

**Method  
1650**

***Adsorbable Organic Halides  
by Adsorption and Coulometric Titration***

***Revision C  
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## **Acknowledgments**

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## **Disclaimer**

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# Method 1650

## *Adsorbable Organic Halides by Adsorption and Coulometric Titration*

### **1.0 SCOPE AND APPLICATION**

- 1.1** This method is for determination of adsorbable organic halides (AOX) associated with the Clean Water Act, the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other organic halides amenable to combustion and coulometric titration. The method is designed to meet the survey and monitoring requirements of the Environmental Protection Agency (EPA).
- 1.2** The method is applicable to the determination of AOX in water and wastewater. This method is a combination of several existing methods for organic halide measurements (References 1 through 7).
- 1.3** The method can be used to measure organically-bound halides (chlorine, bromine, iodine) present in dissolved or suspended form. Results are reported as organic chloride ( $\text{Cl}^-$ ). The detection limit of the method is usually dependent on interferences rather than instrumental limitations. A method detection limit (MDL; Reference 8) of 6.6  $\mu\text{g/L}$ , and a minimum level (ML; Section 18) of 20  $\mu\text{g/L}$ , can be achieved with no interferences present.
- 1.4** This method is for use by or under the supervision of analysts experienced in the use of a combustion/micro-coulometer. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedures described in Section 9.2.
- 1.5** Any modification of the method beyond those expressly permitted (Section 9.1.2) is subject to application and approval of an alternate test procedure under 40 *CFR* 136.4 and 136.5.

### **2.0 SUMMARY OF METHOD**

- 2.1** Sample preservation: Residual chlorine that may be present is removed by the addition of sodium thiosulfate. Samples are adjusted to a  $\text{pH} < 2$  and maintained at 0 to 4°C until analysis.
- 2.2** Sample analysis: Organic halide in water is determined by adsorption onto granular activated carbon (GAC), washing the adsorbed sample and GAC to remove inorganic halide, combustion of the sample and GAC to form the hydrogen halide, and titration of the hydrogen halide with a micro-coulometer, as shown in Figure 1.
- 2.3** Micro-coulometer.
- 2.3.1** This detector operates by maintaining a constant silver-ion concentration in a titration cell. An electric potential is applied to a solid silver electrode to produce silver ions in the cell. As hydrogen halide produced from the combustion of organic halide enters the cell, it is partitioned into an acetic acid electrolyte where it precipitates as silver halide. The current produced is integrated over the combustion period. The electric charge is proportional to the number of moles of halogen captured in the cell (Reference 6).

- 2.3.2** The mass concentration of organic halides is reported as an equivalent concentration of organically bound chloride (Cl<sup>-</sup>).

### **3.0 DEFINITIONS**

- 3.1** Adsorbable organic halides is defined as the analyte measured by this method. The nature of the organo-halides and the presence of semi-extractable material will influence the amount measured and interpretation of results.
- 3.2** Definitions for terms used in this method are given in the glossary at the end of the method (Section 18).

### **4.0 INTERFERENCES**

- 4.1** Solvents, reagents, glassware, and other sample processing hardware may yield elevated readings from the micro-coulometer. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks initially and with each sample batch (samples started through the adsorption process in a given eight-hour shift, to a maximum of 20 samples). Specific selection of reagents and purification of solvents may be required.
- 4.2** Glassware is cleaned by detergent washing in hot water, rinsing with tap water and distilled water, capping with aluminum foil, and baking at 450°C for at least one hour. For some glassware, immersion in a chromate cleaning solution prior to detergent washing may be required. If blanks from glassware without cleaning or with fewer cleaning steps show no detectable organic halide, the cleaning steps that do not eliminate organic halide may be omitted.
- 4.3** Most often, contamination results from methylene chloride vapors in laboratories that perform organic extractions. Heating, ventilating, and air conditioning systems that are shared between the extraction laboratory and the laboratory in which organic halide measurements are performed transfer the methylene chloride vapors to the air in the organic halide laboratory. Exposure of the activated carbon used in the analysis results in contamination. Separate air handling systems, charcoal filters, and glove boxes can be used to minimize this exposure.
- 4.4** Activated carbon.
- 4.4.1** The purity of each lot of activated carbon must be verified before each use by measuring the adsorption capacity and the background level of halogen (Section 9.5). The stock of activated carbon should be stored in its granular form in a glass container that is capped tightly. Protect carbon at all times from sources of halogen vapors.
- 4.4.2** Inorganic substances such as chloride, chlorite, bromide, and iodide will adsorb on activated carbon to an extent dependent on their original concentration in the aqueous solution and the volume of sample adsorbed. Treating the activated carbon with a solution of nitrate causes competitive desorption of inorganic halide species. However, if the inorganic halide concentration is greater than 2,000 times the organic halide concentration, artificially high results may be obtained.

- 4.4.3** Halogenated organic compounds that are weakly adsorbed on activated carbon are only partially recovered from the sample. These include certain alcohols and acids such as chloroethanol and chloroacetic acid that can be removed from activated carbon by the nitrate wash.
- 4.5** Polyethylene gloves should be worn when handling equipment surfaces in contact with the sample to prevent transfer of contaminants that may be present on the hands.

## **5.0 SAFETY**

- 5.1** The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical substance should be treated as a potential health hazard. Exposure to these substances should be reduced to the lowest possible level. 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 (MSDSs) should be made available to all personnel involved in the chemical analysis. Additional information on laboratory safety can be found in References 9 through 11.
- 5.2** This method employs strong acids. Appropriate clothing, gloves, and eye protection should be worn when handling these substances.
- 5.3** Field samples may contain high concentrations of toxic volatile compounds. Sample containers should be opened in a hood and handled with gloves that will prevent exposure.

## **6.0 EQUIPMENT AND SUPPLIES**

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**NOTE:** *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

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- 6.1** Sampling equipment.
- 6.1.1** Bottles: 100- to 4000-mL, amber glass, sufficient for all testing (Section 8.2). Detergent water wash, chromic acid rinse, rinse with tap and distilled water, cover with aluminum foil, and heat to 450°C for at least one hour before use.
- 6.1.2** PTFE liner: Cleaned as above and baked at 100 to 200°C for at least one hour.
- 6.1.3** Bottles and liners must be lot certified to be free of organic halide by running blanks according to this method.
- 6.2** Scoop for granular activated carbon (GAC): Capable of precisely measuring 40 mg ( $\pm 5$  mg) GAC (Dohrmann Measuring Cup 521-021, or equivalent).
- 6.3** Batch adsorption and filtration system.
- 6.3.1** Adsorption system: Rotary shaker, wrist action shaker, ultrasonic system, or other system for assuring thorough contact of sample with activated carbon. Systems different from the one described below must be demonstrated to meet the performance requirements in Section 9 of this method.
- 6.3.1.1** Erlenmeyer flasks: 250- to 1500-mL with ground-glass stopper, for use with rotary shaker.
- 6.3.1.2** Shake table: Sybron Thermolyne Model LE "Big Bill" rotator/shaker, or equivalent.



- 6.5.1.3** Boat sampler: Capable of holding 35 to 45 mg of activated carbon and a polycarbonate filter, and fitting into the combustion tube (Section 6.5.1.1). Some manufacturers offer an enlarged boat and combustion tube for this purpose. Under a time-controlled sequence, the boat is first moved into an evaporation zone where water and other volatiles are evaporated, and then into the combustion zone where the carbon and all other organic material in the boat are burned in a flowing oxygen stream. The evolved gases are transported by a non-reactive carrier gas to the micro-coulometer cell.
- 6.5.1.4** Motor driven boat sampler: Capable of advancing the combustion boat into the furnace in a reproducible time sequence. A suggested time sequence is as follows:
- A. Establish initial gas flow rates: 160 mL/min CO<sub>2</sub>; 40 mL/min O<sub>2</sub>.
  - B. Sequence start.
  - C. Hold boat in hatch for five seconds to allow integration for baseline subtraction.
  - D. Advance boat into vaporization zone.
  - E. Hold boat in vaporization zone for 110 seconds.
  - F. Establish gas flow rates for combustion: 200 mL/min O<sub>2</sub>; 0 mL/min CO<sub>2</sub>; advance boat into pyrolysis zone (800°C).
  - G. Hold boat in pyrolysis zone for six minutes.
  - H. Return gas flow rates to initial values; retract boat into hatch to cool and to allow remaining HX to be swept into detector (approximately two minutes).
  - I. Stop integration at 10 minutes after sequence start.

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**NOTE:** *If the signal from the detector does not return to baseline, it may be necessary to extend the pyrolysis time.*

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The sequence above may need to be optimized for each instrument.

- 6.5.1.5** Absorber: Containing sulfuric acid to dry the gas stream after combustion to prevent backflush of electrolyte is highly recommended.
- 6.5.2** Micro-coulometer system: Capable of detecting the equivalent of 0.2 µg of Cl<sup>-</sup> at a signal-to-noise ratio of 2; capable of detecting the equivalent of 1 µg of Cl<sup>-</sup> with a relative standard deviation less than 10%, and capable of accumulating a minimum of the equivalent of 500 µg of Cl<sup>-</sup> before a change of electrolyte is required.
- 6.5.2.1** Micro-coulometer cell: The three cell designs presently in use are shown in Figure 1. Cell operation is described in Section 2.
- 6.5.2.2** Cell controller: Electronics capable of measuring the small currents generated in the cell and accumulating and displaying the charge produced by hydrogen halides entering the cell. A strip-chart recorder is desirable for display of accumulated charge.

- 6.6 Miscellaneous glassware—nominal sizes are specified below; other sizes may be used, as necessary.
  - 6.6.1 Volumetric flasks: 5-, 10-, 25-, 50-, 100-, and 1000-mL.
  - 6.6.2 Beakers: 100-, 500-, and 1000-mL.
  - 6.6.3 Volumetric pipets: 1- and 10-mL with pipet bulbs.
  - 6.6.4 Volumetric micro-pipets: 10-, 20-, 50-, 100-, 200-, and 500- $\mu$ L with pipet control (Hamilton 0010, or equivalent).
  - 6.6.5 Graduated cylinders: 10-, 100-, and 1000-mL.
- 6.7 Micro-syringes: 10-, 50-, and 100- $\mu$ L.
- 6.8 Balances.
  - 6.8.1 Top-loading, capable of weighing 0.1 g.
  - 6.8.2 Analytical, capable of weighing 0.1 mg.
- 6.9 pH meter.
- 6.10 Wash bottles: 500- to 1000-mL, PTFE or polyethylene.
- 6.11 Strip-chart recorder: suggested but not required—useful for determining end of integration (Section 11.4.2).

## 7.0 REAGENTS AND STANDARDS

- 7.1 Granular activated carbon (GAC): 75 to 150  $\mu$ m (100 to 200 mesh); (Dohrmann, Mitsubishi, Carbon Plus, or equivalent), with chlorine content less than 1  $\mu$ g  $\text{Cl}^-$  per scoop (< 25  $\mu$ g  $\text{Cl}^-$  per gram), adsorption capacity greater than 1000  $\mu$ g  $\text{Cl}^-$  (as 2,4,6-trichlorophenol) per scoop (>25,000  $\mu$ g/g), inorganic halide retention of less than 1  $\mu$ g  $\text{Cl}^-$  per scoop in the presence of 10 mg of inorganic halide (< 20  $\mu$ g  $\text{Cl}^-$  per gram in the presence of 2500 mg of inorganic halide), and that meets the other test criteria in this method.
- 7.2 Reagent water: Water in which organic halide is not detected by this method.
  - 7.2.1 Preparation: Reagent water may be generated by:
    - 7.2.1.1 Activated carbon: Pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).
    - 7.2.1.2 Water purifier: Pass tap water through a purifier (Millipore Super Q, or equivalent).
  - 7.2.2 pH adjustment: Adjust the pH of the reagent water to < 2 with nitric acid for all reagent water used in this method, except for the acetic acid solution (Section 7.13).
- 7.3 Nitric acid ( $\text{HNO}_3$ ): Concentrated, analytical grade.
- 7.4 Sodium chloride ( $\text{NaCl}$ ) solution (100  $\mu$ g/mL of  $\text{Cl}^-$ ): Dissolve 0.165 g  $\text{NaCl}$  in 1000 mL reagent water. This solution is used for cell testing and for the inorganic halide rejection test.
- 7.5 Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) solution (100  $\mu$ g/mL of  $\text{Cl}^-$ ): Dissolve 0.1509 g  $\text{NH}_4\text{Cl}$  in 1000 mL reagent water.
- 7.6 Sulfuric acid: Reagent grade (specific gravity 1.84).
- 7.7 Oxygen: 99.9% purity.
- 7.8 Carbon Dioxide: 99.9% purity.
- 7.9 Nitrate stock solution: In a 1000-mL volumetric flask, dissolve 17 g of  $\text{NaNO}_3$  in approximately 100 mL of reagent water, add 1.4 mL nitric acid (Section 7.3) and dilute to the mark with reagent water.

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- 7.10** Nitrate wash solution: Dilute 50 mL of nitrate stock solution (Section 7.9) to 1000 mL with reagent water.
- 7.11** Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution (1 N): Weigh 79 grams of  $\text{Na}_2\text{S}_2\text{O}_3$  in a 1-L volumetric flask and dilute to the mark with reagent water.
- 7.12** Trichlorophenol solutions.
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*NOTE: The calibration solutions in this section employ 100-mL volumes. For determinations requiring a larger or smaller volume, increase or decrease the size of the volumetric flasks commensurately. For example, if a 1-L sample is to be analyzed, use 1000-mL flasks (Sections 7.12.3.1 and 7.12.4) and 10 times the volume of reagent water (Sections 7.12.3.1 and 7.12.4). The volume of stock solution added to the calibration solutions and precision and recovery (PAR) test solution remain as specified (Sections 7.12.3.2 and 7.12.4) so that the same amount of chloride is delivered to the coulometric cell regardless of the volume of the calibration and PAR solutions.*

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- 7.12.1** Methanol: HPLC grade.
- 7.12.2** Trichlorophenol stock solution (1.0 mg/mL of  $\text{Cl}^-$ ): Dissolve 0.186 g of 2,4,6-trichlorophenol in 100 mL of halide-free methanol.
- 7.12.3** Trichlorophenol calibration solutions.
- 7.12.3.1** Place approximately 90 mL of reagent water in each of five 100-mL volumetric flasks.
- 7.12.3.2** Using a calibrated micro-syringe or micro-pipets, add 2, 5, 10, 30, and 80  $\mu\text{L}$  of the trichlorophenol stock solution (Section 7.12.2) to the volumetric flasks and dilute each to the mark with reagent water to produce calibration solutions of 2, 5, 10, 30, and 80  $\mu\text{g Cl}^-$  per 100 mL of solution (20, 50, 100, 300, and 800  $\mu\text{g/L}$ ).
- 7.12.3.3** Some instruments may have a calibration range that does not extend to 800  $\mu\text{g/L}$  (80  $\mu\text{g of Cl}^-$ ). For those instruments, a narrower dynamic range may be used. However, if the concentration of halide in a sample exceeds that range, the sample must be diluted to bring the concentration within the range calibrated.
- 7.12.4** Trichlorophenol precision and recovery (PAR) test solution (10  $\mu\text{g/L}$  of  $\text{Cl}^-$ ): Partially fill a 100-mL volumetric flask, add 10  $\mu\text{L}$  of the stock solution (Section 7.12.2), and dilute to the mark with reagent water.
- 7.13** Acetic acid solution: Containing 30 to 70% acetic acid in deionized water, per the instrument manufacturer's instructions.

## **8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE**

### **8.1** Sample preservation.

- 8.1.1** Residual chlorine: If the sample is known or suspected to contain free chlorine, the chlorine must be reduced to eliminate positive interference that may result from continued chlorination reactions. A knowledge of the process from which the sample is collected may be of value in determining whether dechlorination is necessary. Immediately after sampling, test for residual chlorine using the following method or an alternative EPA method (Reference 12):



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- 9.1.5** The laboratory shall, on an ongoing basis, demonstrate through the analysis of the precision and recovery (PAR) standard that the analysis system is in control. These procedures are described in Section 9.10.
- 9.1.6** The laboratory shall perform quality control tests on the granular activated carbon. These procedures are described in Section 9.5.
- 9.1.7** Samples are analyzed in duplicate to demonstrate precision. These procedures are described in Section 9.6.
- 9.2** Initial demonstration of laboratory capability
- 9.2.1** Method Detection Limit (MDL)—To establish the ability to detect AOX, the laboratory should determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in Section 1.3 should be achieved prior to the practice of this method.
- 9.2.2** Initial precision and recovery (IPR): To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:
- 9.2.2.1** Analyze four aliquots of the PAR standard (Section 7.12.4) and a method blank according to the procedures in Sections 9.4 and 11.
- 9.2.2.2** Using the blank-subtracted results of the set of four analyses, compute the average percent recovery ( $X$ ) and the standard deviation of the percent recovery ( $s$ ) for the results.
- 9.2.2.3** The average percent recovery shall be in the range of 81 to 114  $\mu\text{g/L}$  and the standard deviation shall be less than 8  $\mu\text{g/L}$ . If  $X$  and  $s$  meet these acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however,  $s$  exceeds the precision limit or  $X$  falls outside the range for recovery, system performance is unacceptable. In this case, correct the problem and repeat the test.
- 9.3** Matrix spikes: The laboratory shall spike a minimum of 10% of samples from a given matrix type (e.g., C-stage filtrate, produced water, treated effluent) in duplicate (MS/MSD). If only one sample from a given matrix type is analyzed, an additional two aliquots of that sample shall be spiked.
- 9.3.1** The concentration of the analytes spiked into the MS/MSD shall be determined as follows:
- 9.3.1.1** If, as in compliance monitoring, the concentration of OX is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at one to five times higher than the background concentration determined in Section 9.3.2, whichever concentration is higher.
- 9.3.1.2** If the concentration of OX is not being checked against a regulatory limit, the spike shall be at the concentration of the precision and recovery standard (PAR; Section 7.12.4) or at one to five times higher than the background concentration determined in Section 9.3.2, whichever concentration is higher.
- 9.3.2** Analyze one sample out of each batch of 10 samples from each site to determine the background concentration of AOX. If necessary, prepare a solution of 2,4,6-trichlorophenol appropriate to produce a level in the sample one to five

times the background concentration. Spike two additional sample aliquots with spiking solution and analyze them to determine the concentration after spiking.

**9.3.2.1** Compute the percent recovery of each analyte in each aliquot:

$$\% \text{ Recovery} = \frac{100 (\text{Found} - \text{Background})}{T}$$

where:

*T* is the true value of the spike

**9.3.2.2** Compute the relative percent difference (RPD) between the two results (not between the two recoveries) as described in Section 12.4.

**9.3.2.3** If the RPD is less than 20%, and the recoveries for the MS and MSD are within the range of 78 to 116%, the results are acceptable.

**9.3.2.4** If the RPD is greater than 20%, analyze two aliquots of the precision and recovery standard (PAR).

**9.3.2.4.1** If the RPD for the two aliquots of the PAR is greater than 20%, the analytical system is out of control. In this case, repair the problem and repeat the analysis of the sample batch, including the MS/MSD.

**9.3.2.4.2** If, however, the RPD for the two aliquots of the PAR is less than 20%, dilute the sample chosen for the MS/MSD by a factor of 2 - 10 (to remain within the working range of the analytical system) and repeat the MS/MSD test. If the RPD is still greater than 20%, the result may not be reported for regulatory compliance purposes. In this case, choose another sample for the MS/MSD and repeat analysis of the sample batch.

**9.3.2.5** If the percent recovery for both the MS and MSD are less than 78% or greater than 116%, analyze the precision and recovery (PAR) standard.

**9.3.2.5.1** If the recovery of the PAR is outside the 78 to 116% range, the analytical system is out of control. In this case, repair the problem and repeat the analysis of the sample batch, including the MS/MSD.

**9.3.2.5.2** If the recovery of the PAR is within the range of 78 to 116%, dilute the sample, MS, and MSD by a factor of 2 - 10 (to remain within the working range of the analytical system) and re-analyze. If the results of the dilute analyses remain outside of the acceptable range, these results may not be reported for regulatory compliance purposes. In this case, choose another sample for the MS/MSD and repeat the analysis of the sample batch.

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- 9.4** Blanks.
- 9.4.1** Reagent water blanks: Analyzed to demonstrate freedom from contamination.
- 9.4.1.1** Analyze a reagent water blank with each batch of samples. The blank must be analyzed immediately preceding calibration verification to allow for blank subtraction and to demonstrate freedom from contamination and memory effects, and must include all details of the procedure to be followed when analyzing samples.
- 9.4.1.2** Prepare the reagent water blank using a volume of reagent water equivalent to the volume used for sample preparation (Section 11.1). If using the micro-column procedure, adsorb the method blank using two columns, as described in Section 11. Combust the GAC from each column separately, as described in Section 11.
- 9.4.1.3** If the result from the blank from the batch method or the sum of the results from two columns is more than 20 µg/L, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.
- 9.4.2** Nitrate-washed GAC blanks: Analyzed daily to demonstrate that the GAC is free from contamination.
- 9.4.2.1** Nitrate-washed GAC blank for the batch procedure: Analyze a batch nitrate-washed GAC blank by adding a scoop of dry GAC to the assembled filter apparatus containing the polycarbonate membrane and washing the GAC with the nitrate wash solution (Section 7.10) using the procedure in Section 11.2.6.
- 9.4.2.2** Nitrate-washed GAC blank for the column procedure: Analyze a column nitrate-washed GAC blank by assembling two carbon columns in series and washing the columns with the nitrate wash solution (Section 7.10) using the procedure in Section 11.3.4.2. Analyze the GAC in each column separately. The results of the second analysis must be within  $\pm 0.2$  µg Cl<sup>-</sup> of the first. A difference greater than 0.2 µg Cl<sup>-</sup> indicates a lack of homogeneity in the GAC that could introduce unacceptable variability. If the difference exceeds this amount, the GAC should be replaced.
- 9.4.3** The result for the reagent water blank (Section 9.4.1) shall not exceed the result for the nitrate wash blank (Section 9.4.2.1 or 9.4.2.2) by more than 0.5 µg Cl<sup>-</sup>.
- 9.5** Granular activated carbon (GAC) batch testing: Each lot number or batch of activated carbon received from a supplier is tested once before use to ensure adequate quality. Use only GAC that meets the test criteria below.
- 9.5.1** Contamination test: Analyze a scoop of GAC. Reject carbon if the amount of OX exceeds 1 µg (25 µg Cl<sup>-</sup>/g).
- 9.5.2** Inorganic chloride adsorption test: Attempt to adsorb NaCl from 100 mL of a solution containing 100 mg/L in reagent water. Wash with nitrate solution and analyze. The amount of halide should be less than 1 µg Cl<sup>-</sup> larger than the blank. A larger amount indicates significant uptake of inorganic chloride by the carbon. Reject carbon if the 1 µg level is exceeded.
- 9.6** Samples that are being used for regulatory compliance purposes shall be analyzed in duplicate.

- 9.6.1** The procedure for preparing duplicate sample aliquots is described in Section 11.5.
  - 9.6.2** Calculate the RPD by following the same procedure described in Section 12.4.
  - 9.6.3** If the RPD is greater than 20%, the analyses must be repeated.
  - 9.6.4** If the RPD remains greater than 20%, the result may not be reported for regulatory compliance purposes.
- 9.7** The specifications in this method can be met if the apparatus used is calibrated properly and maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 9.9), and for initial (Section 9.2.2) and ongoing (Section 9.10) precision and recovery should be identical, so that the most precise results will be obtained.
- 9.8** Depending on specific program requirements, field duplicates may be collected to determine the precision of the sampling technique.
- 9.9** At the beginning and end of each eight-hour shift during which analyses are performed, system performance and calibration are verified. Verification of system performance and calibration may be performed more frequently, if desired.
  - 9.9.1** If performance and calibration are verified at the beginning and end of each shift (or more frequently), samples analyzed during that period are considered valid.
  - 9.9.2** If performance and calibration are not verified at both the beginning and end of a shift (or more frequently), samples analyzed during that period must be reanalyzed.
  - 9.9.3** If calibration is verified at the beginning of a shift, recalibration using the five standards described in Section 10.6 is not necessary; otherwise, the instrument must be recalibrated prior to analyzing samples (Section 10).
  - 9.9.4** Cell maintenance and other changes to the analytical system that can affect system performance may not be performed during the eight-hour (or shorter) shift.
- 9.10** Calibration verification and ongoing precision and recovery: Calibration and system performance are verified by the analysis of the 100 µg/L PAR standard.
  - 9.10.1** Analyze a blank (Section 9.4) and analyze the PAR standard (Section 7.12.4) immediately thereafter at the beginning and end of each shift. Compute the concentration of organic halide in the blank and in the PAR standard using the procedures in Section 12. The blank shall be less than 2 µg Cl<sup>-</sup> (20 µg/L equivalent).
  - 9.10.2** Subtract the result for the blank from the result of the PAR standard using the procedures in Section 12, and compute the percent recovery of the blank-subtracted PAR standard. The percent recovery shall be in the range of 78 to 116%.
  - 9.10.3** If the recovery is within this range, the analytical process is in control and analysis of blanks and samples may proceed. If, however, the recovery is not within the acceptable range, the analytical process is not in control. In this event, correct the problem and repeat the ongoing precision and recovery test (Section 9.10), or recalibrate (Sections 10.5 through 10.6).

- 9.10.4** If the recovery is not within the acceptable range for the PAR standard analyzed at the end of the eight-hour shift, correct the problem, repeat the ongoing precision and recovery test (Section 9.10), or recalibrate (Sections 10.5 through 10.6), and reanalyze the sample batch that was analyzed during the eight-hour shift.
- 9.10.5** If the recovery is within the acceptable range at the end of the shift, and samples are to be analyzed during the next eight-hour shift, the end of shift verification may be used as the beginning of shift verification for the subsequent shift, provided the next eight-hour shift begins as the first shift ends.
- 9.11** It is suggested but not required that the laboratory develop a statement of data quality for AOX and develop QC charts to form a graphic demonstration of method performance. Add results that pass the specification in Section 9.10.2 to initial and previous ongoing data. Develop a statement of data quality by calculating the average percent recovery ( $R$ ) and the standard deviation of percent recovery ( $s_r$ ). Express the accuracy as a recovery interval from  $R - 2s_r$  to  $R + 2s_r$ . For example, if  $R = 95\%$  and  $s_r = 5\%$ , the accuracy is 85 to 105%.

## **10.0 CALIBRATION AND STANDARDIZATION**

- 10.1** Assemble the OX system and establish the operating conditions necessary for analysis. Differences between various makes and models of instruments will require different operating procedures. Laboratories should follow the operating instructions provided by the manufacturer of their particular instrument. Sensitivity, instrument detection limit, precision, linear range, and interference effects must be investigated and established for each particular instrument. Calibration is performed when the instrument is first set up and when calibration cannot be verified (Section 9.9).
- 10.2** Cell performance test: Inject 100  $\mu\text{L}$  of the sodium chloride solution (10  $\mu\text{g Cl}^-$ ; Section 7.4) directly into the titration cell electrolyte. Adjust the instrument to produce a reading of 10  $\mu\text{g Cl}^-$ .
- 10.3** Combustion system test: This test can be used to assure that the combustion/micro-coulometer systems are performing properly without introduction of carbon. This test should be used during initial instrument setup and when instrument performance indicates a problem with the combustion system.
- 10.3.1** Designate a quartz boat for use with the ammonium chloride ( $\text{NH}_4\text{Cl}$ ) solution only.
- 10.3.2** Inject 100  $\mu\text{L}$  of the  $\text{NH}_4\text{Cl}$  solution (Section 7.5) into this boat and proceed with the analysis.
- 10.3.3** The result shall be between 9.5 and 10.5  $\mu\text{g Cl}^-$ . If the recovery is not between these limits, the combustion or micro-coulometer systems are not performing properly. Check the temperature of the combustion system, verify that there are no leaks in the combustion system, confirm that the cell is performing properly (Section 10.2), and then repeat the test.
- 10.4** Trichlorophenol combustion test: This test can be used to assure that the combustion/micro-coulometer systems are performing properly when carbon is introduced. It should be used during instrument setup and when it is necessary to isolate the adsorption and combustion steps.

- 10.4.1** Inject 10  $\mu\text{L}$  of the 1 mg/mL trichlorophenol stock solution (Section 7.12.2) onto one level scoop of GAC in a quartz boat.
  - 10.4.2** Immediately proceed with the analysis to prevent loss of trichlorophenol and to prevent contamination of the carbon.
  - 10.4.3** The result shall be between 9.0 and 11.0  $\mu\text{g Cl}^-$ . If the recovery is not between these limits, the combustion/micro-coulometer system shall be adjusted and the test repeated until the result falls within these limits.
- 10.5** Background level of  $\text{Cl}^-$ : Determine the average background level of  $\text{Cl}^-$  for the entire analytical system as follows:
  - 10.5.1** Using the procedure in Section 11 (batch or column) that will be used for the analysis of samples, determine the background level of  $\text{Cl}^-$  in each of three portions of reagent water. The volume of reagent water used shall be the same as the volume used for analysis of samples.
  - 10.5.2** Calculate the average (mean) concentration of  $\text{Cl}^-$  and the standard deviation of the concentration.
  - 10.5.3** The sum of the average concentration plus two times the standard deviation of the concentration shall be less than 20  $\mu\text{g/L}$ . If not, the water or carbon shall be replaced, or the adsorption system moved to an area free of organic halide vapors, and the test (Section 10.5) shall be repeated. Only after this test is passed may calibration proceed.
- 10.6** Calibration by external standard: A calibration line encompassing the calibration range is developed using solutions of 2,4,6-trichlorophenol.
  - 10.6.1** Analyze each of the five calibration solutions (Section 7.12.3) using the procedure in Section 11 (batch or column) that will be used for the analysis of samples, and the same procedure that was used for determination of the system background (Section 10.5). Analyze these solutions beginning with the lowest concentration and proceeding to the highest. Record the response of the micro-coulometer to each calibration solution.
  - 10.6.2** Prepare a method blank as described in Section 9.4. Subtract the value of the blank from each of the five calibration results, as described in Section 12.
  - 10.6.3** Calibration factor (ratio of response to concentration): Using the blank subtracted results, compute the calibration factor at each calibration point, and compute the average calibration factor and the relative standard deviation (coefficient of variation;  $C_v$ ) of the calibration factor over the calibration range.
  - 10.6.4** Linearity: The  $C_v$  of the calibration factor shall be less than 20%; otherwise, the calibration shall be repeated after adjustment of the combustion/micro-coulometer system and/or preparation of fresh calibration standards.
  - 10.6.5** Using the average calibration factor, compute the percent recovery at each calibration point. The recovery at each calibration point shall be within the range of 80 to 111%. If any point is not within this range, a fresh calibration standard shall be prepared for that point, this standard shall be analyzed, and the calibration factor (Section 10.6.3) and calibration linearity (Section 10.6.4) shall be computed using the new calibration point. All points used in the calibration must meet the 80 to 111% recovery specification.

## 11.0 PROCEDURE

**11.1** Sample dilution: Many samples will contain high concentrations of halide. If analyzed without dilution, the micro-coulometer can be overloaded, resulting in frequent cell cleaning and downtime. The following guidance is provided to assist in estimating dilution levels.

**11.1.1** Paper and pulp mills that employ chlorine bleaching: Samples from pulp mills that use a chlorine bleaching process may overload the micro-coulometer. To prevent system overload, the maximum volume suggested paper industry samples that employ halide in the bleaching process is 100 mL. An adsorption volume as small as 25 mL may be used, provided the concentration of AOX in the sample can be measured reliably, as defined by the requirements in Section 9.11. To minimize volumetric error, an adsorption volume less than 25 mL may not be used. If AOX cannot be measured reliably in a 100-mL sample volume, a sample volume to a maximum of 1000 mL must be used. The sample and adsorption volumes are suggested for paper industry samples employing chlorine compounds in the bleaching process:

<i>Paper or pulp mill stream</i>	<i>Sample volume (mL)*</i>	<i>Adsorption volume (mL)</i>
Evaporator condensate	100	100
Process water	100	100
Pulp mill effluent	30	50
Paper mill effluent	10	25
Combined mill effluent	5	25
Combined bleach effluent	1	25
C-stage filtrate	0.5	25
E-stage filtrate	0.5	25

\* Assumes dilution to final volume of 100 mL. All sample aliquots (replicates, diluted samples) must be analyzed using the same fixed final volume (sample volume plus reagent water, as needed).

**11.1.2** Sample dilution procedure.

**11.1.2.1** Partially fill a precleaned volumetric flask with pH < 2 reagent water, allowing for the volume of sample to be added.

**11.1.2.2** Mix sample thoroughly by tumbling or shaking vigorously.

**11.1.2.3** Immediately withdraw the required sample aliquot using a pipet or micro-syringe.

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**NOTE:** Because it will be necessary to rinse the pipet or micro-syringe (Section 11.1.2.5), it may be necessary to pre-calibrate the pipet or micro-syringe to assure that the exact volume desired will be delivered.

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**11.1.2.4** Dispense or inject the aliquot into the volumetric flask.



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- 11.3.1.3** Insert a Cerafelt plug into the open end of the column to hold the carbon in place.
- 11.3.1.4** Store the columns in a glass jar with PTFE lined screw-cap to prevent infiltration of halide vapors from the air.
- 11.3.2** Column setup.
- 11.3.2.1** Install two columns in series in the adsorption module.
- 11.3.2.2** If the sample is known or expected to contain particulates that could prevent free flow of sample through the micro-columns, a Cerafelt plug is placed in the tubing ahead of the columns. If a measurement of the OX content of the particulates is desired, the Cerafelt plug can be washed with nitrate solution, placed in a combustion boat, and processed as a separate sample.
- 11.3.3** Adjusting sample flow rate: Because the flow rate used to load the sample onto the columns can affect the ability of the GAC to adsorb organic halides, the flow rate of the method blank is measured, and the gas pressure used to process samples is adjusted accordingly. The flow rate of the blank, which is composed of acidified reagent water and contains no particulate matter, should be greater than the flow rate of any sample containing even small amounts of particulate matter.
- 11.3.3.1** Fill the sample reservoir with the volume of reagent water chosen for the analysis (Section 9.4.1.2) that has been preserved and acidified as described in Section 8. Cap the reservoir.
- 11.3.3.2** Adjust the gas pressure per the manufacturer's instructions. Record the time required for the entire volume of reagent water to pass through both columns. The flow rate must not exceed 3 mL/min over the duration of the time required to adsorb the volume. If this flow rate is exceeded, adjust gas pressure, prepare another blank, and repeat the adsorption.
- 11.3.3.3** Once the flow rate for the blank has been established, the same adsorption conditions must be applied to all subsequent samples during that eight-hour shift, or until another method blank is processed, whichever comes first. To aid in overcoming breakthrough problems, a lower gas pressure (and, therefore, flow rate) may be used for processing of samples, if desired. If the sample adsorption unit is disassembled or cleaned, the flow rate must be checked before processing additional samples.
- 11.3.3.4** Elute the pair of columns with 2 mL of nitrate wash solution. The flow rate of nitrate wash solution must not exceed 3 mL/min.
- 11.3.3.5** Separate the columns and mark for subsequent analysis.
- 11.3.4** The adsorption of sample volumes is performed in a similar fashion. Fill the sample reservoir with the sample volume chosen for the analysis (Section 11.1), that has been preserved as described in Section 8. All analyses must be performed with this volume (sample volume plus reagent water, as needed) in order to maintain a flow rate no greater than that determined for the blank (see Section 11.3.3).



- 11.5.2** Adsorb the sample using the same technique (batch or column) used for the first sample volume. Combust the GAC from the second volume as described in Section 11.4, and calculate the results as described in Section 12. Compare the results of the two analyses as described in Section 12.4.
- 11.5.3** Duplicate analyses are not required for method blanks, as different dilution levels are not possible.
- 11.5.4** Duplicate analyses of the PAR standard used for calibration verification (Section 9.10) are not required.

## 12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1** Batch Adsorption Method: Calculate the blank-subtracted concentration of adsorbable organic halide detected in each sample (in micrograms of chloride per liter) using the following equation:

$$AOX (\mu\text{g/L}) = \frac{(C - B)}{V}$$

where:

$C$  =  $\mu\text{g Cl}^-$  from micro-coulometer for the sample

$B$  =  $\mu\text{g Cl}^-$  from micro-coulometer for the reagent water blank (Section 9.4.1)

$V$  = volume of sample in liters

This calculation is performed for each of the two dilution levels analyzed for each sample.

- 12.2** Column Adsorption Method: Calculate the blank-subtracted concentration of adsorbable organic halide detected in each sample (in micrograms of chloride per liter) using the following equation:

$$AOX (\mu\text{g/L}) = \frac{[(C_1 + C_2) - (B_1 + B_2)]}{V}$$

where:

$C_1$  =  $\mu\text{g Cl}^-$  from micro-coulometer for first column from the sample

$C_2$  =  $\mu\text{g Cl}^-$  from micro-coulometer for second column from the sample

$B_1$  =  $\mu\text{g Cl}^-$  from micro-coulometer for first column from the reagent water blank (Section 9.4.1)

$B_2$  =  $\mu\text{g Cl}^-$  from micro-coulometer for second column from the reagent water blank (Section 9.4.1)

$V$  = volume of sample in liters

- 12.3** Percent breakthrough: For each sample analyzed by the column method, calculate the percent breakthrough of halide from the first column to the second column, using the following equation:

$$\% \text{ Breakthrough} = \frac{(C_2 - B_2)(100)}{[(C_1 - B_1) + (C_2 - B_2)]}$$

- 12.3.1** For samples to be reported for regulatory compliance purposes, the percent breakthrough must be less than or equal to 25% for both of the two analyses performed on each sample (see Section 11.5).

- 12.3.2** If the breakthrough exceeds 25%, dilute the affected sample further, maintaining the amount of halide at least three times higher than the level of blank, and reanalyze the sample. Ensure that the sample is also analyzed at a second level of dilution that is at least a factor of 2 different (and still higher than three times the blank).
- 12.4** Relative percent difference (RPD): Calculate the relative percent difference between the results of the two analyses of each sample, using the following equation:
- $$RPD = \frac{200|(AOX_1 - AOX_2)|}{[(AOX_1 + AOX_2)]}$$
- 12.5** High concentrations of AOX: If the amount of halide from either analysis exceeds the calibration range, dilute the sample and reanalyze, maintaining at least a factor of 2 difference in the dilution levels of the two portions of the sample used.
- 12.6** Low concentrations of AOX: The blank-subtracted final result from the batch procedure or the sum of the blank-subtracted results from the two carbon columns should be significantly above the level of the blank.
- 12.6.1** If the instrument response for a sample exceeds the instrument response for the blank by a factor of at least 3, the result is acceptable.
- 12.6.2** If the instrument response for a sample is less than three times the instrument response for the blank, and the sample has been diluted, analyze a less dilute aliquot of sample.
- 12.6.3** If the instrument response of an undiluted sample containing AOX above the minimum level is less than three times the instrument response for the blank, the result is suspect and may not be used for regulatory compliance purposes. In this case, find the cause of contamination, correct the problem, and reanalyze the sample under the corrected conditions.
- 12.7** Report results that meet all of the specifications in this method as the mean of the blank-subtracted values from Section 12.1 or 12.2 for the two analyses at different dilution levels, in  $\mu\text{g/L}$  of  $\text{Cl}^-$  (not as 2,4,6-trichlorophenol), to three significant figures. Report the RPD of the two analyses. For samples analyzed by the column procedure, also report the percent breakthrough.

### **13.0 METHOD PERFORMANCE**

The specifications contained in this method are based on data from a single laboratory and from a large-scale study of the pulp and paper industry.

### **14.0 POLLUTION PREVENTION**

- 14.1** The solvents used in this method pose little threat to the environment when recycled and managed properly.
- 14.2** Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

**15.0 WASTE MANAGEMENT**

- 15.1** It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.
- 15.2** Samples preserved with HCl or H<sub>2</sub>SO<sub>4</sub> to pH < 2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste. Acetic acid and silver acetate solutions resulting from cell flushing must be disposed of in accordance with all applicable federal, state, and local regulations.
- 15.3** For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction," both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

## **16.0 REFERENCES**

- 16.1** "Total Organic Halide, Methods 450.1—Interim," Prepared by Stephen Billets and James J. Lichtenberg, USEPA, Office of Research and Development, Physical and Chemical Methods Branch, EMSL-Cincinnati, Cincinnati, OH 45268, EPA 600/4-81-056 (1981).
- 16.2** Method 9020, USEPA Office of Solid Waste, "Test Methods for Evaluating Solid Waste, SW-846," Third Edition, 1987.
- 16.3** "Determination of Adsorbable Organic Halogens (AOX)," "German Standard Methods for the Analysis of Water, Waste Water and Sludge—General Parameters of Effects and Substances," Deutsche Industrie Norm (DIN) Method 38 409, Part 14, DIN German Standards Institute, Beuth Verlag, Berlin, Germany (1987).
- 16.4** "Water Quality—Determination of Adsorbable Organic Halogens (AOX)," International Organization for Standard/Draft International Standardization (ISO/DIS) Method 9562 (1988).
- 16.5** "Organically Bound Chlorine by the AOX Method," SCAN-W 9:89, Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-11486, Stockholm, Sweden (1989).
- 16.6** Method 5320, "Dissolved Organic Halogen," from "Standard Methods for the Examination of Water and Wastewater," 5320, American Public Health Association, 1015 15th St. NW, Washington, DC 20005 (1989).
- 16.7** "Canadian Standard Method for the Determination of Adsorbable Organic Halides (AOX) in Waters and Wastewaters," Environment Canada and The Canadian Pulp and Paper Association (1990).
- 16.8** 40 CFR Part 136, Appendix B.
- 16.9** "Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206, (Aug 1977).
- 16.10** "OSHA Safety and Health Standards, General Industry" OSHA 2206, 29 CFR 1910 (Jan 1976).
- 16.11** "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety (1979).
- 16.12** "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL-Cincinnati, Cincinnati, OH 45268, EPA-4-79-020 (March 1979).
- 16.13** "Validation of Method 1650: Determination of Organic Halide," Analytical Technologies Inc., ERCE Contract 87-3410, November 15, 1990. Available from the EPA Sample Control Center, DynCorp, 300 N. Lee St, Alexandria, VA 22314 (703-519-1140).

## **17.0 DIAGRAMS**

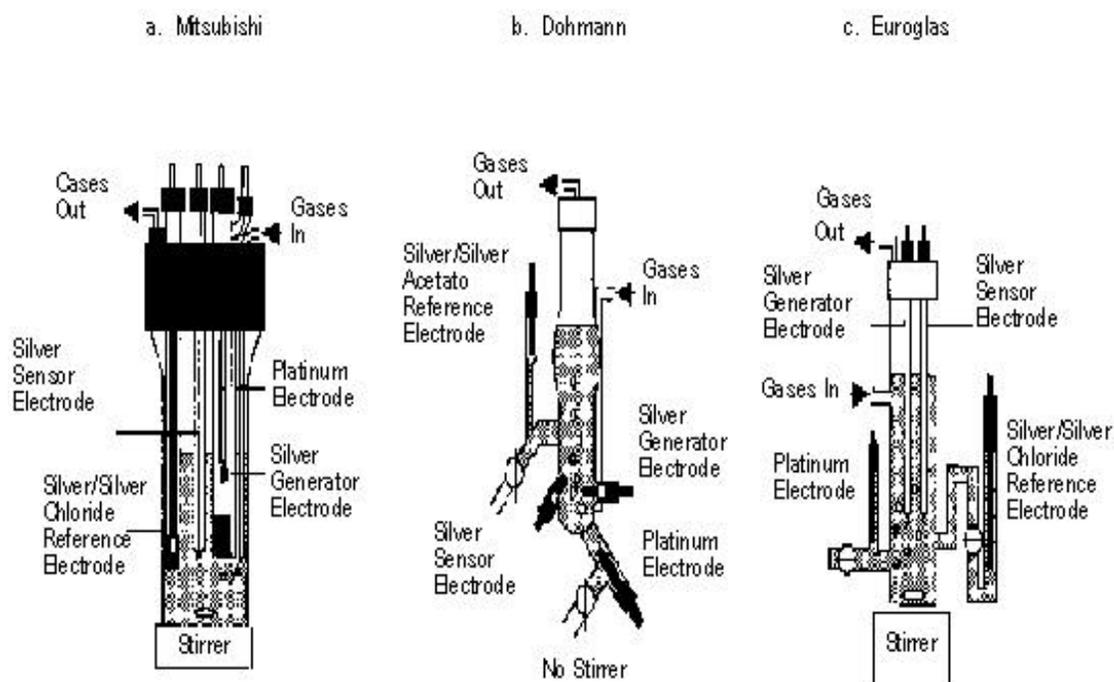


Figure 1. Microcoulometric Titration Cells (from Reference 7)

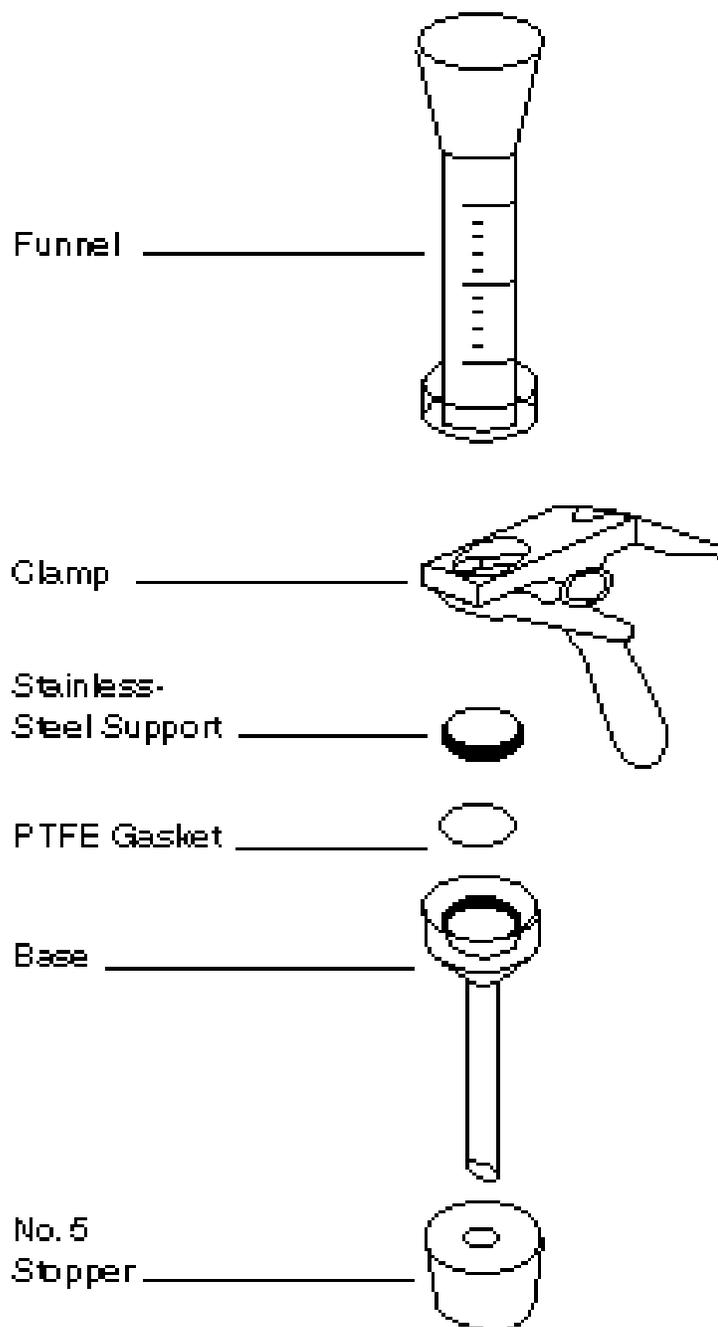
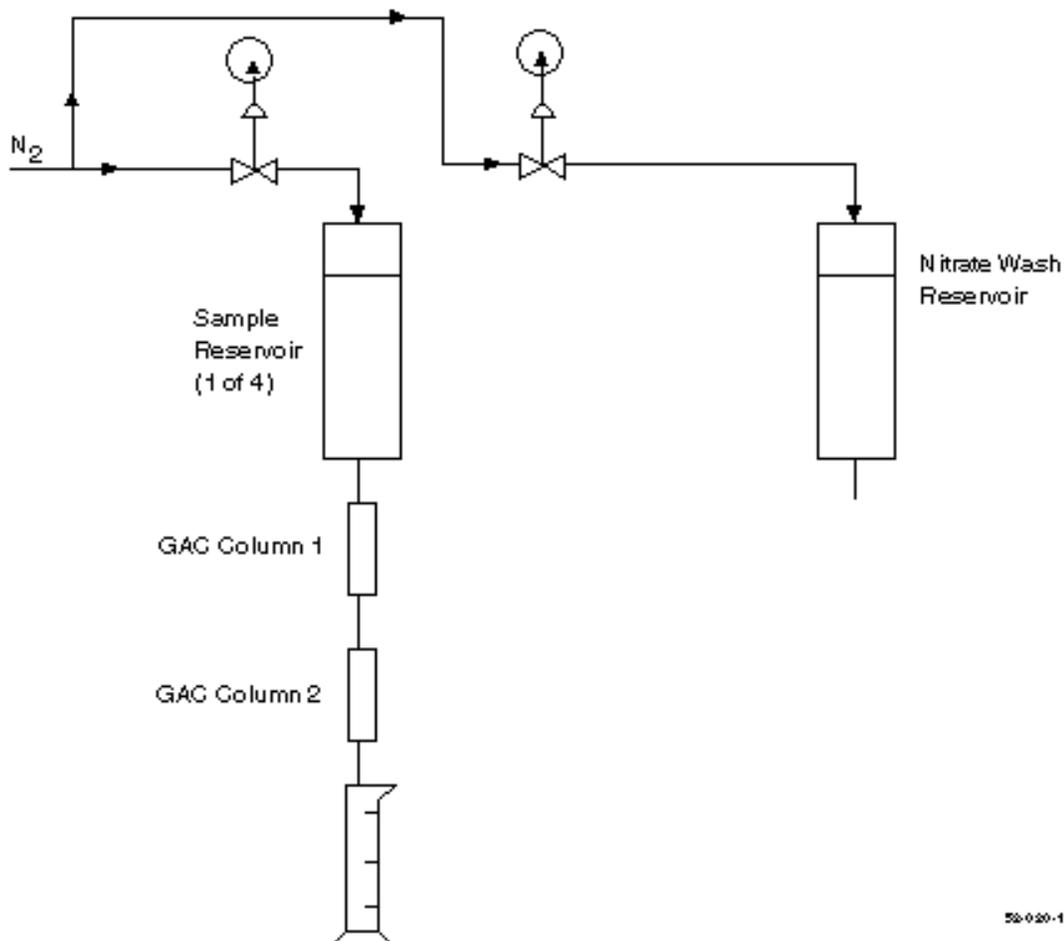
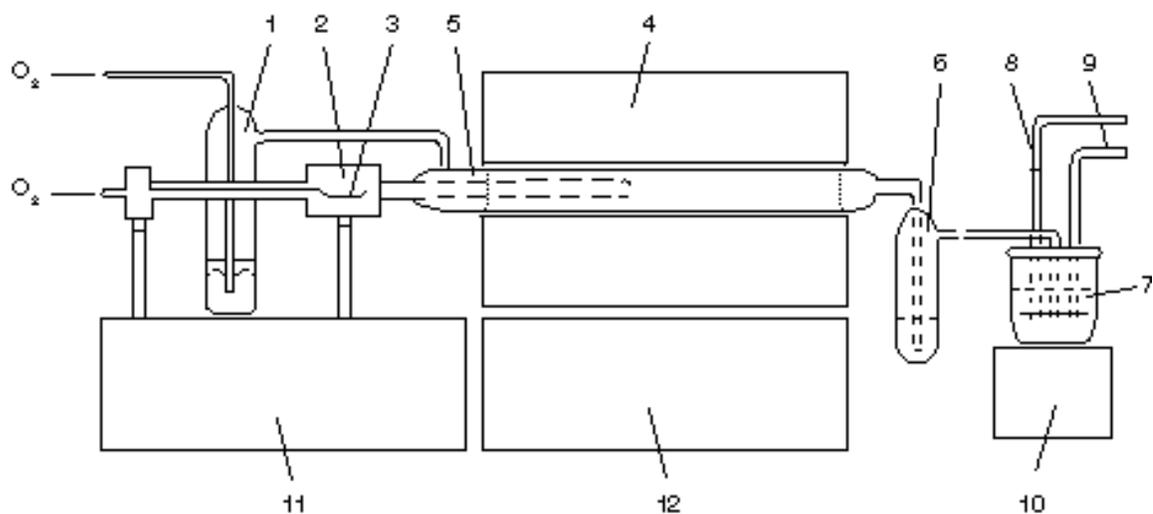


Figure 2. Filter Apparatus



52-020-133

Figure 3. Schematic of the Column Adsorption System



1. Stripping Device
2. Sample inlet for AOX
3. AOX Sample
4. Furnace
5. Combustion Tube
6. Absorber filled with H<sub>2</sub>SO<sub>4</sub>
7. Titration cell
8. Working electrodes
9. Measuring electrodes
10. Stirrer
11. Titration micro-processor
12. Gas flow and temperature control device

Figure 4. Schematic of an AOX Apparatus

## 18.0 GLOSSARY OF DEFINITIONS AND PURPOSES

These definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

### 18.1 Units of weight and measure and their abbreviations.

#### 18.1.1 Symbols

°C	degrees Celsius
μg	microgram
μL	microliter
<	less than
>	greater than
%	percent

#### 18.1.2 Alphabetical characters

cm	centimeter
g	gram
h	hour
ID	inside diameter
in	inch
L	liter
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
ppb	part-per-billion
ppm	part-per-million
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

### 18.2 Definitions and acronyms (in alphabetical order).

Analyte—AOX tested for by this method.

Calibration standard (CAL)—A solution prepared from a secondary standard and/or stock solution which is used to calibrate the response of the instrument with respect to analyte concentration.

Calibration verification standard (VER)—The mid-point calibration standard (CS3) that is used to verify calibration.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all

respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

IPR—Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory blank—See Method blank.

Laboratory control sample (LCS)—See Ongoing precision and recovery sample (OPR).

Laboratory reagent blank—See Method blank.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum level (ML)—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

Must—This action, activity, or procedural step is required.

OPR—Ongoing precision and recovery standard; a laboratory blank spiked with a known quantity of analyte. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PAR—Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

Preparation blank—See Method blank.

Primary dilution standard—A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

Quality control check sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent water—Water demonstrated to be free from the analyte of interest and potentially interfering substances at the method detection limit for the analyte.

Relative standard deviation (RSD)—The standard deviation multiplied by 100, divided by the mean.

RSD—See Relative standard deviation.

Should—This action, activity, or procedural step is suggested but not required.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

VER—See Calibration verification standard.