample and standard to 1.0 ± 0.3 . Dilute to 50 mL with deionized H_2O and mix.
4. Add 1.0 mL water analysis diphenylcarbazide reagent to each sample and standard and mix.
5. Let stand five minutes but no more than 15 minutes.
6. Measure absorbance at 540 nm using a 1.0 cm sipper cell.

C. Air Analysis - Soluble Chromates and Chromic Acid

1. Calibrate the 50 mL side arm test tubes by pipetting 20.0 mL deionized H_2O into each and marking the bottom of the meniscus. Empty and dry the tubes.
2. Remove the sample filter from the screw cap vial and place it in the Buchner funnel set up as shown. Cover the filter with 5 mL 0.25 M H_2SO_4 and let stand for 5 min.

3. Using the vacuum, pull the H_2SO_4 through the filter into the tube. Rinse the filter and vial twice with small amounts of 0.25 M H_2SO_4 and adjust the sample volume to the 20 mL mark with additional H_2SO_4 as needed.
 4. Prepare a spike by pipetting 20 μL of the 50 $\mu\text{g}/\text{mL}$ Cr^{+6} standard onto a PVC filter place in a Buchner funnel. Proceed as in Steps 2 and 3.
 5. Prepare standards by pipetting 10, 20, 50, 100, and 200 μL of the 50 $\mu\text{g}/\text{mL}$ Cr^{+6} standard into calibrated tubes and diluting to the 20 mL mark with 0.25 M H_2SO_4 . This gives standards containing 0.5, 1.0, 2.5, 5, and 10 μg Cr^{+6} .
 6. Add 0.5 mL air analysis diphenylcarbazide reagent to each sample and standard and mix.
 7. Within 5-15 min measure the absorbance at 540 nm using 1 cm sipper cell.
- D. Air Analysis - insoluble chromates and all Cr^{+6} in the presence of iron or other reducing agents.
1. Calibrate the 50 mL side arm test tubes as for soluble chromate analysis (Section C.1).
 2. Remove the sample filter from the screw cap vial and place it in a 100 mL beaker.
 3. Rinse the vial with 5 mL of filter extract solution and add this to the beaker.
 4. Prepare a spike by pipetting 20 μL of the 50 $\mu\text{g}/\text{mL}$ Cr^{+6} standard onto a PVC filter placed in a 100 mL beaker. Add 5 mL of filter extract solution and proceed as with the samples.
 5. Purge the head space above the solutions with nitrogen and repeat the purge 2-3 times during the extraction.
 6. Cover the beakers with watchglasses and heat to near boiling on a hot plate. Continue heating, with occasional swirling and purging, for 30-45 minutes. DO NOT allow the solution to evaporate to dryness as Cr^{+6} may be lost. A brown colored PVC filter is an indication of such loss.
 7. Cool the solutions and filter through a 5 μ PVC filter using a Buchner funnel and precalibrated 50 mL side arm test tube. Rinse the filter and beaker with deionized H_2O , keeping the final volume below 18 mL.
 8. Add 1.9 mL of 6N H_2SO_4 to each sample and swirl carefully to mix. Let the samples sit for several minutes, until the vigorous gas evolution ceases. Occasional swirling will help speed up the gas removal.

9. When gas evolution ceases dilute the solution volumes to 20 mL.
10. Prepare standards and proceed with color development as for soluble chromates (Section C, Steps 5-7).

Calculation

1. Plot $\mu\text{g}/\text{Cr}^{+6}$ vs absorbance.
2. Determine $\mu\text{g}/\text{Cr}^{+6}$ in the sample from the calibration curve.
3. Calculate air or water concentrations as follows:

$$\text{Air} \quad \text{mg/m}^3 \text{ Cr}^{+6} = \frac{\mu\text{g Cr}^{+6}}{\text{L air}}$$

$$\text{Water} \quad \text{mg/L Cr}^{+6} = \frac{\mu\text{g Cr}^{+6}}{40 \text{ mL H}_2\text{O}}$$

Method No. EHS C-3

Title: Cyanide - Colorimetric Water & Air

Date Issued: Before 2-17-83 Approved by: MK Hamilton MKH

Written by: MK Hamilton

Supersedes Method No. _____

Date	Reviewed By	Date	Revised By
<u>1-2-86</u>	<u>MKH</u>	<u>2-17-83</u>	<u>MKH</u>

Replaced by Method No. _____ Date: _____

2-17-83

CYANIDE - COLORIMETRIC - WATER & AIR

Reference

1. Manual of Methods for Chemical Analysis of Water & Wastes, EPA-600-14-79-020 U.S. Environmental Protection Agency, 1979, Method 335.1.
2. Analytical Chemistry, Vol. 44, No. 11, 1972, pp. 1845-46, "Determination of Nanogram Quantities of Simple & Complex Cyanides in Water," P. D. Goulden, et. al.
3. NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 3, S250, 1977.

Principle

Cyanides in the aqueous solution are converted to hydrogen cyanide by distillation with acid and are absorbed in NaOH solution. Air samples are collected on membrane filters (particulate) plus 0.1N NaOH absorbing solution (HCN). The CN^- in the distillate, absorbing solution or desorbed filter is converted to cyanogen chloride, $CNCl$, by reacting with chloramine-T at a pH less than eight. $CNCl$ forms a colored dye on addition of pyridinebarbituric acid, the absorbance of which is measured at 578 nm.

Limitations

Because most cyanides are highly reactive and unstable, water samples should be made alkaline immediately after collection by adding 4 mL of 6N NaOH per Liter. The cyanide analysis should be performed within 24 hours of collection. Preliminary treatment may be necessary to remove interferences from sulfides and oxidizing agents. The distillation is important not only for removing interferences from varying salt concentrations, but also for converting any complex cyanides to simple CN^- . Only the cobalticyanide complex is not converted by this procedure. Filters from air sampling should be desorbed as soon as possible after sampling. Samples should be analyzed within 2 hours of desorption.

Equipment

1. Distillation apparatus shown on next page or equivalent (aqueous)

Cyanide Distillation Apparatus

1. Electric heating mantle
 2. 1-Liter, two neck distilling flask
 3. Inlet tube tapered to 8 mm i.d. at lower end
 4. Friedrichs condensor
 5. Glass connecting tube
 6. Scrubber-50ml buret with side arm at bottom and overflow bulb at top. Partially filled with glass beads.
 7. Rubber stopper with glass tube for connecting system to hood vacuum.
 8. Tygon tubing to attach connecting tube to buret side arm.
2. Spectrophotometer for use at 578 nm with 1.0 or 4.0 cm cells
 3. 250 ml volumetric flasks (aqueous)

4. 100 mL volumetric flasks
5. Whatman #41 filter paper (aqueous)
6. Long-stemmed funnels (aqueous)
7. GF/A glass fiber filter paper (aqueous)
8. Personal sampling pumps (air)
9. Styrene cassettes (air)
10. Midget impingers (air)
11. 0.8 μ cellulose acetate filters and cellulose backup pads (air)
12. Large test tubes (air)

Reagents (Stock)

1. Starch
2. Potassium iodide, KI
3. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$
4. Lead carbonate, PbCO_3
5. Ascorbic acid
6. Sodium hydroxide, NaOH
7. Cuprous chloride, Cu_2Cl_2
8. Sulfuric acid, con. H_2SO_4
9. Hydrochloric acid, conc., HCl
10. Sodium dihydrogen phosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
11. Potassium cyanide, KCN
12. Potassium hydroxide, KOH
13. Chloramine-T
14. Pyridine

15. Barbituric acid
16. Silver nitrate, AgNO_3
17. Paradimethylaminobenzalrhodanine [5-(p-Dimethylamino benzylidene) rhodamine]
18. Acetone

Reagents (Prepared)

A. Water Analysis

1. Starch-iodide paper - Stir 5 g of starch into 100 mL of deionized H_2O , boil and add 0.5 g KI. Impregnate strips of Whatman #41 filter paper with this solution, dry and store in glass bottle.
2. Lead acetate paper - Prepare a saturated solution of lead acetate in deionized H_2O (~45 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}/100 \text{ ml}$). Impregnate strips of Whatman #41 filter paper with this solution, dry and store in glass bottle.
3. 1 N NaOH - Dissolve 40.0 g NaOH in deionized H_2O and dilute to 1 Liter. Prepare annually.
4. Cuprous chloride reagent - Weight 20 g Cu_2Cl_2 into an 800 mL beaker. Wash twice, by decantation, with 250 mL portions of dilute (1+49) H_2SO_4 and twice with deionized H_2O . Add about 250 mL deionized H_2O , followed by small additions of conc. HCl until the Cu_2Cl_2 dissolves. (At this point the solution should be clear and pale green. Brown or dark discoloration indicates presence of cupric salts and solution must be discarded.) Dilute to 1 Liter with deionized H_2O adding conc. HCl as needed to keep the Cu_2Cl_2 in solution. Store in a tightly stoppered bottle containing a few lengths of pure copper wire extending from the bottom to the mouth of the bottle. Prepare fresh when solution darkens.

B. Air or Water Analysis

1. Sodium dihydrogen phosphate (1M) - Dissolve 13.8 g $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in deionized water and dilute to 100 mL. Store in refrigerator. Prepare every 6 months.
2. Chloramine-T solution - Dissolve 1.0 g chloramine-T in deionized H_2O and dilute to 100 mL. Store in refrigerator. Prepare weekly.
3. Pyridine-barbituric acid reagent - Place 15 g barbituric acid in a 250 mL volumetric flask and add just enough deionized H_2O to wash down the sides of the flask and wet the barbituric acid.

Add 75 mL pyridine, mix, add 15 mL conc. HCl, mix until dissolved, cool and dilute to volume with deionized H₂O. (Dissolution complete only after adding H₂O). Store in dark. Prepare weekly.

4. CN⁻ Rhodanine indicator - dissolve 0.02 g paradimethylaminobenzal-rhodanine in acetone and dilute to 100 mL. Prepare annually.

C. Air Analysis

1. 0.1 N NaOH - Dissolve 4.0 g NaOH in deionized H₂O and dilute to 1 Liter. Prepare annually.

Standards

1. Standard AgNO₃ (0.0141N) - Dissolve 2.395 g AgNO₃ in deionized H₂O and dilute to 1 Liter. Store in brown bottle. Standardize monthly against standard NaCl as in EHS C-5.
2. Stock cyanide solution - Dissolve 2.51 g KCN and 2 g KOH in deionized H₂O, dilute to 1 Liter and standardize as follows:

Pipet 10.0 mL of KCN solution into a 250 mL conical beaker. Add 100 mL deionized H₂O and adjust pH to 11 or above with 1 N NaOH. Add 0.5 mL CN indicator and titrate with standardized AgNO₃ solution to first color change from canary yellow to a salmon hue. Also titrate a reagent blank.

$$\begin{aligned}
 & \text{Ag}^+ + 2\text{CN}^- \rightarrow \text{Ag}(\text{CN})_2^- \\
 \text{mg/mL CN}^- &= \frac{(\text{mL AgNO}_3)(\text{N AgNO}_3)}{10.0 \text{ mL CN}} \times \frac{52.02 \text{ mg CN/mL}}{1 \text{ N CN}} \\
 &= (\text{mL AgNO}_3)(\text{N AgNO}_3) \times 5.202
 \end{aligned}$$

Stock CN⁻ solution must be restandardized weekly.

2. Intermediate cyanide solution - Dilute 5.0 mL of stock cyanide solution (or the amount necessary to contain 5000 µg CN⁻) to 100 mL with deionized H₂O. 1 mL = 50 µg CN⁻. Prepare fresh daily.
3. Working cyanide solution - Dilute 2.0 mL of intermediate cyanide solution to 100 mL with deionized H₂O. 1 mL = 1 µg CN⁻. Prepare fresh daily.

Procedure

A. Water Analysis

I. Collection

1. Collect the sample in glass or plastic containers.
2. Add 4mL of 6 N NaOH per Liter of sample and refrigerate. Analyze within 24 hours.

II. Pretreatment and Distillation

Carry an alkaline CN standard (~ 0.02 mg/L) through the entire procedure to determine recovery.

1. Sulfide removal - place a drop of sample on a strip of lead acetate test paper. If the test is negative (no darkening), skip to Step 2 for oxidizing agent removal. If the test is positive (dark color), add small increments of PbCO_3 to 502 mL of the alkaline sample. Repeat until no more blank PbS forms. Avoid excess PbCO_3 or long period of contact. Filter through GF/A filter paper into a 1-Liter two neck distilling flask, rinse precipitate with 10 mL deionized H_2O and add washings to the filtrate.
2. Oxidizing agent removal - check the filtrate from sulfide removal with starch-iodide paper. If test is positive (blue-black color), add ascorbic acid crystals until a negative test (no color) is obtained. Add an additional 0.3 g ascorbic acid to each sample.
3. Set up distillation apparatus in a well ventilated hood.
4. Add 30 mL of 1 N NaOH to the 50 mL buret scrubber.
5. Connect the flask containing the sample (502 mL) to the distillation apparatus and adjust the vacuum so that air enters at a rate of about 2-3 bubbles per second. (This should be fast enough to prevent sample backup in the delivery tube.)
6. Slowly add 25 mL conc. H_2SO_4 through the air inlet tube, rinse the tube with deionized H_2O and allow airflow to mix the flask contents for 3 minutes.
7. Add 10 mL Cu_2Cl_2 reagent through the air inlet tube and again rinse with deionized H_2O .
8. Heat to rapid boiling but do not flood the condensor. Watch the air flow rate closely as the solution begins to boil and adjust it if necessary to prevent sample backup in the inlet tube. Reflux for one hour, then turn off heat but continue air flow for 15 minutes.

9. Transfer the 1 N NaOH scrubber solution to a 250 mL volumetric flask. Rinse the buret and the connecting tube from condensor to buret and add the rinsings to the volumetric flask. Dilute to 250 mL with deionized H₂O.

If stable complex cyanides are present, repeat the distillation.

III. Colorimetric Determination

1. Prepare a series of standards by pipeting 0, 0.5, 1.0, 3.0, and 5.0 mL of the 1 µg/mL CN⁻ standard into 100 mL volumetric flasks. Add 6 mL of 1 N NaOH to each flask plus enough deionized H₂O to give 50 mL of solution. This gives standards containing 0, 0.5, 1.0, 3.0, and 5.0 µg CN.
2. Pipet a 50 mL aliquot of sample distillate into a 100 mL volumetric flask.
3. To each sample and standard add 15 mL NaH₂PO₄ solution and 2.0 mL chloramine-T and mix.
4. Immediately add 5.0 mL pyridine-barbituric acid reagent, mix, dilute to volume with deionized H₂O and mix again.
5. After 8 minutes, but before 15 minutes, measure the absorbance of the solution at 578 nm using 1.0 or 4.0 cm cells and deionized H₂O as reference.

B. Air Analysis

I. Collection

1. Using a personal sampling pump precalibrated at 0.5 - 1 Lpm pull air through a sampling train consisting of a 37mm cassette containing an 0.8 µm cellulose acetate filter followed by a midget impinger containing 15 mL of 0.1 N NaOH. Sample for at least 30 minutes.
2. Place the membrane filter in a small jar or tube and desorb with 25 mL of 0.1 N NaOH. Stir occasionally for 30 minutes to complete the dissolution. Analyze the solution within 2 hours.
3. Prepare Blank and spiked filters and desorb in a similar manner.

II. Colorimetric determination

1. Pipet 5.0 mL of absorbing solution from each desorbed filter and impinger into a large test tube.

2. Prepare a series of standards by pipetting 0, 50, 100, 300 & 500 μL of the 1 $\mu\text{g}/\text{mL}$ CN standard into large test tubes and diluting to 5.0 mL with 0.1N NaOH. This gives standards containing 0, 0.05, 0.1, 0.3, and 0.5 μg CN.
3. To each sample and standard add 1.5 mL NaH_2PO_4 solution and 0.2 mL chloramine - T and mix.
4. Immediately add 0.5 mL pyridine-barbituric acid reagent and mix.
5. Add 2.8 mL deionized H_2O and mix again.
6. After 8 minutes but before 15 minutes measure the absorbance of the samples and standards at 578 nm using 1.0 or 4.0 cm cells and deionized H_2O as reference.

Calculation:

A. Water

1. Plot μg CN^- present in the 50 mL aliquot vs. absorbance.
2. Determine μg CN^- present in the sample aliquots from the above curve.

$$\begin{aligned}\text{mg/L } \text{CN}^- &= \frac{\text{aliquot } \mu\text{g } \text{CN}^-}{500 \text{ mL}} \times \frac{250 \text{ mL}}{50 \text{ mL}} \\ &= \text{aliquot } \mu\text{g } \text{CN}/100\end{aligned}$$

Use the standard carried through the distillation to determine % recovery and correct results for this if less than 100%.

B. Air

1. Plot μg CN present in the 5 mL aliquot versus absorbance
2. Determine μg CN present in each sample aliquot from the above curve.

Particulate CN

$$\text{mg/m}^3 \text{CN} = \frac{(\text{aliquot } \mu\text{g } \text{CN})(A)}{B \times V}$$

A = mL 0.1 N NaOH used to desorb filter. (25 mL)
 B = Sample aliquot (5mL)
 V = m³ air sampled

Gaseous HCN

$$\text{mg/m}^3\text{CN} = \frac{(\text{aliqu. } \mu\text{gCN})(A)}{B \times V}$$

A = mL 0.1N NaOH impinger absorbing soln. (15 mL)
 B = Sample aliquot (5 mL)
 V = m³ air sampled
 2 3-15-83 p

Revised 2/83 MK Hamilton

Method No. EHS A-7

Title: Inorganic Anions in Water Using Ion Chromatography

Date Issued: 1-9-90

Approved by: M.K. Hamilton

Written by: P.A. Thurman

Supersedes Method No. New

Date	Reviewed By	Date	Revised By

Replaced by Method No. _____

Date: _____

INORGANIC ANIONS IN WATER USING ION CHROMATOGRAPHY

Reference

1. EPA Methods for Chemical Analysis of Water and Wastes, Method 300.0, EPA-600/4-84-017, March 1984.
2. Standard Methods for the Analysis of Water and Wastewater, 17th Ed., 1989, pp 4-2 through 4-6, Section 411C.
3. Nelson Analytical Model 4660X Operators Manual, 1986, pp 1-1 -> 13-8.
4. Dionex System 2010i Operator's Manual.

Principles

Use of ion chromatography provides a rapid simultaneous analyses of many common anions, with fluoride, chloride, nitrate, nitrite, phosphate, and sulfate being the most common. The method can also be used for other anions such as sulfite.

The sample is injected into a carbonate/bicarbonate eluent stream and passed through a series of ion exchangers. The anions are separated by a strongly basic anion exchanger (separator or guard column) and then converted to their highly conductive acidic form by an acidic cation exchanger (suppressor column). The separated acidified anions are measured by conductivity.

Limitations

This method is not approved for the analysis of fluoride in drinking water samples. That analysis must be done by specific ion electrode (EHS F-2).

Substances which have retention times coinciding with any of the anions of interest will interfere, such as, low molecular weight organic acids in high concentrations. Due to small sample volumes used, contamination from dirty and/or turbid samples must be avoided. All samples are filtered through a Millex-HV 0.45 μ filter unit when injected to prevent column plugging.

Equipment

1. Ion Chromatograph (Dionex 2010i) connected via analog to digital converter to a data station (Hewlett Packard Model 300, Series 9000).
2. Anion separator column, with styrene divinybenzene-based low-capacity pellicular anion exchange resin (HPIC-AS4A).
3. Guard column, same as separator column except 4 x 50 mm HPIC-AG4A.
4. Micro Membrane Suppressor.
5. Auto regen accessory for suppressor column.

6. High pressure in-line filter to protect guard column.
7. Deionized water finishing system--Millipore MilliQ-Plus.
8. Syringes, 10cc leur slip tip.
9. Sample filters (Millipore Millex HV 0.45 μ m).
10. 100 mL volumetric flasks, misc pipets, etc.

Reagents (stock)

1. Sodium Bicarbonate (NaHCO_3)
2. Sodium Carbonate (Na_2CO_3)
3. Sulfuric Acid, conc.--(H_2SO_4)
4. Sodium Sulfate (Na_2SO_4)
5. Potassium Nitrate (KNO_3), 99.99+%
6. Sodium Chloride (NaCl), 99.99+%
7. Sodium Fluoride (NaF), 99.99+%
8. Potassium Phosphate, Monobasic (KH_2PO_4), 99.99+%
9. Potassium Sulfate (K_2SO_4), 99.99+%
10. Sodium Nitrite (NaNO_2), 99.99+%
11. Nitrogen

Reagents--Prepared

1. Eluant solution: 1.7mM NaHCO_3 --1.8 mM Na_2CO_3

Dissolve 0.5712g NaHCO_3 and 0.7632g Na_2CO_3 in deionized water and dilute to 4 liters with Millipore water.

2. Regenerant solution: 0.025 N H_2SO_4

Dilute 0.7 mL conc. H_2SO_4 to 1 liters with deionized water.

3. Column Cleaning Solution--0.1M Na_2CO_3

Dissolve 10.6g Na_2CO_3 in deionized water and dilute to 1 liter. Prepare fresh when needed.

4. Column cleaning solution--0.1M Na_2SO_4 --Dissolve 14.2g Na_2SO_4 in deionized water and dilute to 1 liter. Prepare fresh when needed.

Standards

1. Stock standards (prepare all with Millipore finished deionized water)

- a. Nitrate, 100 $\mu\text{g/mL}$ $\text{NO}_3\text{-N}$ or 445 $\mu\text{g/mL}$ NO_3 . Dissolve 0.361g dried KNO_3 in deionized water and dilute to 500 mL. (Stable for six months).
- b. Chloride, 500 $\mu\text{g/mL}$. Dissolve 0.412g dried NaCl in deionized water and dilute to 500 mL. (Stable for 6 months)
- c. Fluoride--1000 $\mu\text{g/mL}$. Dissolve 1.1106g NaF in deionized water and dilute to 500 mL. Store in polyethylene. (Stable for six months.)
- d. Phosphate--500 $\mu\text{g/mL}$. Dissolve 0.3582g KH_2PO_4 in deionized water and dilute to 500 mL. Store in polyethylene. (Stable for three months.)
- e. Sulfate--1000 $\mu\text{g/mL}$. Dissolve 0.4517g of 100.4 percent K_2SO_4 in deionized water and dilute to 250 mL. Store in polyethylene. (Stable for six months.)
- f. Nitrite--1000 $\mu\text{g/mL}$ NO_2 or 305 $\mu\text{g/mL}$ $\text{NO}_2\text{-N}$. Dissolve 0.750g dried NaNO_2 in deionized water and dilute to 500 mL. (Stable for three months.)

2. Intermediate Standards (Prepare with Millipore finished deionized water.)

- a. To a 100 mL volumetric flask add:

20.0 mL of 500 ppm Cl	= 100 $\mu\text{g/mL}$
9.0 mL of 445 ppm NO_3	= 40 $\mu\text{g/mL}$
20.0 mL of 1000 ppm SO_4	= 200 $\mu\text{g/mL}$
20 mL of 500 ppm PO_4	= 100 $\mu\text{g/mL}$
4.0 mL of 1000 ppm NO_2	= 40 $\mu\text{g/mL}$

Dilute to volume with deionized water

- b. In a separate 100 mL volumetric flask pipet, 2 mL of 1000 ppm F. Dilute to 100 mL with deionized water (20 $\mu\text{g/mL}$). Prepare intermediate standards monthly.

3. Working Standards

Pipet the following amounts of the appropriate intermediate standards into 100 mL volumetric flasks and dilute to 100 mL with Millipore finished deionized water. (Prepare weekly.)

mL Intermediate Standard	Conc. $\mu\text{g/mL}$					
	<u>F</u>	<u>Cl</u>	<u>NO₃</u>	<u>PO₄</u>	<u>SO₄</u>	<u>NO₂</u>
0	0	0	0	0	0	0
0.5	too low	0.5	0.2	0.5	1.0	0.2
1.0	0.2	1.0	0.4	1.0	2.0	0.4
2.0 (2.5 Fluoride)	0.5	2.0	0.8	2.0	4.0	0.8
5.0	1.0	5.0	2.0	5.0	10.0	2.0
20.0 (25 Fluoride)	5.0	20.0	8.0	20.0	40.0	8.0

Procedure

1. Instrument Start-up

See Laboratory Operating Guides L-8.4 for instrument start-up instructions.

2. Instrument Calibration

Run standards first to establish the initial calibration curve. See Appendix 1 to set-up calibration curve on the data station.

- a. It is not always necessary to recalibrate the instrument each day it is run. Check the existing calibration by running 2 or 3 standards and calculating their values using the existing calibration curve-if the true values are within ten percent of the calculated values, the calibration curve is still valid and may be used. If calculated values are not within ten percent of the true values, rerun standards and make a new calibration curve.

3. Sample injections: All samples and standards are filtered through Millex HV 0.45 μ filters. For data acquisition set-up see Laboratory Operating Guide L-8.4, Section C.

- a. Turn auto offset-on.
- b. Fill a 10 mL leur tip syringe with standard or sample.
- c. Attach syringe to the sample port.

- d. Inject 1-2 mL of the sample.
- e. Press the load-inject button to inject. At the same time start the computer by pushing the start button on the A/D box 707.

4. Sample Protocol

- a. Run every tenth sample in duplicate. (At least one sample must be run if there are less than ten samples.)
- b. Spike at least one sample or one for every ten samples run.
- c. Run a standard after every fifth sample to validate the calibration curves.
- d. Dilute as necessary samples with concentrations outside the calibration range.
- e. Run 2-3 standards at the end of the run to validate the calibration curves.

Calculations

Sample concentrations are normally calculated by the computer and printed out at the end of each sample run. Manually check the calculated sample values against the calibration curve. Verify that any dilution factors are calculated in the result. Also check validity of all QC and standard check data.

Appendix 1

Preparing a calibration curve using the "Metgen" program (method generation program).

1. Run each standard in duplicate. Record and average the heights for each component at each concentration level.
2. Proceed to the "Metgen" program by pressing the F1 key.
3. Enter the "Method File Name" (2010IC2 is currently being used).
4. Select the menu by pressing the key corresponding to "Metgen Menu" on the menu bar.
5. Select "Quant. Opts" by pressing the F5 key.
6. Select "Review Opts" by pressing the F1 key.
7. Select "Comp. Names" by pressing the F4 key.
8. Select "Cal. Amt. List" by pressing the F5 key.
9. Enter the averaged heights for each component at each concentration level as follows.
 - a. Position the cursor in the height column by pressing "Return."
 - b. Enter the averaged height for the component at the current level.
 - c. Move to the next level by pressing "Return" until the cursor is in the appropriate height column.
 - d. Press "Return" after the last height is entered.
 - e. Select "Cal. Amt. List" by pressing the F5 key.
 - f. Repeat Step 9 until all heights have been entered for all components.
10. Select the key corresponding to "Quant Menu" on the menu bar.
11. Select the key corresponding to "Metgen Menu" on the menu bar.
12. Select "Store Method" by pressing the F7 key.
 - a. Press "Return" when the name of the method (2010IC2) is displayed.
 - b. Press "Return" at the "Overwrite this File" prompt. (Method is now saved.)
13. Press the key corresponding to "New Program" on the menu bar.
14. Press "Return" at the next prompt. (XTRA CHROM II--Core program menu will appear.)
15. Proceed to the "Acquire" program.

OT

Method No. EHS F-2-1

Title: Fluoride - Specific Ion Electrode

Date Issued: February 1973

Approved by: M. K. Hamilton *MKH*

Written by: M. K. Hamilton

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

FLUORIDE - SPECIFIC ION ELECTRODE

References

1. Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985, pp. 357-359.
2. Instruction Manual - pH/Ion Meter, 135 Corning, 1979.
3. Instruction Manual - Fluoride Electrode Model 94-09, Orion Research, Incorporated, 1970.

Principles

A fluoride ion activity electrode with a laser-type doped single lanthanum fluoride crystal is used with a saturated calomel reference electrode to measure fluoride concentration. This is done by measuring the potential established across the electrode crystal in the presence of fluoride ions.

Limitations

Polyvalent cations such as Al (III), Fe (III), and Si (IV) complex fluoride ions. In alkaline solutions, the hydroxyl ion also interferes with the electrode response to fluoride ions. Variations in the total ionic strength of the solutions being measured cause fluctuations in results. All of these problems can be overcome by diluting 1:1 with TISAB (Total Ionic Strength Adjustment Buffer).

Equipment

1. pH/Specific ion meter - Corning 135 or equivalent.
2. Single junction sleeve-type reference electrode.
3. Fluoride specific ion electrode.
4. Magnetic stirrer and small stirring bars.
5. 100 mL plastic beakers.

Reagents (stock)

1. Anhydrous sodium fluoride, NaF.
2. Glacial acetic acid.
3. Sodium chloride, NaCl.
4. Sodium citrate dihydrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$.
5. Sodium hydroxide, NaOH.
6. Reference electrode filling solution.

Reagents (prepared)

1. 6N NaOH - dissolve 120g NaOH in deionized H₂O and dilute to 500 mL. Prepare annually.
2. TISAB buffer solution - add the following to approximately 500 mL deionized H₂O in a 1-Liter beaker:
57 mL glacial acetic acid
58g NaCl
12g sodium citrate (Na₃C₆H₅O₇ · 2H₂O)

Stir to dissolve. Use a pH meter NaOH pellets and 6N NaOH to adjust the pH to 5.0-5.5. Cool and dilute to one Liter. Prepare every 6 months.

Standards

1. Stock fluoride solution - dissolve 1.105g anhydrous NaF in deionized H₂O and dilute to 500 mL. 1 mL = 1000 µg F. Prepare every 6 months.
2. Intermediate fluoride dilution - dilute 1.0 mL of stock fluoride solution to 100 mL with deionized H₂O. 1 mL = 10 µg F. Prepare monthly.
3. Working fluoride standards - pipet 0.5, 2.5, 5.0, 25.0, and 50.0 mL of intermediate fluoride dilution into 100 mL volumetric flasks. Add 50 mL TISAB solution and dilute to volume with deionized H₂O. Store in polyethylene bottles. These are equivalent to 0.1, 0.5, 1.0, 5.0, and 10.0 µg/mL F standards before addition of TISAB. Prepare monthly.

ProcedureA. Sample collection

Collect in polyethylene bottles which have been rinsed with deionized H₂O. Store at 4°C up to 7 days. No preservative.

B. Analysis

1. Set Corning 135 meter to "activity" mode and reset. Be sure the temperature probe is in place.
2. Rinse electrodes and blot dry with soft tissue, being careful not to scratch the LaF crystal.
3. Calibrate the meter as follows, using plastic beakers for all fluoride measurements:
 - a) Enter 5.0 for "Cal.1", 0.1 for "Blank" and 0.5 for "Cal. 2". Also enter the slope value of -60.000.
 - b) Immerse the electrodes and temperature probe in the 5.0 µg/mL F standard. Stir for 3 minutes and then press "Cal.1" when stabilized.

- c) Rinse and dry the electrodes and get readings on the 0.1 and 0.5 $\mu\text{g/mL}$ F standards after stirring each for 3 minutes. Press "Blank" after the 0.1 $\mu\text{g/mL}$ standard stabilizes and "Cal. 2" after the 0.5 $\mu\text{g/mL}$ standard.
 - d. Read and record the new slope which should be near - 60mV.
 - e. Take readings on all five standards (0.1 to 10.0 $\mu\text{g/mL}$ F).
- 4. Prepare samples by pipetting 10.0 mL of sample plus 10.0 mL TISAB solution into a plastic beaker. Run every 10th sample in duplicate.
 - 5. Measure the fluoride concentration by immersing the electrodes in the buffered solution, stirring three minutes and recording the meter reading. Check instrument calibration by running a standard after every 5th sample. Rerun the entire calibration curve at the end of the analysis.

Calculation

- 1. Prepare a calibration curve by plotting $\mu\text{g/mL}$ F vs meter reading on 2 cycle log paper.
- 2. Determine the sample concentration in $\mu\text{g/mL}$ (mg/L) from the calibration curve.

Precision

In the EHS laboratory using drinking water samples at concentrations of 0.2 to 9.0 $\mu\text{g/mL}$ F, the standard deviation was 2% of the average (± 0.04 to ± 0.15). Precision of a single determination at 95% confidence level is $\pm 5\%$ at concentrations of 0.2 to 9.0 $\mu\text{g/mL}$ F.

Accuracy

In the EHS laboratory using drinking water samples at concentrations of 0.822 and 8.50 $\mu\text{g/mL}$ F, recoveries were 99.3 ($\pm 1.2\%$) and 100.1% ($\pm 1\%$) respectively.

Method No. EHS F-8

Title: Flashpoint Determination

Date Issued: 8-81

Approved by: MK Hamilton *[Signature]*

Written by: Susan Kinsey

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

FLASH POINT DETERMINATION

Reference

1. Hazardous Waste Testing Manual, Millipore, pp. 63-86 (includes ASTM D93-79 Method on pp. 74+).
2. Test Methods for Evaluating Solid Wastes: Physical and Chemical Methods SW-846 3rd Ed, USEPA, 1986, volume 1C, chapter 8, Methods 1010 (ASTM D93-85) and 1020 (ASTM D3278-82).

Principles

These methods, prepared by the American Society for Testing and Materials (ASTM), are designed for the determination of flash point, using either the Pensky-Martens Closed Cup Tester or the Setaflash Closed Cup Tester. The flash point of an organic material is defined as the temperature, (under controlled conditions), at which the concentration of the material in the vapor phase has reached the lower explosive limit. In such a flammable atmosphere the introduction of a spark will ignite the vapor. This ignition results in a flame that instantaneously propagates itself across the surface of the sample. Vapor pressure is a fundamental physical property of any chemical, determined largely by intermolecular attractions. Vapor pressure is also affected by the equilibrium state of the system. Consequently, in this analysis volume, temperature, and time are important variables.

For the purposes of Department of Transportation (DOT) compliance, liquids with a flash point below 100 °F (37.8 °C) are regulated as flammable. Under RCRA regulations for ignitability, substances are considered hazardous when the flash point is below 60°C. When testing samples with unknown flash points, the test flame must be applied at regular intervals, from the initial temperature to 100 °C or until the flash point is reached.

Limitations

These procedures are specifically designed for fuel oils, lube oils, solvents, greases, some solids, suspensions of solids, and liquids that tend to form a surface film under test conditions.

Exact reproducibility of the flash point testers, and their comparability has not been proven at this point.

Setaflash Closed Cup Tester

This method requires 2 mL of sample material. It is best used when there is little sample material, a rapid analysis time is desired, trace cross contamination must be avoided, and an accuracy of 5 °C intervals is acceptable. Accuracy comparable to that of the Pensky-Martens method requires iterative analysis (see section on finite testing). This is the procedure routinely used by the EHS laboratory.

Equipment

1. Setaflash Closed Cup Tester
2. 2 mL glass syringe
3. tissue wipes, acetone
4. cooling block (kept in freezer)

Procedure-finite flash point (Primary Method)

1. This procedure is used to determine the exact flash point of a test material. The ASTM method calls for an iterative approach where the flash point is first approximated and then the analysis is repeated with the temperature adjusted to just below that of the first observed flash. In our laboratory we have modified this approach more closely to that of the Pensky-Martens method described above. This is a valid approximation if the sample chamber is heated at such a rate so that there is time for vapor and liquid phases to reach equilibrium. For samples of low volatility and low volume (<70 mL), use the iterative approach.
2. Begin the test with the sample chamber at, or, by using the cooling block, below ambient temperature. Sample material is introduced into the sample chamber via the 2 mL glass syringe. For viscous or solid samples the 2 mL volume may have to be estimated using other means.
3. The temperature dial is set to some value that produces a 5 °C/minute increase. Additional adjustments may be necessary as the tester reaches the set value and begins to cycle on and off. The pilot and ignition flames are set as described above but are not shut down after adjustment. The temperature of the sample cup is monitored and the sample tested for flashpoint at every 5 °C increase. After the flash has been observed, the temperature dial is reset to the beginning value, the lid of the sample chamber opened, and excess material wiped from the testercup. Use acetone as necessary to remove remaining residues, if any. To cool the sample cup down to ambient temperatures, the aluminum block is removed from the freezer and fitted into the sample cup. When the sample cup has returned to ambient temperature, the next sample can be tested.

Procedure-flash/no flash (Alternative Procedure)

1. This method is for testing a material at a predetermined temperature.
2. Basic procedure--the power switch of the tester is turned on and the temperature dial set to the value corresponding to the desired temperature. The coarse and fine knobs allow adjustment to within 1 °C. The temperature of the tester cup is indicated on the built-in thermometer. While the tester cup is heating, light and adjust the pilot and ignition flames. Use the pinch clamp to shut off gas without changing flow rates. When the temperature has stabilized at the desired setting the indicator light will cycle on and off. Fill the syringe with 2 mL of sample material and dispense through injection port in lid of tester chamber. Start the 1 minute timer. Release the pinch clamp and light the gas streams. When the timer tones, trip the release lever and observe for the flash/no-flash condition. Shut off gas flow, turn temperature dial back to its original setting, and clean the sample cup as described above.
3. Multiple analyses--the temperature dial is not reset after an analysis, rather the tester cup is cleaned, the lid shut and the cup allowed to again reach thermal equilibrium. The steps outlined under the basic procedure are repeated. If a temperature other than that currently in equilibrium is desired the temperature dial is set accordingly. For temperatures less than the current setting, the cooling block can be used.

Pensky-Martens Closed Cup Tester

This method is employed when low volatile samples are encountered (i.e. tar, heavy oils), where greater accuracy (flash point to within 2 °C) is desired and trace cross contamination is not a problem. This method requires 70 mL of organic material.

Equipment

1. Pensky-Martens Closed Cup Tester
2. Motorized stirrer with flexible belt
3. Thermometers
4. 2 beakers, 1 large enough to hold brass sample cup
5. Materials to clean brass sample cup: tissue wipes, detergent solution, small nylon bottle brush, acetone.

Procedure

1. Fill clean, dry brass cup to mark with sample; place cup in well and secure cover apparatus by tightening attachment screws; adjust thermometer in provided port so that stirring mechanism does not strike it; check all gas connections and adjust larger needle valve for gas

flow; connect belt; turn gas on, light pilot flame, and adjust smaller needle valve for test flame; turn stirrer on. (Stop stirring when apply test flame.)

2. Basic procedure--adjust the Ful-Kontrol dial for a temperature increase of 5-6°C/min. (approximately 70 increasing to 90 by the end of test); set the belt on the smaller pulley to achieve a stirring rate of approximately 115 rpm. Test the sample at 2°C intervals beginning 17-28°C below expected flash point (lower test flame in 0.5 sec., hold 1 sec., raise quickly); if flash point is unknown, test in similar manner, except start at ambient temperature. Record the flash point as the temperature at which there is a distinct flash in the cup (there may be a bluish halo present in the reading preceding the flash).
3. Multiple analyses--after the flash has been observed perform the following: shut off gas, shut off stirrer, disconnect belt, remove cover, remove sample cup from well and place in water bath (water filled beaker), turn Ful-Kontrol knob back to start position. For routine samples the test cup should be placed in the water bath immediately after the end of the test. The sample cup is cleaned as follows: return remaining sample to original container, use nylon brush to scrub cup with detergent solution, rinse first with water then with acetone, use tissue to dry sample cup. The sample cup is then refilled with the next sample and placed in the tester. The Ful-Kontrol is reset to 70 and the sample tested in thew manner already described.
4. Notes--samples with low flash points can be tested by cooling the sample cup in a freezer prior to analysis. A second sample cup is useful in this situation; one can be kept in the freezer while the other is in use.

An important consideration in disassembling the tester: Place the test cup in the water immediately after the test is completed. If this is not done, the sample will continue to receive heat from the cup and sample well, consequently, the sample may superheat once the stirrer has been disconnected. In this situation, sample material can be violently ejected from the cup. This is especially the case with aqueous/organic mixed samples. Such samples should be analyzed only in the Setaflash tester.

Quality control

Quality control records for the flash point analysis are maintained in the "Waste" volume of quality control data. There are separate sections for the Pensky-Martens and for the Setaflash methods. Compounds of known purity and flashpoint are used to check the accuracy of the tester and analyst. Currently undecane, with a flash point of 65 °C is used as our reference standard. The observed flashpoint of the standard, the date of the test, the analyst's initials, and the customer order number of the associated sample set are recorded.

DWS

SEIAT LASH I

Closed-Cup Tester

PENSKY-MARTENS

Closed-Cup Tester

Method No. EHS H-7

Title: TGS ANSA Method for the Determination of Nitrogen Dioxide in the Atmosphere

Date Issued: 2-79

Approved by: HK Hamilton *[Signature]*

Written by: K. Norton

Supersedes Method No. _____.

[illegible]

Replaced by Method No. _____

Date: _____

TGS ANSA METHOD FOR THE DETERMINATION OF NITROGEN

References

1. TGS ANSA Method for the Determination of Nitrogen Dioxide in the Atmosphere, EPA Designated Equivalent Method No. EQN-1277-028.

Principles

Ambient nitrogen dioxide (NO_2) is collected by bubbling air through a 50 mL solution of triethanolamine, o-methoxyphenol (Guaiacol), and sodium metabisulfite in a two port polypropylene tube. The inlet port is fitted with an 8 mm O.D., 6 mm I.D. glass tube with the end drawn out to form an orifice with an I.D. of 0.3 - 0.6 mm.

The concentration of nitrite ion (NO_2^-) produced during sampling is determined colorimetrically by reacting the nitrite ion with sulfanilamide and 8-anilino-1-naphthalenesulfonic acid ammonium salt and measuring the absorbance of the highly colored AZO dye at 550 nm.

The method is applicable to 24-hour integrated sampling of NO_2 in ambient air with a sampling rate of $200 \text{ cm}^3/\text{min}$.

Limitations

At an NO_2 concentration of $100 \mu\text{g}/\text{m}^3$ (0.05 ppm) the following pollutants, at the levels indicated, do not interfere: ammonia, $205 \mu\text{g}/\text{m}^3$ (0.29 ppm); carbon monoxide, $154,000 \mu\text{g}/\text{m}^3$ (134 ppm); formaldehyde, $750 \mu\text{g}/\text{m}^3$ (0.61 ppm); nitric oxide, $734 \mu\text{g}/\text{m}^3$ (0.60 ppm); phenol, $150 \mu\text{g}/\text{m}^3$ (0.04 ppm); ozone, $400 \mu\text{g}/\text{m}^3$ (0.020 ppm); and sulfur dioxide, $439 \mu\text{g}/\text{m}^3$ (0.17 ppm).

Equipment

1. Two port polypropylene tubes (164 mm x .32 mm).
2. Approximately 152 mm long bubbler tubes (8 mm O.D., 6 mm I.D. with an orifice of I.D. 0.3 - 0.6 mm).
3. Test tubes (150 mm long X 20 mm diameter).
4. RAC 24-hour sequential samplers.
5. Spectrophotometer capable for measuring absorbance at 550 nm using 1 cm. optical path length cells or sipper cell and/or autosampler.
6. Autosampler tubes.

Reagents (Stock)

1. Triethanolamine
2. o-methoxyphenol (guaiacol) - reagent grade
3. Sodium Metabisulfite

4. Sulfanilamide
5. 8-anilino-1-naphthalenesulfonic acid ammonium salt (ANSA)
6. Hydrogen peroxide, 30%
7. Absolute Methanol
8. Hydrochloric Acid, concentrated (HCl)
9. Sodium Nitrite - NaNO_2

Reagents (Prepared) Reagents should be prepared in amounts which will be used within the holding times. This is in keeping with waste reduction efforts.

1. Absorbing Solution - Dissolve 90 mL of triethanolamine, 2.25 mL of o-methoxyphenol (guaiacol) and 1.25 g of sodium metabisulfite consecutively in 3L of deionized water. Dilute to 5L with deionized water. Stable for 3 weeks if protected from light.
2. Sulfanilamide Solution - Add 20g of sulfanilamide to 1,000 mL volumetric flask containing approximately 500 mL of deionized water. Slowly add 330 mL of concentrated HCl and dilute to 1,000 mL with deionized water. Stable for 4 weeks under normal laboratory conditions.
3. ANSA Solution - Dissolve 1.0 g of ANSA in 500 mL of absolute methanol. Dilute to 1,000 mL with absolute methanol in a volumetric flask. Mix thoroughly. Stable for 3 weeks when stoppered and stored under normal laboratory conditions. Should not be exposed to temperatures of 30°C or higher for 8 hours or more.
4. Hydrogen Peroxide Solution - Dilute 0.2 mL of 30% hydrogen peroxide to 250 mL with deionized water. Stable for 1 month if refrigerated and protected from light.

Standards

1. Sodium Nitrite Stock Solution - (500 $\mu\text{g NO}_2/\text{mL}$) - Dissolve 0.7732 g of oven dried NaNO_2 in deionized water and dilute to 1L with deionized water. Can be stored for 6 weeks, if refrigerated.
2. Sodium Nitrite Working Solution - (10 $\mu\text{g NO}_2/\text{mL}$) Pipet 5.0 mL of the stock solution into a 250 mL volumetric flask and dilute to volume with absorbing solution. Prepare fresh daily.
3. Working Standards - Transfer 0, 1.0, 3.0, 5.0, 8.0, and 10.0 mL of the sodium nitrite working solution to 100 mL volumetric flasks and dilute to volume with absorbing solution. This yields standards of 0, 0.1, 0.3, 0.5, 0.8, and 1.0 $\mu\text{g NO}_2/\text{mL}$.

ProcedureA. Sample collection

1. Place 50 mL absorbing solution into a polypropylene tube, 164 mm long x 32 mm diameter. The tube is fitted with a polypropylene two-port closure equipped with an 8 mm O.D., 6 mm I.D. glass tube having an end drawn out to form the specified orifice.
2. Draw air through the bubbler using a convenient flow control device, such as a critical orifice and RAC sequential sampler. The device must be capable of maintaining a constant flow through the sampling solution between 180 and 220 cm³/min. Sample for 24 hours and record the volume of air samples based on the actual calibration sampling rate.

B. Analysis

1. Replace any water lost by evaporation during sampling by adding deionized water up to 50 mL calibration mark.
2. Pipet 5 mL of each standard and collected sample into a test tube.
3. Add 0.5 mL of hydrogen peroxide solution and mix for approximately 15 seconds.
4. Add 2.7 mL of sulfanilamide solution and mix vigorously for about 30 seconds.
5. Add 3.0 mL of ANSA solution and mix vigorously for about 30 seconds (the ANSA must be added within 6 minutes after adding the sulfanilamide solution. Longer time intervals will result in lower absorbance values.)
6. Transfer aliquots of the samples and standards to autosampler tubes. If not using autosampler, use sipper cell.
7. Measure and record the absorbance of the blank and each standard and sample at 550 nm, using the autosampler (see Lab Operating Procedure L-8.2 for set up instructions). The absorbance measurement can be made anytime from 1 to 40 minutes after the addition of the ANSA.

Calculations

1. Use the standard values to plot absorbance vs. $\mu\text{g}/\text{NO}_2/\text{mL}$ absorbing solution.
2. Use the calibration curve to determine $\mu\text{g NO}_2$ present in the sample aliquot.
3. Calculate NO_2 in air as follows:

$$\mu\text{g NO}_2/\text{m}^3 = \frac{\mu\text{g NO}_2/\text{mL} \times 50 \text{ mL} \times D}{V (\text{M}^3) \times 0.93}$$

Where:

$\mu\text{g NO}_2/\text{mL}$ = NO_2 concentration in analyzed sample

50 = volume of absorbing reagent used in sampling

V = volume of air sample (m^3)

0.93 = Sampling efficiency

D = Dilution factor = for no dilution
= 2 for 1:1 dilution

4. The NO_2 concentration may be calculated as ppm using:

$$\text{ppm NO}_2 = (\mu\text{gNO}_2/\text{m}^3) \times 5.32 \times 10^{-4}$$

NOTE: Calculations may also be performed with an IBM-PC using Lotus 1-2-3 and the program written by S. R. Somers (Appendix I).

APPENDIX I

COMPUTER INSTRUCTIONS FOR LOTUS NO₂ PROGRAMINTRODUCTION

The following instructions allow the user to manipulate data generated from the weekly NO₂ air surveillance program on the IBM PC using the LOTUS 1-2-3 software. All calculations are programmed so all the user has to do is enter the appropriate measurements in the designated location and the program will convert absorption to ppm NO₂.

START UP

Turn the computer on using the multiple outlet switch.

Insert the LOTUS 1-2-3 diskette into the left drive, which will be referred to as drive A. Close the A drive door. Wait a few moments while the computer loads (boots) LOTUS. When the red light is on, this indicates the computer is obtaining information from the diskette or manipulating information. DO NOT REMOVE THE DISKETTE WHEN THIS LIGHT IS ON.

Insert the data diskette labeled (NO₂ CALCULATIONS) into the right drive or drive B. Close the door.

If the computer is already on, and not in use, there will be an A prompt (A) in the upper left corner of the screen. When the A > appears it is ready to accept commands. Simply type: LOTUS, return (↵) and the software will automatically boot.

When LOTUS is activated, follow the instructions for date and time, striking the return (↵) key after each entry. Make sure that the date is entered correctly because it will be used later in the program, i.e., mn-day-yr (5-01-85).

LOTUS will now list a menu. This menu shows the user different options within the LOTUS network. Use the 1-2-3--LOTUS spreadsheet program. Strike return when the highlighted command cursor is centered on 1-2-3.

Next a copyright will appear, strike any key to continue.

If the appropriate diskette is placed in drive B, the program will automatically load the NO₂ spreadsheet and generate a list of commands needed to utilize the program.

The spreadsheet program is now loaded; letters should appear in the vertical direction (rows) and numbers in horizontal (columns). Notice that the letters and numbers make up a matrix so the user can identify each cell.

The beginning of the program appears and is ready to be manipulated. Notice the greenish and white areas. Data can only be entered to the cells that appear greenish or those that have been designated for data input; all other cells are internally protected and will not accept entries.

IMPORTANT: Striking the **Alt** **M** keys simultaneously causes a menu directly relating to the NO₂ spreadsheet to appear. This menu lists most of the commands needed to manipulate the spreadsheet. The commands are set up so the user can move from one end to another (down the line) to complete the objective. The menu should appear as follows:

EXIT DATE INPUT LAB NO PRINT FILE SAVE QUIT

DATING THE WORKSHEET

By striking **Alt** **M** keys and selecting DATE, the cursor will automatically move to cell B22 and wait until the user enters the weekly date. The date should be entered as shown here: 1/28 - 2/05; followed by a return (↵). The easiest way to change the date is by striking the F-2 key (edit), making the necessary changes and erasing with the delete key.

DATA ENTRY

To start the input mode, go to menu **Alt** **M**, select INPUT, (notice another menu appears). Select INPUT again and the cursor automatically moves to enter the standard absorption curve for Run 1 and Run 2; manipulate the cursor using the keys located to the right of the key board (primarily ↓, down). This in essence will give you the fundamental rudiments of latter calculations deriving ppm from absorption.

To enter the data for each respected site, locate the site and its information cells as shown below.

<u>ABS.</u>	<u>CONC.</u>	<u>LAB NO</u>
<u>(550 nm)</u>	<u>(ppm/NO)</u>	<u>E85-01-</u>

SITE:
DATE:
PUMP NO:
ORIFICE NO:
FLOW (cc/m):
AIR VOLUME:
CAL. DATE:

DUP:
AVG:

Check all pertinent information in the first column to make sure all pump characteristics are correct and current (especially flow and air volume). All ABS entries will then be placed under the ABS column. Continue to enter the absorption for each site using the cursor movement keys to advance the spreadsheet. After all absorption entries are entered, to break the program loop strike **Ctrl** **Break** simultaneously.

CALCULATING

After all data has been entered and the pump characteristics checked, the entries need to be calculated. Simply recall the menu, select INPUT, followed by CALCULATE.

LABORATORY NUMBER SYSTEM

The lab number identifies each sample and is responsible for the integrity of quality assurance. To add the laboratory numbers in chronological order, retrieve the menu (ALT M) and enter command LAB NO.

To operate, the program will ask the user to enter the address (site) to go to. Type in the appropriate site (Ale, 200W, 100B, 100D, 615C, AB, Wye, FFTF, or SB). Enter the starting lab no., strike return (↵), and the program will supply the log numbers for the rest of the cell. Again, the program will ask the cell address. Type the next site on which data was collected (↵) and the lab no. (↵). Repeat until all sites are accounted for. NOTE: If only five samples were collected, then your worksheet should represent this; hence, the ABS columns and the laboratory number must coincide. To break the program strike Ctrl Break simultaneously. IMPORTANT: A cross check against the log book will determine if the process was done correctly.

PRINTING WEEKLY REPORT

When all data entries are finished a weekly printout is essential, and must be done before the FILE and SAVE commands. This printout will be placed in the NO₂ notebook for future reference. Before printing make sure the printer is on, paper loaded, and ready to accept information. The ON-LINE light must be lit. The printer settings should be the following:

MARGINS

Left: 7	Top: 0	Page Length: 64
Right: 136	Bottom: 2	Footer:!! Date: @

IMPORTANT: Before sending information to the printer, the paper must first be aligned so that the top perforation "lines-up" with the printer head. This will allow for a weekly report that is bondable, legible, and neat.

To print the data sheet, recall the menu and select PRINT. After this is complete, remove the printout from the printer and store in the notebook. Record data in the log and QC books.

FILE

After the absorbance numbers have been converted to parts per million NO₂, the data needs to be stored in a calendar matrix for future manipulations.

Recall the menu (ALT M) and select FILE, the cursor will automatically move to R5 and ask the user to "align cursor at appropriate date". Strike return (↵) to continue. Using the cursor movement keys or page down, move the cursor accordingly. Once the starting date is located, position the cursor in column R (ALE) and strike return (↵). The data will be automatically placed in the matrix for the remaining sites, and a range is set for later use.

SAVING WEEKLY ENTERIES

After all data has been entered, printed, and filed the last operation is to store the results in a calendar matrix for yearly summations. To do this, go to the menu (Alt M) and select SAVE (↵). The computer will then perform this command and presents another menu:

EXIT FILE SAVE QUIT

Select FILE (↵), notice the same calendar appears as in the previous spreadsheet. The comment "Align cursor at appropriate Date" appears. Strike return (↵) and move the cursor accordingly. When the cursor is properly aligned in the 'C' (ALE) column, strike return (↵) and the weekly results are combined, but not saved. After the data is combined, select SAVE (↵) to protect and complete the process. Selecting Quit will exit the user from the spread sheet.

RETURN TO FILE

The computer will then present the beginning menu. Strike EXIT, followed by a self check (Y/N). Strike Yes if you want to leave the LOTUS Access System. The final result will be an A. Retrieve the diskettes from drives A and B, place in protective wrappers, and store in respective location. Turn the computer off using the multiple outlet switch.

PROTECTION SYSTEM

The protection status minimizes the chance that unintentional harm will be done to the spreadsheet. Basically, those areas which appear greenish are unprotected and the rest (white) are internally protected. To break the internal protection, which would be needed to change pump characteristics, simply strike Slash (/), Worksheet (W), Global (G), Protection (P), Disable (D), and make corrections. It is wise to turn the protection back on after the necessary corrections are entered to protect the integrity of the spreadsheet. To turn the protection system back on, strike /WGPE.

ERASING

This operation will be used to delete characters that change within the weeks time. To do this, strike slash (/), Range (R), Erase (E), color in range to be erased, return (↵), and continue. The deleted material is not lost until the spreadsheet is saved.

OTHER IMPORTANT KEYS AND INDICATORS IN LOTUSKeys

Control break: Allows the user to escape from an internal program ("Loop").
F-1: Help key

ESC: Escape, allows the user to back-out and exit the command.

Indicators

Upper left corner of screen identifies the current location within the spread sheet, i.e., E31.
Upper right corner of the screen indicates the command mode (ready, wait, command, error, etc.).

Method No. EHS 5-6

Title: SO₂ In Air and Stack Samples Using Barium Perchlorate Titration

Date Issued: 4-78

Approved by: MK Hamilton

Written by: MK Hamilton

Supersedes Method No. _____

Date	Reviewed By	Date	Revised By
<u>10/80</u>	<u>MKH</u>	<u>10/1/85</u>	<u>MKH</u>
<u>11/11/82</u>	<u>MKH</u>		
<u>7-29-89</u>	<u>QAT</u>		

Replaced by Method No. _____

Date: _____

SO₂ IN AIR AND STACK SAMPLES USING BARIUM PERCHLORATE TITRATION

References

1. Sulfur Dioxide in Air, NIOSH Analytical Method P&CAM 163.
2. Tentative Test Method for Sulfur Dioxide in Workplace Atmospheres (Barium Perchlorate Method), ASTM Designation D3449-75T.
3. EPA Method 6: Determination of Sulfur Dioxide Emissions from Stationary Sources, 40 CFR Part 60.

Principles

Sulfur dioxide in the air is absorbed in 0.3N H₂O₂ (3 percent H₂O₂ if stack) and oxidized to sulfate. After the pH of the solution has been adjusted with perchloric acid, the resulting sulfate is titrated with barium perchlorate using thorin as the indicator.

Limitations

Particulate sulfates, sulfuric acid and SO₃ will all cause erroneously high SO₂ values. This problem can be eliminated by placing a 0.8μ membrane prefilter ahead of the impinger for ambient sampling or by using an initial scrub of 80 percent isopropanol, as is the case when stack sampling. Metal ion and phosphate ion interferences are also eliminated by using a prefilter. Oxidizing material trapped on the prefilter could cause erroneously low SO₂ results but is not often a problem.

Equipment

1. 125 mL erlenmeyer flasks
2. 10 and 50 mL graduated burettes
3. Stack sampling train as described in EPA Method 6, or
4. Midget impingers, 0.8μ membrane filters and cassettes, and personal sampling pump
5. pH meter

Reagents (Stock)

1. Barium perchlorate - Ba(ClO₄)₂·3H₂O
2. Isopropyl alcohol (isopropanol)
3. Perchloric Acid, conc. - HClO₄
4. Sulfuric Acid, conc. - H₂SO₄

5. Thorin indicator
6. Hydrogen peroxide, 30 percent - H_2O_2
7. Sodium hydroxide - NaOH
8. Potassium acid phthalate (KHP), primary standard
9. Phenolphthalein indicator
10. Ethyl alcohol (ethanol)

Reagent (Prepared)

1. Hydrogen peroxide absorbing solution (0.3N) - dilute 17 mL of 30 percent H_2O_2 to 1 liter using deionized H_2O . Prepare daily.
2. 80 percent isopropanol (stack sampling only) - dilute 800 mL isopropanol to 1 liter with deionized H_2O . Prepare annually.
3. Perchloric acid (1.8%) - dilute 25 mL conc. $HClO_4$ to 1 liter with deionized H_2O . Prepare annually.
4. Thorin indicator solution - dissolve 0.1-0.2g thorin in 100 mL deionized H_2O . Prepare annually.
5. Phenolphthalein indicator - dissolve 0.01g phenolphthalein in 50 mL ethanol + 50 mL deionized water. Prepare annually.
6. Hydrogen peroxide absorbing solution (3%) - dilute 100 mL of 30 percent H_2O_2 to 1 liter with deionized H_2O . Prepare daily. (Stack sampling only)

Standards

1. 0.0100N KHP - Dissolve 0.2042g oven dried potassium hydrogen phthalate in deionized H_2O and dilute to 100 mL. Prepare monthly.
2. -0.01 N NaOH - dissolve 0.4g NaOH in deionized H_2O and dilute to 1 liter. Standardize every three months as follows: Pipet two 25.0 mL aliquots of 0.0100N KHP into 125 mL erlenmeyer flasks. Prepare a blank from 25 mL deionized H_2O . Add 2-4 drops phenolphthalein to each and titrate with the NaOH to a pink end point.

$$N_{NaOH} = \frac{mL_{KHP} \times N_{KHP}}{mL_{NaOH}}$$

$$mL_{NaOH} = (mL \text{ to titrate KHP}) - (mL \text{ to titrate Blk})$$

3. -0.01N H_2SO_4 - Add 0.3 mL conc. H_2SO_4 to deionized H_2O and dilute to 1 liter. Standardize every three months against the standardized NaOH as follows: Pipet two 25.0 mL aliquots of -0.01 N H_2SO_4 into 125 mL erlenmeyer flasks. Prepare a blank from 25 mL deionized H_2O . Add 2-4 drops phenolphthalein to each flask and titrate with the standardized NaOH to a pink end point.

$$\begin{array}{c} \text{N} \\ \text{H}_2\text{SO}_4 \\ 2 \quad 4 \end{array} = \frac{\text{mL} \quad \text{xN}}{\text{mL} \quad \text{NaOH}} \quad \frac{\text{NaOH}}{\text{H}_2\text{SO}_4}$$

$$\text{mL NaOH} = (\text{mL to titrate } \text{H}_2\text{SO}_4) - (\text{mL to titrate blank})$$

4. -0.01N $\text{Ba}(\text{ClO}_4)_2$ - Dissolve 1.95g $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in 200 mL deionized H_2O . Add 800 mL isopropanol, mix well and adjust the pH to -3.5 with dilute HClO_4 . Standardize every three months as follows: Pipet two 10.0 mL aliquots of standardized H_2SO_4 into 125 mL erlenmeyer flasks and add 40 mL isopropanol. Prepare a blank from 10.0 mL deionized H_2O + 40 mL isopropanol. Adjust the pH of the solutions to -3.5 using dilute HClO_4 and add 4-6 drops thorin to each. Titrate with the $\text{Ba}(\text{ClO}_4)_2$ to an end point color change from yellow to pink.

$$\begin{array}{c} \text{N} \\ \text{Ba}(\text{ClO}_4)_2 \\ 4 \quad 2 \end{array} = \frac{\text{mL} \quad \text{H}_2\text{SO}_4 \quad \text{x} \quad \text{N} \quad \text{H}_2\text{SO}_4}{\text{mL} \quad \text{Ba}(\text{ClO}_4)_2}$$

$$\begin{array}{c} \text{mL} \\ \text{Ba}(\text{ClO}_4)_2 \\ 4 \quad 2 \end{array} = (\text{mL to titrate } \text{H}_2\text{SO}_4) - (\text{mL to titrate Blk})$$

Procedure

1. Sampling

- A. Stacks - see EPA Method 6
- B. Ambient - Place 15 mL 0.3N peroxide absorbing solution in a midge impinger and sample at 1.0 Lpm for a minimum of 100 min. Use a 0.8μ membrane prefilter when necessary.

2. Analysis

- A. Transfer the samples to volumetric flasks (25 mL for ambient samples, 500 mL for stack samples) and dilute to volume with deionized H_2O .

B. Pipet a 10.0 mL aliquot to a 125 mL erlenmeyer flask and add 40 mL isopropanol plus 4-6 drops thorin. Prepare a blank using 10.0 mL of appropriate absorbing solution in place of the sample aliquot. Adjust pH to -3.5 using dilute HClO_4 .

C. Titrate to pink end point using standardized $\text{Ba}(\text{ClO}_4)_2$.

Calculations

1. Stack samples - see EPA Method 6 or computer program written by B. K. Grogan.

2. Ambient Samples

$$\text{mg/m}^3 \text{ SO}_2 = \frac{\text{mL}_B \times M_B \times \text{MW}_{\text{SO}_2} \times F}{V}$$

mL_B = mL $\text{Ba}(\text{ClO}_4)_2$ to titrate sple minus amount to titrate Blk

M_B = Molarity $\text{Ba}(\text{ClO}_4)_2$ = 1/2 normality

MW_{SO_2} = molecular wt SO_2 = 64.06

F = dilution factor = $\frac{\text{total sol. vol.}}{\text{aliquot vol.}}$

V = m^3 air sampled

ppm SO_2 = $\text{mg/m}^3 \text{ SO}_2 \times 0.382$

0.382 = $\frac{24.45 \text{ mL/m mole}}{64.06 \text{ mg/m mole}}$

Method No. EHS N-1

Title: Determination of NO_x IN Stack Gas

Date Issued: 6-25-74

Approved by: NK Hamilton *NK-H*

Written by: MK Hamilton

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

DETERMINATION OF NO_x IN STACK GAS

References

1. Federal Register, Vol. 42, No. 160, August 18, 1977, pp. 41784-41786.
2. EPA Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources, October 4, 1982.
3. Environmental Sciences & Technology 9 (10), 979-981, October 1975.

Principles

A grab sample of air is collected in an evacuated flask containing a dilute H₂SO₄-H₂O₂ absorbing solution. Nitrogen oxides, except nitrous oxide, are collected in this solution which is treated with phenoldisulfonic acid and neutralized with NH₄OH to give a yellow color, the absorbance of which is measured at 405 nm. Results are reported as ppm NO₂.

Limitations

This method is applicable for the determination of nitrogen oxides, except nitrous oxide, from stationary sources at concentrations greater than 10 ppm NO₂.

Equipment

1. 1 liter evacuable round bottom flasks (500 mL and 2000 mL flasks may also be used).
2. Pyrex glass sampling probe
3. Vacuum pump and manometer
4. Steam bath
5. 100 mL beakers
6. Red or neutral litmus paper
7. 100 mL volumetric flasks
8. Spectrophotometer for use at 405 nm with 1.0 cm cells or sipper cell

Reagents (stock)

1. Sulfuric acid, conc. - H₂SO₄
2. Hydrogen peroxide, 30% - H₂O₂
3. Sodium hydroxide - NaOH
4. Phenoldisulfonic acid
5. Ammonium hydroxide, conc. - NH₄OH

6. Potassium nitrate, analyzed reagent - KNO_3 Reagents (prepared)

1. Absorbing solution - add 2.8 mL conc. H_2SO_4 to 1 liter deionized H_2O and mix well. Add 0.6 mL 30% H_2O_2 to 5.4 mL deionized H_2O and mix. Add the H_2O_2 solution to the H_2SO_4 solution and mix. Store away from extreme heat or direct sunlight. Prepare weekly.
2. 1 N NaOH - dissolve 40g NaOH in deionized H_2O and dilute to 1 liter.

Standards

1. Stock NO_2 solution (1 mL = 250 μg NO_2) - dissolve 0.2748g oven dried KNO_3 in deionized H_2O and dilute to 500 mL. Prepare monthly.
2. Intermediate NO_2 dilution (1 mL = 25 μg NO_2) - transfer 10.0 mL stock NO_2 solution to a 100 mL volumetric flask and dilute to volume with deionized H_2O . Prepare weekly.

ProcedureA. Sample collection

1. Fill the collection flask completely with H_2O and measure the volume of water used. This gives the volume of the flask at room temp.
2. Place 25 mL absorbing solution in the flask and evacuate to at least 3 inches of Hg. Measure the negative pressure (vacuum) just before using the flask and record (P_1).
3. Purge the sample probe, then open the flask for about 15 seconds to collect a sample.
4. Close the flask and shake for 5 minutes. Allow to stand at least 16 hours.
5. Shake the flask for 2 minutes and measure the flask pressure (P_f) at room temperature.

B. Analysis

1. Transfer the 25 mL absorbing solution from the sampling flask to a 100 mL beaker. Rinse the flask twice with 10 mL aliquots of deionized H_2O and add rinsings to beaker.
2. Prepare standards by pipetting 0, 1.0, 3.0, 6.0, 10.0, 15.0 and 20.0 mL intermediate NO_2 standard (25 $\mu\text{g}/\text{mL}$) into 100 mL beakers. Add 25 mL absorbing solution and enough deionized H_2O to give a volume of about 45 mL. NOTE: If analyst is new to the procedure, standards should be carried through the entire procedure before starting samples to be sure techniques are mastered and procedure is working.

3. Neutralize samples and standards to litmus using 1 N NaOH. Be careful not to add excess NaOH as it will cause low results.
4. Evaporate all solutions to dryness on steam bath. (Avoid over-baking the samples once dryness is reached).
5. Add 2 mL phenoldisulfonic acid and use a plastic rod to crush and wet the residue thoroughly.
6. Add 1 mL deionized H₂O (use to rinse plastic rod) and 4 drops conc. H₂SO₄.
7. Heat on steam bath for 3 minutes with occasional stirring and cool.
8. Add 20 mL deionized H₂O, mix, and add 15 mL conc. NH₄OH. (A yellow color should develop in the presence of NO₂).
9. Transfer the solutions to 100 mL volumetric flasks and dilute to volume with deionized H₂O. If the sample color is darker than the highest standard, dilute as needed.
10. Measure absorbance of samples and standards at 405 nm using 1.0 cm cells and deionized H₂O reference. Sipper cell may also be used. (Color is stable for several hours.)

Calculations

1. From the standard values plot absorbance vs $\mu\text{g NO}_2/100 \text{ mL}$.
2. Using this calibration curve determine the $\mu\text{g NO}_2$ present in the samples.
3. Determine ppm NO₂ in the air samples as follows:

$$\text{ppm NO}_2 = \frac{A(\mu\text{g NO}_2/100 \text{ mL})}{V_1} \times 0.532$$

A = dilution factor

V_1 = liter air sampled

$$= \frac{P_2 V_2}{P_1}$$

P_1 = 760 mm standard pressure = 29.9 in. Hg

P_2 = measured flask pressure ($P_{\text{initial}} - P_{\text{final}}$) as in. Hg

V_2 = (mL flask volume - 25 mL absorbing solution)/1000 = L air sampled

0.532 = factor to convert $\mu\text{g/L}$ to $\mu\text{L/L}$ (ppm) at 25°C

$$= \frac{24.45 \mu\text{L}}{46.01 \mu\text{g}}$$

24.45 μL = volume of 1 μmole at 25°C

$$= \frac{V_1 T_2}{T_1}$$

V_1 = 22.4 $\mu\text{L}/\mu\text{mole}$ at 0°C

T_1 = 273°K = 0°C

T_2 = 298°K = 25°C

46.01 μg = weight of 1 μmole NO_2

NO_x SAMPLING BULB VOLUMES (BULB + CAP)

<u>Bulb No.</u>	<u>Vol, mL</u>	<u>Bulb No.</u>	<u>Vol, mL</u>	<u>Bulb No.</u>	<u>Vol, mL</u>
101	550	131	545	199	535
102	552	132	548		
103	548	134	532	200	1035
105	535	135	535	201	1041
108	550	137	548	203	1033
109	535	139	526	204	1037
110	535	140	555	205	1028
112	545	141	535		
113	531	142	547	300	2220
115	530	143	538	301	2095
117	557	144	549	302	2100
118	559	147	532	303	2310
123	535	148	540	304	2120
124	530	149	541		
125	575	152	548		
128	552	153	535		
130	540	154	535		

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NO SAMPLING BULB VOLUMES (BULB + CAP)

<u>Bulb No.</u>	<u>Vol, mL</u>	<u>Bulb No.</u>	<u>Vol, mL</u>	<u>Bulb No.</u>	<u>Vol, mL</u>
101	550	131	545	199	535
102	552	132	548		
103	548	134	532	200	1035
105	535	135	535	201	1041
108	550	137	548	203	1033
109	535	139	526	204	1037
110	535	140	555	205	1028
112	545	141	535		
113	531	142	547	300	2220
115	530	143	538	301	2095
117	557	144	549	302	2100
118	559	147	532	303	2310
123	535	148	540	304	2120
124	530	149	541		
125	575	152	548		
128	552	153	535		
130	540	154	535		

Method No. EHS H-1-1

Title: Hardness (EDTA)

Date Issued: Before 1983 Approved by: M. K. Hamilton

Written by: M. K. Hamilton

Supersedes Method No. _____

[illegible]

Replaced by Method No. _____

Date: _____

HARDNESS (EDTA)..

Reference

1. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, pp. 2-52 -> 2-57.

Principles

Calcium and magnesium, when present in an aqueous solution at pH 10, will produce a wine-red color in the presence of the dye Eriochrome Black T. The addition of ethylenediamine tetraacetic acid (EDTA) will complex the calcium and magnesium. When the complexation is complete, the solution will change from wine-red to blue. If the EDTA has been standardized with a known concentration of calcium carbonate, the results of the EDTA hardness titration will be reported as mg/L CaCO_3 .

Limitations

Magnesium ions must be present to yield a satisfactory endpoint in the titration. To meet this requirement, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer. An indistinct or fading endpoint may result from the presence of metal ions such as Fe, Cu, Co, Al, Ni, etc. This problem may be overcome by the addition of an inhibitor such as hydroxylamine hydrochloride. Barium, and strontium, if present, will also titrate as EDTA hardness. Suspended or colloidal organic matter may also interfere with the endpoint. This can be overcome by evaporating the sample to dryness, heating at 550°C , dissolving the residue in 1N HCl and neutralizing with 1N NaOH.

Equipment

1. 10 mL buret
2. 250 mL erlenmeyer flasks
3. Magnetic stirrer and stirring bars

Reagents (stock)

1. Disodium ethylenediamine tetraacetate dihydrate (EDTA)--also called disodium (Ethylenedinitrilo) tetraacetate--analyzed reagent grade.
2. Ammonium chloride-- NH_4Cl
3. Ammonium hydroxide, conc.-- NH_4OH
4. (Ethylenedinitrilo) tetraacetic acid, magnesium salt

5. Eriochrome Black T dye (sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid).
6. Triethanolamine
7. Anhydrous calcium carbonate-- CaCO_3 --primary standard or ACS reagent grade.
8. Hydrochloric acid, conc.-- HCl
9. Methyl orange

Reagents (Prepared)

1. Buffer--dissolve 6.75g NH_4Cl in 57.2 mL conc. NH_4OH , add 0.5g magnesium salt of EDTA and dilute to 100 mL with deionized water. Store in a polyethylene bottle, kept tightly closed when not in use. Prepare monthly.
2. Indicator--dissolve 0.5 g Eriochrome Black T in 100g triethanolamine. Prepare annually.
3. EDTA titrant--dissolve 3.723 g disodium EDTA in deionized water and dilute to one liter. Standardize monthly against a standard calcium solution, following the sample procedure below. Store in a polyethylene bottle. Prepare annually.
4. 3N NH_4OH --dilute 50 mL conc. NH_4OH to 250 mL with deionized water. Prepare annually.

Standards

1. Standard calcium solution--1.0 mL = 1.0 mg CaCO_3 --weigh 1.000 g anhydrous CaCO_3 into a 500 mL erlenmeyer and add 1:1 HCl gradually until the CaCO_3 dissolves. Add 200 mL deionized water and boil a few minutes. Cool, add a few drops methyl orange and adjust to the intermediate orange endpoint with 3N NH_4OH or 1:1 HCl . Transfer quantitatively to a 1-Liter volumetric flask and dilute to volume with deionized water. Prepare every six months.

Procedure

1. Transfer a sample aliquot, requiring less than 10 mL EDTA titrant, to a 250 mL erlenmeyer flask and dilute to 100 mL, if necessary, with deionized water.
2. Add two mL buffer and 4-5 drops of indicator solution.

3. Begin stirring and titrate immediately with EDTA until the last reddish tinge disappears from the solution. (If the endpoint color change is not sharp, the indicator may have deteriorated, or a different inhibitor may be needed. See Standard Methods, for a list of additional indicators.)
4. Titrate a blank, using 100 mL deionized water instead of sample.

Calculation

1. Standardization of EDTA solution:

$$A = \frac{B \times C}{D}$$

A = mg CaCO₃ equivalent to 1.0 mL EDTA

B = mL standard CaCO₃ solution titrated

C = 1.0 mg/mL concentration of CaCO₃ solution

D = mL EDTA needed in titration (mL_{std} - mL_{blk})

2. Calculation of EDTA hardness:

A. Hardness as mg/L CaCO₃ = $\frac{A \times B \times 1000}{C}$

A = mg CaCO₃ equivalent to 1.0 mL EDTA

B = mL EDTA to titrate sample (mL_{sple} - mL_{blk})

1000 = mL/L

C = mL sample titrated

B. Hardness as grains/gal = $\frac{\text{mg/L CaCO}_3}{17.1}$

EPA Quality criteria for water hardness:

0 - 75 mg/L = soft

75 - 150 gm/L = mod. hard

150 - 300 mg/L = hard

300 mg/L = very hard

W. Hamilton

FILTRABLE RESIDUE
(TOTAL DISSOLVED SOLIDS)

Reference

1. Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985, pp 95-96.

Principle

The sample is filtered and the filtrate is evaporated on a steam bath. The residue remaining after evaporation, dried to a constant weight, is equal to the filtrable residue.

Limitations

Because of the many variables due to the chemical and physical nature of the sample which affect filtration, the filtrable residue value obtained is not subject to the usual criteria for accuracy. The drying temperature also affects the results. At 180°C, some water of crystallization may remain, and the organic matter may be reduced by volatilization; however, the results agree more closely with those obtained by summing the individually determined mineral salts than residue values obtained by drying at a lower temperature.

Equipment

1. Oven for drying samples at 179-181°C.
2. 9 cm Porcelain filtering funnel
3. 9 cm Whatman GF/C or equivalent glass fiber filters.
4. 150-mL porcelain evaporating dishes
5. 250 or 500 mL suction flasks
6. Hot plate or steam bath

Procedure

1. Dry the evaporating dishes in an oven at 180°C, cool in a desiccator, and weigh.
2. Assemble filtering apparatus. Rinse a glass fiber filter with about 50 mL of the water sample and discard the rinse.
3. Filter about 150 mL of the water sample through the glass fiber filter.
4. Place a 100 mL aliquot of the filtered sample in a dried and weighed evaporating dish. Evaporate to dryness on a steam bath or low temperature hot plate, being careful to avoid splattering.

5. After the water is completely evaporated, place the dish in an oven at 180°C for at least one hour. Cool in desiccator and weigh. Repeat drying step until a constant weight is obtained. Record the temperature at which the dishes were dried on the analyst worksheet.

Calculation

For 100 mL aliquot:

$$\text{mg/L filtrable residue} = \text{mg residue} \times 10$$

Report results as:

mg/L filtrable residue on drying at 180°C

Method No. EHS C-11

Title: CHEMICAL OXYGEN DEMAND (COD)--HACH CLOSED-TUBE METHOD

Date Issued: 1-11-90

Approved by: MK Hamilton, CIH

Written by: P. A. Thurman

Supersedes Method No. EHS C-8

<u>Date</u>	<u>Reviewed By</u>	<u>Date</u>	<u>Revised By</u>

Replaced by Method No. _____

Date: _____

CHEMICAL OXYGEN DEMAND (COD)--HACH CLOSED TUBE METHOD

References

1. Hach COD Reactor Model 16500 Instruction Manual.
2. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Section 5220C, pp 5-14 & 15.

Principles

Chemical Oxygen Demand (COD) is a measure of the oxygen equivalent of the material present in the sample subject to oxidation by a strong chemical oxidant, namely dichromate. The sample is refluxed in a closed tube with a known amount of potassium dichromate and sulfuric acid to oxidize most organic matter present. The excess dichromate is titrated with standard ferrous ammonium sulfate. The amount of oxidizable organic matter present is proportional to the amount of dichromate consumed.

Limitations

Volatile straight chain aliphatic hydrocarbons and pyridine and related materials may not be significantly oxidized by this procedure. Samples containing more than 2000 mg/L chloride cannot be analyzed by this procedure. The presence of significant amounts of reduced inorganic species such as ferrous iron and sulfide may produce high results as they will also be oxidized by the dichromate. This method uses reagent vials for 2 concentration ranges approved by EPA:

0-150 mg/L COD (Hach Catalog #21258) 0-1500 mg/L COD (Hach catalog #21259)

Equipment

1. Hach COD reactor, Model 16500
2. Buret--10 mL
3. stirring bars, teflon-coated (10 mm x 3 mm)
4. magnetic stirrer
5. small test tube rack
6. water purification system Millipore--Milli-Q-Plus

Reagents (stock)

1. Potassium dichromate, primary standard grade-- $K_2Cr_2O_7$
2. Sulfamic acid

3. Ferrous ammonium sulfate-hexahydrate-- $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
4. 1,10-phenanthroline monohydrate
5. Ferrous sulfate heptahydrate-- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
6. Potassium acid phthalate, primary standard grade
7. Sulfuric acid conc.-- H_2SO_4

Reagents (Prepared)

1. Ferroin indicator solution

Dissolve 1.485 g 1,10-phenanthroline monohydrate and 0.695 g $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ in deionized/Milli-Q water and dilute to 100 mL. Use a 1:10 dilution of this for 0-150 mg/L range.

2. Ferrous Ammonium Sulfate 0.125 N

Dissolve 12.25 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in deionized/Milli-Q water. Add 1 mL conc. H_2SO_4 and dilute to 250 mL with deionized/Milli-Q water. Standardize with each use.

3. Ferrous Ammonium Sulfate--0.0125N

Dissolve 1.225 g Ferrous Ammonium sulfate in deionized/Milli-Q water. Add 1 mL concentrated sulfuric acid and dilute to 250 mL with deionized/Milli-Q water. Must be standardized with each use.

4. Potassium Dichromate--0.25 N

Dissolve 1.226 g primary standard $\text{K}_2\text{Cr}_2\text{O}_7$, previously dried for 2 hours at 100-105°C in deionized/Milli-Q water. Add 12 mg sulfamic acid and dilute to 100 mL with deionized Milli-Q water. Prepare every 6 months.

5. Potassium Dichromate--0.025 N

Dissolve 0.1226 g dried primary standard $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized/Milli-Q water. Add 12 mg sulfamic acid and dilute to 100 mL with deionized/Milli-Q water. Prepare every 6 months.

6. Potassium acid phthalate (KHP) standard, 500 mg/L COD equivalent

Dissolve 0.4251 g oven dried primary standard KHP in deionized/Milli-Q water and dilute to 1 liter. Prepare fresh when needed.

7. Hach vials with COD digestion solution for 0-150 mg/L (#21258) and 0-1500 mg/L (#21259).

Procedure

A. Sample collection and preservation

1. Collect samples in glass containers that have been rinsed with sulfuric acid and Milli-Q deionized water.
2. If samples cannot be run immediately, acidify to pH <2 using conc. H_2SO_4 (~2 mL/L sample) and refrigerate at 4°C. Cooled, acidified samples are stable for 7-28 days.
3. Homogenize samples containing solid material just prior to analysis.

B. Digestion

1. Turn on Hach COD reactor and preheat to reach a temperature of 150°C for 30 minutes.
2. Slowly pipet 2.0 mL of sample into a Hach digestion vial containing reagents for the desired COD range. Do not use any vials which have had reagents spilled from them. Caution: Vials contain concentrated sulfuric acid, dichromate, and mercuric sulfate--handle carefully.
3. Replace vial cap tightly and holding vial by the cap, gently sever the vial until contents are well mixed. These vials become hot--do not grab the vial itself!
4. Prepare a reagent blank using 2.0 mL of Milli-Q water instead of sample. Also prepare a standard in the proper range using the KHP 500 mg/L COD equivalent standard.
5. Place vials in the preheated reactor.
6. Heat vials for 2 hours at 150°C. Turn off reactor and allow vials to cool in place to 120° or less. This takes approximately 20 minutes.
7. While still warm, invert each vial several times. Place in a test tube rack and allow to cool completely. If a pure green color is obtained in the reactor sample, the sample concentration is too high for the range of the vials (150 mg/L [low range] or 1500 mg/L [high range]). If the low range is exceeded, rerun a diluted sample or use the high range vials. If the high range is exceeded, rerun using a diluted sample. (Do not directly pipet less than 1 mL of sample of a greater dilution is needed, make dilution in another flask and pipet 2 mL of the dilution into the reaction vial.)

C. Titration Procedure 0-150 mg/L COD range

1. Remove cap and rinse the inside walls of the digestion vial with less than 1 mL of Milli-Q deionized water.
2. Add a small stirring bar and one drop of the diluted Ferroin indicator to the vial. If the color changes to brown at this point, the COD is greater than 150 mg/L. Rerun with 2 mL of a diluted sample.
3. Place vial on the magnetic stirrer and begin stirring.
4. Titrate with 0.0125 N ferrous ammonium sulfate to the color change from greenish-blue to orange-brown.
5. Record the volume in mL of the ferrous ammonium sulfate used.
6. Standardize the ferrous ammonium sulfate (0.0125) as follows:
 - a. Pipet 2.0 mL of 0.025 N Standard Potassium Dichromate into a clean via.
 - b. Add 3 mL conc. sulfuric acid and swirl to mix. Allow to cool until comfortable to touch.
 - c. Add a stirring bar and one drop of the diluted Ferroin indicator.
 - d. Place on a magnetic stirrer and titrate with 0.0125N ferrous ammonium sulfate to the color change greenish-blue to orange-brown.
 - e. Record the volume in mL of ferrous ammonium sulfate used for standardization.
7. Dispose of waste in the inorganic waste container.

D. Titration Procedure 0-1500 mg/L range

1. Remove cap and rinse the inside walls of the digestion vial with less than 1 mL of Milli-Q deionized water.
2. Add a stirring bar and one drop of ferroin indicator. If the color of the sample changes to brown at this point, the COD is greater than 1500 mg/L. Rerun using a diluted sample. (Use 2 mL of a dilution of the sample rather than using less than 1 mL of the original sample.)
3. Place vial on the magnetic stirrer and begin stirring

4. Titrate with 0.125 N ferrous ammonium sulfate until color changes from greenish-blue to orange-brown. ..
5. Record the volume in mL of the ferrous ammonium sulfate used.
6. If the volume of ferrous ammonium sulfate used by the sample is within 0.2 mL of the volume used for the blank, the sample is too low for accurate analysis using high range reagents. Rerun sample using the low range vials.
7. Standardize the 0.0125 N ferrous ammonium sulfate as follows:
 - a. Pipet 2.0 mL of 0.25 N standard potassium dichromate into a clean vial.
 - b. Add 3 mL conc. sulfuric acid and swirl to mix. Allow to cool until comfortable to touch.
 - c. Add a stirring bar and one drop ferroin indicator.
 - d. Place on a magnetic stirrer and titrate with 0.125 N ferrous ammonium sulfate to a color change of greenish-blue to orange-brown.
 - e. Record the volume in mL of the ferrous ammonium sulfate used for standardization.
8. Discard waste in the inorganic waste container.

Calculation

A. 0-150 mg/L range:

$$(A-B) \times \frac{200}{C} = \text{mg/L COD}$$

A = mL titrant used for blank

B = mL titrant used for sample

C = mL titrant used to standardize the 0.0125 N ferrous ammonium sulfate

0-1500 mg/L range:

$$(A-B) \times \frac{2000}{C} = \text{mg/L COD}$$

A = mL titrant used for blank

B = mL titrant used for sample

C = mL titrant used to standardize the 0.125 N ferrous ammonium sulfate

DT

Method No. EHs B-4

Title: BIOCHEMICAL OXYGEN DEMAND (BOD) - DO PROBE

Date Issued: Before 5/80 Approved by: M K Hamilton *MKH*

Written by: P A Swoboda

Supersedes Method No. EHs B-1

Date	Reviewed By	Date	Revised By
<i>5/29/80</i>	<i>MKH</i>	<i>1/18/83</i>	<i>MKH</i>
<i>10/27/82</i>	<i>MKH</i>	<i>1/12/90</i>	<i>PA Sworman</i>
<i>9/22/85</i>	<i>MKH.</i>		
<i>1-15-88</i>	<i>MKH (Reprint w/minor changes)</i>		

Replaced by Method No. _____ Date: _____

BIOCHEMICAL OXYGEN DEMAND (BOD)--DO PROBE

1. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Section 5210, pp. 5-2 through 5-10.
2. YSI Dissolved Oxygen Meter--Instruction Manual.
3. Introduction to Biological Oxygen Demand, Technical Information Series--Booklet No. 7, Hach, 1989.

Principles

The biochemical oxygen demand is an empirical test to determine the relative oxygen requirements of waste waters, effluents, and polluted waters. This is done by determining the dissolved oxygen (DO) present initially and after a five-day incubation at 20°C. The difference in these two values equals the BOD. The amount of dissolved oxygen present is determined using the YSI Model 58 Dissolved Oxygen Meter. Dissolved oxygen measurements are taken using the membrane covered probe. This membrane allows oxygen and certain other gases to pass through so that when a polarizing voltage is applied across the sensor, oxygen that has passed through reacts at the cathode causing a current. This is read on the scale as ppm dissolved oxygen.

Limitations

The BOD values obtained cannot be compared with other BOD results unless they were obtained under identical test conditions. Any oxidizing or reducing materials which are present could cause interferences in the DO analysis. Residual chlorine, which may be present, is destroyed by adding an equivalent amount of sodium sulfite. If the samples are supersaturated with DO, they should be reduced to saturation by aerating with compressed air to prevent loss of oxygen during incubation.

Equipment

1. YSI Model 58 dissolved oxygen meter
2. YSI Model 5720A BOD bottle probe
3. Air incubator thermostatically controlled at 20°C ± 1°C
4. Flared mouth BOD bottles, 300 mL
5. Various size graduated cylinders
6. 11-liter glass container
7. Tubing for siphons
8. Deionized water finishing system--Millipore Milli-Q Plus

Reagents (Stock)

1. Sodium hydroxide (NaOH)

2. Sodium sulfite (Na_2SO_3)
3. DPD free chlorine reagent
4. Sulfuric Acid, Cond. (H_2SO_4)
5. Glucose
6. Glutamic acid
7. Nutrient buffer pillows (Hach #14861-98)

Reagents (Prepared)

1. 1N NaOH--dissolve 40.0 g NaOH in deionized water and dilute to one liter. Prepare annually.
2. 1N H_2SO_4 --add 28 mL conc. H_2SO_4 to deionized water and dilute to one liter. Prepare annually.
3. BOD dilution water--place the necessary amount of Milli-Q deionized water into a large glass container. For every 3 liters of water, add one Hach 3-liter nutrient buffer pillow. Mix well to assure complete dissolution of the reagents (some residue may remain with some pillows). Saturate with DO by aerating with compressed air. The temperature should be $20^\circ\text{C} \pm 1^\circ\text{C}$. Prepare dilution water the day of use.
4. Glucose-Glutamic acid control solution--dissolve 0.150 g dried glucose and 0.150 g dried glutamic acid in deionized water and dilute to 1 liter with Milli-Q deionized water. Prepare as needed.

Procedure

A. Dilution Preparation

1. Check the pH of the samples and adjust to pH 6.5 - 7.5, using 1N H_2SO_4 or 1N NaOH.
2. Add a DPD free chlorine reagent pillow to 5 mL of sample to check for residual chlorine. If the test is positive (pink color), add a small amount of Na_2SO_3 to the original sample. Mix (DO NOT SHAKE). Allow to sit a few minutes, then repeat procedure until the test shows no pink color change upon addition of DPD reagent.

3. Make several dilutions of the sample. (See Standard Methods if seeding is necessary.) Suggested dilution ranges for samples are:

0.1 - 1.0%	strong trade waste
1 - 5%	raw and settled sewage
5 - 25%	oxidized effluents
25 - 100%	polluted river water

Make the dilutions as follows:

Siphon BOD dilution water into a 1000 mL graduated cylinder until the cylinder is about half full. Siphon the desired amount of mixed sample into an appropriate graduated cylinder and carefully add it to the cylinder of dilution water. Adjust volume to 1000 mL with dilution water and mix well with a glass rod. IMPORTANT: DURING THE ENTIRE DILUTION PROCESS, BE CAREFUL TO AVOID TRAPPING AIR IN THE SOLUTIONS.

4. Siphon each of the mixed dilutions into one BOD bottle and stopper tightly, covering the seal with solution. Read the initial DO, then incubate sample bottle for five days at 20°C. Replace any lost solution with dilution water as needed to maintain the water seal.
5. Fill a BOD bottle with dilution water for a blank and treat as a sample.
6. Prepare a control by carefully pipetting 20.0 mL of the glucose-glutamic acid solution into a 1000 mL volumetric flask and diluting to volume with Milli-Q deionized water. Fill a BOD bottle and proceeding as with a sample.
7. After five days, determine the final DO of the incubated samples.

B. Determination of DO

1. Preparation of probe and meter:

- a) See Appendix 1 for filling probe with electrolyte and membrane placement. Membrane should be replaced every month or sooner if bubbles and discoloration appear under the membrane or if the meter cannot be calibrated.
- b) Allow 15 minutes for instrument warm up and probe stabilization before calibrating. This is done with the meter turned to the 0.01 mg/L range. Steps b and c must be performed whenever the instrument has been off or the probe has been disconnected.

- c) Switch the meter to the zero position and adjust the O₂ zero control knob to give a meter reading of 00.0.

2. Calibration--Air Calibration--Fresh Water

- a) The probe is kept stored in a partially filled BOD bottle. This provides moist air necessary for the calibration and prevents dehydration of the electrolyte.
- b) Switch the meter to the temperature position and note the temperature. Refer to Table 1 and determine the dissolved oxygen calibration value.
- c) Determine the atmospheric correction factor using Table 2.
- d) Multiply the calibration value from Table 1 by the correction factor from Table 2 (correction factor for Tri-Cities area = 0.98).

Example: At a temperature of 22°C (from Table 1) the calibration value is 8.8 ppm. 8.8×0.98 (correction factor) = 8.62.

- e) Switch to the 0.01 mg/L range and adjust the calibrate knob so that the meter reads the corrected calibration value from Step d. Wait 2 minutes to verify stability. Readjust, if necessary.

3. Dissolved oxygen measurement

- a) Place the probe in the sample BOD bottle, being careful not to trap air bubbles, and turn on probe stirrer.
- b) Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen (approximately 2-3 min.).
- c) Read dissolved oxygen in mg/L from the meter.

Calculations

$$\text{mg/L BOD} = \frac{[(D_1 - D_2) - B1k]}{P}$$

D₁ = DO of initial diluted sample

D₂ = DO of diluted sample after incubation

P = dilution factor = $\frac{\text{mL sample used}}{1000 \text{ mL}}$

B1k = (DO_{B1k1} - DO_{B1k2}) - P(DO_{B1k1} - DO_{B1k2})

Example:

20 mL of sample diluted to 1000 mL

$$D_1 = 8.15 \quad D_2 = 4.25 \quad P = 0.02 \text{ (20/1000)}$$

$$DO_{Blk_1} = 8.20 \quad DO_{Blk_2} = 8.05$$

$$\text{mg/L} = \frac{(8.15 - 4.25) - [(8.20 - 8.05) - 0.02(8.20 - 8.05)]}{0.02}$$

$$= \frac{3.90 - (0.15 - 0.003)}{0.02} = 188$$

Quality Control

Routine quality control for this procedure includes monitoring results obtained for the blank and glucose-glutamic acid control solution. Uptake of unseeded blanks should not exceed 0.2 mg/L DO. The control solution should give a BOD equivalent of 198 mg/L $\pm$ 30. If these conditions are not met, evaluate the procedure for possible interference or contamination problems.

Calibration Tables

Table 1 shows the amount of oxygen in PPM that is dissolved in air saturated fresh water at sea level (760 mm Hg atmospheric pressure), as temperature varies from 0° to 45°C.

Table 1
Solubility

Temperature °C	PPM Dissolved Oxygen	Temperature °C	PPM Dissolved Oxygen
0	14.6	23	8.7
1	14.2	24	8.5
2	13.9	25	8.4
3	13.5	26	8.2
4	13.2	27	8.1
5	12.8	28	7.9
6	12.5	29	7.8
7	12.2	30	7.7
8	11.9	31	7.5
9	11.6	32	7.4
10	11.3	33	7.3
11	11.1	34	7.2
12	10.8	35	7.1
13	10.6	36	7.0
14	10.4	37	6.8
15	10.2	38	6.7
16	9.9	39	6.6
17	9.7	40	6.5
18	9.5	41	6.4
19	9.3	42	6.3
20	9.2	43	6.2
21	9.1	44	6.1
22	8.8	45	6.0

Source: Derived from Standard Methods for the Examination of Water and Wastewater.

Table II shows the correction factor that should be used to correct the calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level.) If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

Table II

Correction for Atmospheric Pressure

Atmospheric Pressure mm Hg	or Equivalent Altitude Ft.	= Correction Factor
775	540	1.02
760	0	1.00
745	542	.98
730	1094	.96
714	1688	.94
699	2274	.92
684	2864	.90
669	3466	.88
654	4082	.86
638	4756	.84
623	5403	.82
608	6065	.80
593	6744	.78
578	7440	.76
562	8204	.74
547	8939	.72
532	9694	.70
517	10472	.68
502	11273	.66

Source: Derived from *Standard Methods for the Examination of Water and Wastewater*.

APPENDIX 1

Operating Procedures

PREPARING THE PROBE

All YSI 5700 Series Probes have similar sensors and should be cared for in the same manner. They are precision devices relying on good treatment if high accuracy measurements are to be made. Prepare the probes as follows (see Figure 1):

ALL PROBES ARE SHIPPED DRY--YOU MUST FOLLOW THESE INSTRUCTIONS

1. Prepare the electrolyte by dissolving the KCl crystals in the dropper bottle with deionized water. Fill the bottle to the top.
2. Unscrew the sensor guard from the probe (YSI 5739 only) and then remove the "O" ring and membrane. Thoroughly rinse the sensor with KCl solution.
3. Fill the probe with electrolyte as follows:
 - A. Grasp the probe in your left hand. When preparing the YSI 5739 probe, the pressure compensating vent should be to the right. Successively fill the sensor body with electrolyte while pumping the diaphragm with the eraser end of a pencil or similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. (With practice, you can hold the probe and pump with one hand while filling with the other.) When preparing the YSI 5720A and 5750 probes, simply fill the sensor body until no more air bubbles appear.
 - B. Secure a membrane under your left thumb. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode.

NOTE: Handle membrane material with care, keeping it clean and dust free, and touching it only at the ends.
 - C. With the thumb and forefinger of your other hand, grasp the free end of the membrane.
 - D. Using a continuous motion, stretch the membrane UP, OVER, and DOWN the other side of the sensor. Stretching forms the membrane to the contour of the probe. The membrane can be stretched to approximately 1-1/2 times its normal length.
 - E. Secure the end of the membrane under the forefinger of the hand holding the probe.
 - F. Roll the "O" ring over the end of the probe. There should be no wrinkles (or trapped air bubbles) in the membrane. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the "O" ring.

- G. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.
4. Shake off excess KCl and reinstall the sensor guard.
 5. The YSI 5720A and 5750 probes can be stored in a B.O.D. bottle containing about 1 inch of water.
 6. Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks. However, should the electrolyte be allowed to evaporate and an excessive amount of bubbles form under the membrane, or the membrane become damaged, thoroughly flush the reservoir with KCl and install a new membrane.
 7. Also, replace the membrane if erratic readings are observed or calibration is not stable.
 8. "Home brew" electrolyte can be prepared by making a saturated solution of reagent grade KCl and deionized water, and then diluting the solution to half strength with deionized water. Adding 2 drops of Kodak Photo Flo per 100 mL of solution assures good wetting of the sensor, but is not absolutely essential.
 9. The gold cathode should always be bright and untarnished. To clean, wipe with a clean lint-free cloth or hard paper. NEVER USE ANY FORM OF ABRASIVE OR CHEMICAL. Rinse the sensor several times with KCl, refill, and install a new membrane.
 10. Some gasses contaminate the sensor, evidenced by discoloration of the gold. If the tarnish cannot be removed by vigorous wiping with a soft cloth, lab wipe, or hard paper, return the probe to the factory for service.
 11. Oxides of nitrogen and sulphur, halides, and H_2S are known interfering gases. Helium and Neon are reported to interfere with the oxygen reaction at the cathode. If you suspect erroneous readings, it may be necessary to determine if these are the cause.
 12. If the probe has been operated for extended periods with a loose or wrinkled membrane, the gold cathode may become plated with silver. In this event, return the probe to the factory for refinishing.

APPENDIX 2 ALTERNATE DILUTION WATER PREPARATION

As an alternative to using the Hach nutrient buffer pillows to prepare the dilution water, the following method may be used:

Reagents (Stock)

1. Potassium dihydrogen phosphate (KH_2PO_4).
2. Dipotassium hydrogen phosphate (K_2HPO_4)
3. Disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$)
4. Ammonium chloride (NH_4Cl)
5. Magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or MgSO_4)
6. Calcium chloride (CaCl_2)
7. Ferric chloride ($\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$)

Reagents (Prepared)

1. Phosphate buffer--pH 7.2--dissolve 4.25 g KH_2PO_4 , 10.9 g K_2HPO_4 , 16.7 g $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and 0.85 g NH_4Cl in Milli-Q deionized water and dilute to 500 mL. Prepare annually or when Blank values exceed 0.2 mg/L.
2. Magnesium sulfate solution--dissolve 11.2 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (5.3 g MgSO_4) in Milli-Q deionized water and dilute to 500 mL. Prepare annually or when Blank values exceed 0.2 mg/L.
3. Calcium chloride solution--dissolve 13.75 g CaCl_2 in Milli-Q deionized water and dilute to 500 mL. Prepare annually or when Blank values exceed 0.2 mg/L.
4. Ferric chloride solution--dissolve 0.125 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in Milli-Q deionized water and dilute to 500 mL. Prepare annually or when Blank values exceed 0.2 mg/L.

Dilution Water Preparation

Place the necessary amount of Milli-Q deionized water in a large glass container. Saturate the water with DO by aerating with compressed air. The temperature of the water should be $20^\circ \pm 1^\circ\text{C}$. For each liter of water, add 1 mL each of the phosphate buffer, magnesium sulfate solution, calcium chloride solution and ferric chloride solution. Prepare the dilution water the day of use.

LINEAR ALKYL BENZENE SULFONATE
- METHYLENE BLUE ACTIVE SUBSTANCES - (MBAS)

Reference

1. Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985, pages 581-585.

Principles

Anionic surfactants such as LAS react with methylene blue to form a colored salt. This salt is extractable into chloroform where the absorbance at 652 nm can be measured.

NOTE: CHLOROFORM IS LISTED AS A CLASS 2 SUSPECT HUMAN CARCINOGEN. REFER TO LABORATORY POLICY GUIDE - USE OF CARCINOGENS (L-H.10) FOR PROPER HANDLING OF THIS MATERIAL.

Limitations

The method is limited to water of "drinking quality" and not wastes or sewage. The method is subject to positive interferences from the following compounds: organic sulfates, sulfonates, carboxylates, phosphates, phenols, inorganic cyanates, chlorides, nitrates, and thiocyanates. Negative interferences can be caused by amines. (With the exception of chlorides, interferences from the above compounds can be generally ignored unless the compound is present in "unusually high" quantities.)

Minimum detectable amount: 10 µg LAS

Equipment

1. 250 mL separatory funnels with Teflon stopcorks.
2. 100 mL Volumetric flasks.
3. Spectrophotometer for use at 652 nm providing a light path of one cm or longer.

Reagents (Stock)

1. Linear Alkylbenzene Sulfonate, LAS
2. Phenolphthalein indicator solution.
3. Sodium Hydroxide, Reagent grade, NaOH.
4. Sulfuric Acid, conc., H₂SO₄

5. Chloroform, CHCl_3 - CLASS 2 - SUSPECT HUMAN CARCINOGEN
6. Methylene Blue (Eastman No. P573 or equivalent)
7. Monosodium dihydrogen phosphate monohydrate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

Reagents (Prepared)

1. Methylene Blue Reagent - Dissolve 100 mg of methylene blue in 100 mL deionized water. Transfer 30 mL to a one liter flask, add 500 mL of deionized water, 6.8 mL of conc. sulfuric acid, and 50 grams of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Shake until dissolved and dilute to one liter. Prepare annually.
2. Wash solution - Add 6.8 mL of conc. sulfuric acid to 500 mL of deionized water in one liter flask. Add 50.0 grams of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, shake until dissolved and dilute to one liter. Prepare annually.
3. Sodium Hydroxide, 1N - Dissolve 40 grams NaOH in one liter of water. Prepare annually.
4. Sulfuric Acid, 1N - Dilute 28 mL of conc. H_2SO_4 to one liter. Prepare annually.

Standards

1. Stock LAS - Weigh an amount of the reference material equal to 1.000 grams LAS on a 100% active basis. Dissolve in deionized water and dilute to one liter. 1.00 mL = 1.00 mg LAS. Store in a refrigerator. Prepare weekly.
2. Working standard LAS - Dilute 10.00 mL stock LAS to one liter with deionized water. 1.00 mL = 10.0 μg LAS. Prepare daily.

Procedures

Standard Curve: Pipet 1.00, 3.00, 5.00, 7.00, and 10.00 mL of the LAS working standard into separatory funnels and dilute each to 100 mL. This gives standards equalling 10, 30 50, 70 and 100 μg LAS. Treat as per the following procedure.

1. Add 100 mL of the sample to a separatory funnel. (This may vary depending on the concentration of LAS.)
2. Add one or two drops of phenolphthalein.
3. Add 1N NaOH dropwise until alkaline and then add 1N H_2SO_4 until pink color disappears.
4. Add 10 mL of chloroform and 25 mL of methylene blue reagent and rock vigorously for 30 seconds. (NO NOT agitate vigorously because emulsion may form.) Allow the phase to separate.

NOTE: ALL CHLOROFORM WORK SHALL BE DONE IN A HOOD WHILE WEARING GLOVES.

5. Swirl the sample gently, let settle and draw off lower phase into a secondary funnel. If sample CHCl_3 layer is lighter than low standard, stop here and report less than value of 0.1 mg/L. See end of procedure for disposal of chloroform solutions.
6. Repeat the extraction three times, using 10 mL of chloroform.
Note: If the blue color in the water phase becomes faint and disappears, discard the sample and start over, using a smaller sample size.
7. Combine all extracts in the second separatory funnel. Add 50 mL of wash solution, shake vigorously for 30 seconds and allow to settle. (No emulsions should form.)
8. Draw off the chloroform layer through IPS phase separating paper into a 100 mL volumetric flask.
9. Wash the aqueous solution from step seven twice with 10 mL of chloroform, collecting the chloroform in the 100 mL flask.
10. Rinse the phase separating paper with chloroform, collecting the rinse in the flask. Dilute to 100 mL mark with chloroform.
11. Measure the absorbance at 652 nm with one cm cells against a chloroform blank.

Disposal All chloroform solutions shall be disposed of in the organic solvent and carcinogen waste container.

Calculation

Plot a curve of standard concentration in μg LAS extracted versus absorbance.

Read the value of LAS from the curve and calculate as follows:

$$\frac{\mu\text{g LAS}}{\text{liters of sample extracted}} = \text{mg/liter LAS}$$

Report as "Methylene Blue Active Substances".

END

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