Method 1649 Draft May 1991

Organic Halides in Solid Matrices by Coulometric Titration

1 Scope and application

1.1 This method is designed to meet the survey requirements of the United States Environmental Protection Agency (EPA). It is used to determine organic halides associated with the Clean Water Act; the resources Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liability Act; and other organic halides amenable to combustion and coulometric titration.

1.2 The method is applicable to the determination of organic halides in soils, sludges, and pulp. The method is a combination of existing methods and new technology for organic halide measurement.

1.3 This method is for use by or under the supervision of analysts experienced in the use of a combustion/microcoulometer. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 8.2.

1.4 Any modification of this method beyond those expressly permitted (Section 8.1.2) is subject to the application and approval of alternate test procedures under 40 CFR Parts 134 and 135.

2 Summary of Method

2.1 Sample preparation: organic halides are leached from the sample into water by acidification and sonication. The organic halides in the leachate are adsorbed onto granular activated carbon (GAC). The sample and GAC are collected on a polycarbonate filter.

2.2 Sample analysis--Combustion/microcoulometric: the sample, GAC, and filter are combusted to form the hydrogen halide, and titration of the hydrogen halide with a microcoulometer, as shown in Figure 3. The 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, it is partitioned into the 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.

2.3 The mass concentration of organic halides is reported as an equivalent concentration of organically bound chloride (Cl^-).

3 Contamination and interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield elevated readings from the microcoulometer. 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 set (samples started through the adsorption process in a given 8 hour shift, to a maximum of 20 samples). Specific selection of reagents and purification of solvents may be required.

3.2 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 fewer cleaning steps show no detectable organic halide, the cleaning steps from above that do not eliminate organic halide may be omitted.

3.3 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.

3.4 Activated carbon

3.4.1 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 8.5). 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.

3.4.2 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.

3.4.3 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.

3.5 Polyethylene gloves should be worn when handling equipment surfaces in contact with the sample.

4 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical substance 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 should be available to all personnel involved in the chemical analysis. Additional information on laboratory safety can be found in references 9 - 11.

4.2 This method employs strong acids. Appropriate clothing, gloves, and eye protection should be worn when handling these substances.

4.3 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.

5 Apparatus and materials

5.1 Sampling equipment

5.1.1 4 ounce glass jar-- Chromic acid rinse, detergent water wash, rinse with tap and distilled water, cover with aluminum foil and heat to 450 °C for at least one hour before use.

5.1.2 Teflon liner--cleaned as above and baked at 100 - 200 °C for at least one hour.

5.1.3 Jars and liners must be lot certified to be free of organic halides by running blanks according to this method.

5.2 Scoop of granular activated carbon (GAC)--capable of precisely measuring 0.13 +/- 0.01 cc GAC (Dohrmann Measuring Cup 521-021, or equivalent). This scoop size has been shown to hold 35 - 60 mg of GAC, depending on the carbon source. The variance in GAC mass has been shown to have no affect on method performance (Reference 13).

5.3 Adsorption apparatus

5.3.1 Finger type sonicator capable of developing 100-110 watts at 50% duty-Cycle. (Branon Model 450 or equivalent)

5.3.2 20 mL vials used for sample sonication.

5.3.3 Adsorption system--rotary shaker, wrist action shaker, or other system for assuring thorough contact of sample with activated carbon. The system used shall be demonstrated to meet the performance requirements in Section 8 of this method.

5.3.3.1 Erlenmeyer flasks--250 with ground glass stopper, for use with rotary shaker.

5.3.3.2 Shake table--Sybron Thermolyne Model LE "Big Bill" rotator/shaker, or equivalent.

5.3.3.3 Rack attached to shake table to permit agitation of 16 - 25 samples simultaneously.

5.3.4 Filtration system-- Figure 1

5.3.4.1 Vacuum filter holder--glass, with fritted glass support (Fisher Model 09-753E, or equivalent).

5.3.4.2 Poly carbonate filter--0.45 micron, 25 mm diameter, (Micro Separation Inc, Model K04CP02500, or equivalent).

5.3.4.3 Filter forceps--Fisher Model 09-753-50, or equivalent, for handling filters. Clean by washing with detergent and water, rinsing with tap and deionized water, and air drying on aluminum foil. Two forceps may better aid in handling filters. Clean by washing with detergent and water, rinsing with tap and deionized water, and air drying on aluminum foil.

5.3.4.4 Vacuum flask--500 mL (Fisher 10-1800, or equivalent).

5.3.4.5 Vacuum Source--a pressure/vacuum pump, rotary vacuum pump, or other vacuum source capable of providing at least 610 mm (24 in) Hg vacuum and 30 L/min free air displacement.

5.3.4.6 Stopper and tubing to mate the filter holder to the flask and the flask to the pump.

5.3.4.7 Polyethylene gloves--(Fisher 11-394-110-B, or equivalent).

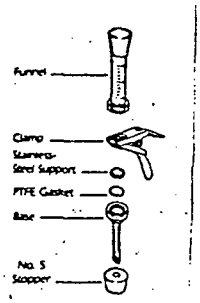

Figure 1 Filter apparatus

5.4 Combustion/micro-coulometer system--commercially available as a single unit or assembled from parts. At the time of writing this method, organic halide units were commercially available from Dorhmann Division of Rosemount Analytical, Santa Clara, California: Euroglas BV, Delft, the Netherlands; and Mitsubishi Chemical Industries Ltd., Tokyo, Japan

5.4.1 Combustion system--older systems may not have all of the features shown in Figure 3. These older systems may be used provided the performance requirements (Section 8) of this method are met.

5.4.1.1 Combustion tube--quartz, capable of being heated to 800 - 1000°C and accommodating a boat sampler. The tube must contain an air lock for introduction of a combustion boat, connections for purge and combustion gas, and connection to the micro-coulometer cell.

5.4.1.2 Tube furnace capable of controlling combustion tube in the range of 800 - 1000 °C.

5.4.1.3 Boat sampler -- capable of holding the 50 mg of sample, 35 - 60 mg of GAC and a polycarbonate filter as well as fitting into the tube (5.4.1.1). 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 organic material in the boat is burned in a flowing oxygen stream. The evolved gases are transported by a nonreactive carrier gas to the microcoulometer cell.

5.5.1.4 Motor driven boat sampler--capable of advancing the combustion boat into the furnace in a reproducible time sequence. A time sequence shown to be effective is:

A. Establish initial gas flow rates: 160 mL/min CO_2; 40 mL/min O_2.

B. Sequence start.

C. Hold boat in hatch for 5 seconds to allow integration for baseline subtraction.

D. Advance boat into vaporization zone.

E. Hold for boat in vaporization zone for 110 seconds.

F. Establish gas flow rates for combustion: 200 mL/min O_2; 0 mL/min CO_2; advance boat into pyrolysis zone (800 °C).

G. Hold boat in pyrolysis zone for 6 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 (approx 2 minutes).

I. Stop integration at 10 minutes after sequence start.

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

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

5.4.1.5 Absorber--containing sulfuric acid to dry the gas stream after combustion to prevent backflush of electrolyte is recommended.

5.4.2 Microcoulometer system--capable of detecting the equivalent of 1 ug of Cl- with a relative standard deviation of less than 10 percent, and capable of accumulating a minimum of the equivalent of 500 ug of Cl- before a change of electrolyte is required.

5.4.2.1 Micro-coulometer cell--the three cell designs presently in use are shown in Figure 2. Cell operation is described in Section 2.

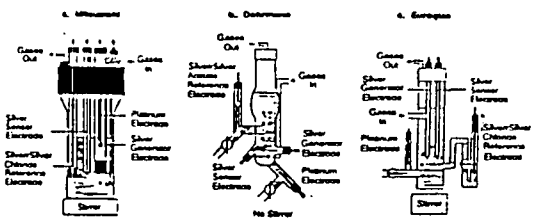

Figure 2 Microcoulometric titration cells [from Ref (7)]

5.4.2.2 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.

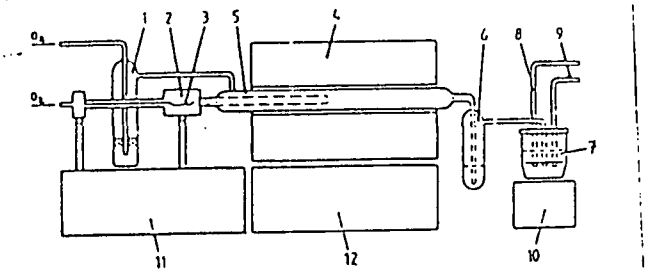

Figure 3: Schematic of an AOX apparatus

1. Stripping Device
2. Sample inlet for AOX
3. AOX sample
4. Furnace
5. Combustion Tube
6. Absorber filled with H_2SO_4
7. Titration cell
8. Working electrodes
9. Measuring electrodes
10. Stirrer
11. Titration micro processor
12. Gas flow and temperature control device

5.6 Miscellaneous glassware

5.6.1 Volumetric flasks--5, 10, 25, 50, 100, and 1000mL

5.6.2 Beakers--100, 500, and 1000 mL

5.6.3 Volumetric pipets--1 and 10 ml with pipet bulbs

5.6.4 Volumetric micro-pipets--10, 20, 50, 100, 200, and 500 ul with pipet control (Hamilton 0010, or equivalent)

5.6.5 Graduated cylinders--10, 100, and 1000 mL

5.7 Micro-syringes--10, 50, and 100 uL

5.8 Balances

5.8.1 Top loading, capable of weighing 0.1 gram

5.8.2 Analytical, capable of weighing 0.1 mg

5.9 Wash bottles--500 - 1000 mL, Teflon or polyethylene

6 Reagents and standards

6.1 Granular activated carbon (GAC)--75 - 150 um (100 to 200 mesh), (Dorhmann 511-877, or equivalent), with chlorine content less than 1 ug Cl- per scoop (<25 ug Cl- per gram), adsorption capacity greater than 1000 ug Cl- (2,4,6-trichlorophenol) per scoop (>25,000 ug per gram), inorganic halide retention of less than 1 ug Cl- per scoop in the presence of 2500 mg of inorganic halide), and that meets the other test criteria in Section 8.5 of this method.

6.2 Reagent water--water in which organic halide is not detected by this method.

6.2.1 Preparation--reagent water may be generated by:

6.2.1.1 Activated carbon--pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

6.2.1.2 Water purifier--pass tap water through a purifier (Millipore Super Q, or equivalent).

6.2.2 pH ajustment--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 (6.8.6).

6.3 Nitric acid (HNO_3)--concentrated, analytical grade

6.4 Nitrate stock solution--in a 1000 mL volumetric flask, dissolve 17 g of $NaNO_3$ in approx 100 mL of water, add 1.4 mL nitric acid (Section 6.3) and dilute to the mark with reagent water.

6.5 Nitrate wash solution--dilute 50 mL of nitrate stock solution (Section 6.4) to 1000 mL with reagent water.

6.6 Sodium thiosulfate ($Na_2S_2O_3$) solution (1 N)--weigh 79 grams $Na_2S_2O_3$ in a 1 liter volumetric flask and dilute to the mark with reagent water.

6.7 Trichlorophenol solutions

6.7.1 Trichlorophenol stock solutions (1.0 mg/mL of Cl-)--dissolve 0.186 g of 2,4,6-trichlorophenol in 100 mL of halide-free methanol.

6.7.2 Trichlorophenol precision and recovery standard--place 50 mg of quartz sand in a 20 mL vial and add 100 uL of trichlorophenol stock solution (6.7.1).

6.8 Reagents and standards for combustion system

6.8.1 Sodium chloride (NaCl) solution--(100 ug/L of Cl-)--dissolve 0.165g NaCl in 1000 ml reagent water. This solution is used for cell testing and for the inorganic halide rejection test.

6.8.2 Ammonium chloride (NH_4Cl) solution (100 ug/mL of Cl-)--dissolve 0.165 g NH_4Cl in 1000 mL reagent water.

6.8.3 Sulfuric acid--reagent grade (specific gravity 1.84)

6.8.4 Oxygen--99.9% purity

6.8.5 Carbon Dioxide--99.9% purity

6.8.6 Acetic acid solution--containing 30 - 70 percent acetic acid in deionized water per the instrument manufacturers instructions.

7 Calibration

7.1 Assemble the OX system and establish the operating conditions necessary for analysis. Differences between various makes and models of instruments will require differing operating procedures. Analysts should follow the operating instructions provided by the manufacturer of their particular 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 set up and when calibration cannot be verified (Section 11).

7.2 Cell performance test--inject 100 uL of the sodium chloride solution (10 ug of Cl-; Section 6.8.1) directly into the titration cell electrolyte. Adjust the instrument to produce a reading of 10 ug Cl-.

7.3 Combustion system test--this test can be used to assure that the combustion/micro-coulometer systems are performing properly without introduction of carbon. It should be used during instrument setup and when instrument performance indicates a problem with the combustion system. Check the temperature of the combustion system and verify that there are no leaks in the combustion system and that the cell is performing properly (Section 7.2), then repeat the test.

7.3.1 Designate a quartz boat for use with the ammonium chloride (NH_4Cl) solution only.

7.3.2 Inject 100 uL of the NH_4Cl solution (6.8.2) into this boat and proceed with the analysis.

7.3.3 The result shall be between 9.5 and 10.5 ug 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 and verify that the cell is performing properly (Section 7.2), then repeat the test.

7.4 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.

7.4.1 Inject 10 uL of the 1 mg/mL trichlorophenol calibration solution (6.7.1) onto one level scoop of GAC in a quartz boat.

7.4.2 Immediately proceed with the analysis to prevent loss of trichlorophenol and to prevent contamination of the carbon.

7.4.3 The result shall be between 9.0 and 11.0 ug 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.

7.5 Background level of Cl- --determine the average background level of Cl- for the entire analytical system as follows:

7.5.1 Using the procedure in Section 10 that will be used for the analysis of samples, determine the background level of Cl^- in each of three 10 mg portions of quartz sand.

7.5.2 Calculate the average (mean) concentration of Cl^- and the standard deviation of the concentration.

7.5.3 The sum of the average concentration plus two times the standard deviation of the concentration shall be less than 2 ug. 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 (7.5) shall be repeated. Only after this is passed may calibration proceed.

7.6 Calibration by external standard--a calibration curve encompassing the calibration range is performed using 2,4,6-trichlorophenol.

7.6.1 Place 50 mg of quartz sand in each of five 20 ml vials.

7.6.2 Pipet 20, 50, 100, 300, and 800 uL of trichlorophenol stock solution (6.7.1) into the vials from 7.6.1. Some instruments may have a calibration range that does not extend to 80 ug of Cl^-. For those instruments, a less 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.

7.6.3 Proceed with the analysis of each sample as per Section 10.

7.6.4 Using the calculations in Section 12.1 determine the halide present in each standard.

7.6.5 Subtract the average value of the background (Section 7.5.2) from each of the five determinations.

7.6.6 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; Cv) of the calibration factor over the calibration range.

7.6.7 Linearity--the Cv of the calibration factor shall be less than 20 percent; otherwise, the calibration shall be repeated after system corrections have been made

8 Quality assurance/quality control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, an ongoing analysis of standards and blanks as tests of continued performance, and analysis of matrix spike and matrix spike duplicate (MS/MSD) samples to assess accuracy and precision. Laboratory performance is compared to establish performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is demonstrated as described in Section 8.2.

8.1.2 The analyst is permitted to modify this method to improve performance or

lower the costs of measurements provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedures in Sections 7.2 to 7.6 and Section 8.2 to demonstrate method performance.

8.1.3 The laboratory shall spike 10 percent of the samples with known concentrations of 2,4,6-trichlorophenol to monitor method performance and matrix interferences (interferences caused by the sample matrix). This test is described in Section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits.

8.1.4 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 8.4.

8.1.5 The laboratory shall, on an on-going basis, demonstrate through the analysis of the precision and recovery standard that the analysis system is in control. These procedures are described in Section 11.

8.1.6 The laboratory shall perform quality control tests on the granular activated carbon. These procedures are described in Section 8.5

8.2 Initial precision and recovery (IPR)--to establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

8.2.1 Analyze four PAR standards (Section 6.7.2) according to the procedure in Section 10.

8.2.2 Using the 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.

8.2.3 The average percent recovery shall be in the range of 7.7 - 10.8 ug and the standard deviation shall be less than 0.7 ug. 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.

8.3 Matrix spikes--the laboratory shall spike a minimum of 10 percent of samples from a given matrix type (e.g., soil, sludges, and pulps) 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.

8.3.1 The concentration of the analytes spiked into the MS/MSD shall be determined as follows:

8.3.1.1 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 8.3.2, whichever concentration is higher.

8.3.1.2 If the concentration of OX is not being checked against a regulatory

limit, the spike shall be at the concentration of the PAR standard (Section 6.7.2) or at one to five times higher than the background concentration determined in Section 8.3.2, whichever concentration is higher.

8.3.2 Analyze one sample out of each set of 10 samples from each matrix to determine the background concentration (B) of OX. Spike two additional sample aliquots with spiking solution and analyze them to determine the concentration after spiking (A).

8.3.2.1 Compute the percent recovery (P) of each analyte in each aliquot:

$$P = 100 (A - B)/T$$

where T is the true value of the spike.

8.3.2.2 Compute the relative percent difference (RPD) between the two results (not between the two recoveries):

$$RPD = | 2(A1 - A2) |/(A1 + A2)$$

8.3.2.3 If the RPD is less than 20 percent, and the recoveries for the MS and MSD are within the range of 71 - 116 percent, the results are acceptable.

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

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

8.3.2.4.2 If, however, the RPD for the two aliquots of the PAR is less than 20 percent, dilute the sample chosen for the MS/MSD by a factor of 10 and repeat the MS/MSD test. If the RPD is still greater than 20 percent, 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 set.

8.3.2.5 If the percent recovery for both the MS and MSD are less than 71 or greater than 116 percent, analyze the precision and recovery (PAR) standard.

8.3.2.5.1 If the recovery of the PAR is outside the 71 - 116 percent range, the analytical system is out of control. In this case, repair the problem and repeat the analysis of the sample set, including the MS/MSD.

8.3.2.5.2 If the recovery of the PAR is within the range of 71 - 116 percent, dilute the sample, MS, and MSD by a factor of 10 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 set.

8.4 Blanks--reagent water blanks are analyzed to demonstrate freedom from contamination.

8.4.1 Analyze a reagent water blank with each set of samples. The blank must be analyzed immediately following calibration verification to demonstrate freedom from contamination and memory effects and must include all details of the procedure to be followed when analyzing samples.

8.4.2 If more than 2 ug is found in the blank, analysis of samples is halted until the source of contamination is

eliminated and a blank shows no evidence of contamination at this level.

8.5 Granular activated carbon (GAC) testing--each batch of activated carbon is tested before use to ensure adequate quality. Use only GAC that meets the test criteria below.

8.5.1 Contamination test--analyze a scoop of GAC. Reject carbon if the amount of OX exceeds 1 ug (25 ug Cl-/g)

8.5.2 Inorganic chloride adsorption test--attempt to adsorb NaCl from 100 mg/l in reagent water. Wash with nitrate solution and analyze. The amount of halide should be less than 1 ug Cl- larger than the blank. A larger amount indicates significant uptake of inorganic chloride by the carbon. Reject carbon if the 1 ug level is exceeded.

8.5.3 Carbon capacity test--prepare an adsorption test standard solution in reagent water to contain 10 mg/l organic carbon (as humic acids of equivalent) and an organic halide concentration of 100 ug/L organochloride (from 2,4,6-trichlorophenol). Prepare a blank solution containing only the 10 mg organic carbon. Analyze 100 mL portions of these solutions. Subtract the result of the blank from the result of the halide spike, compare the blank subtracted result to the true value of the spike. Recovery of the halide should be greater than 85 percent.

8.6 The specifications contained 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 7), calibration verification (Section 11), and for the initial (Section 8.2) and ongoing (Section 11) precision and recovery should be identical, so that the most precise results will be obtained.

8.7 Depending on specific program requirements, field duplicates may be collected to determine the precision of the sampling technique.

9 Sample collection and preservation

9.1 Collect sample in a 4 ounce jar. This will provide a sufficient amount of all quality control testing.

9.2 Cool and maintain sample temperature at 0-4°C from the time of collection until analysis.

9.3 No holding times have been established for this method.

10 Sample preparation

10.1 Composite small amounts of sample by mixing small amounts of sample in a clean beaker. The composited sample should total about 1 g and should be taken from three to five points within the sample container. Mix the sub sample well with a stainless steel spatula or glass rod to insure homogeneity.

10.2 Weigh out three 50 mg aliquots of the composited sample into 20 ml vials.

10.3 Add 5 mL of reagent water to each vial.

10.4 Place sonication horn inside the vial and sonicate for 5 min.

10.5 Quantitatively transfer the contents of each vial into a 250 mL erlenmeyer flask with 95 mL of reagent water.

10.6 Add 100 uL of 1 M $Na_2S_2O_3$ to convert all active Cl to inorganic Cl.

10.7 Acidify the samples to a pH of < 2 with concentrated HNO_3, approximately 200 uL

10.8 Add 5 mL of the nitrate stock solution

10.9 Add one level scoop of activated carbon

10.10 Shake the suspension for at least one hour in a mechanical shaker

10.11 Filter the suspension through a polycarbonate membrane filter. Filter by suction until the liquid level reaches the top of the carbon.

10.12 Wash the inside surface of the filter funnel with approximately 25 mL of nitrate wash solution in several portions. After the level of the final wash reaches the top of the charcoal, filter by suction until the cake is barely dry. The time required for drying should be minimized to prevent exposure of the GAC to halogen vapors in the air, but should be sufficient to permit drying of the cake so that excess water is not introduced into the combustion apparatus. A drying time of approximately 10 seconds under vacuum has been shown to be effective for this operation.

10.13 Carefully remove the top of the filter holder, making sure that no carbon is lost. This operation is most successfully performed by removing the clamp, tilting the top of the filter holder (the funnel portion) to one side, and lifting upward.

10.14 Using a squeeze bottle or micro syringe, rapidly rinse the carbon from the inside of the filter holder onto the filter cake using small portions of wash solution. Allow the cake to dry under vacuum for no more than 10 seconds after the final rinse. Immediately turn the vacuum off.

10.15 Using the tweezers, carefully fold the polycarbonate filter in half, then in fourths, making sure that no carbon is lost.

10.17 Halide determination by combustion

10.17.1 Place the folded polycarbonate filter containing the sample and GAC in a quartz combustion boat, close the airlock, and proceed with the automated sequence.

10.17.2 Repeat automated sequence with second and third sample aliquot.

10.17.3 Record the cumulative signal from the microcoulometer and determine the concentration calibration data per Section 12.

11 System and Laboratory Performance

11.1 At the beginning and end of each eight hour shift during which analyses are performed, system performance and calibration are verified. System performance and calibration may be performed more frequently, if desired.

11.1.1 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.

11.1.2 If performance and calibration are not verified at the beginning and end of the shift (or more frequently), samples analyzed during that period must be reanalyzed.

11.1.3 If calibration is verified at the beginning of the shift, recalibration is not necessary; otherwise, the

instrument must be calibrated prior to analyzing samples.

11.1.4 Cell maintenance and other changes to the analytical system that can affect system performance may not be performed during the eight hour (or shorter) period.

11.2 Calibration verification and ongoing precision and recovery--calibration and system performance are verified by the analysis of the 10 ug PAR standard.

11.2.1 Analyze the PAR standard (Section 6.7.1) and analyze a blank (Section 8.4) immediately thereafter at the beginning and end of each shift. Compute the concentration of organic halide in the PAR standard and in the blank. The blank shall be less than 2 ug Cl^-.

11.2.2 Subtract the result for the blank from the result of the PAR standard, and compute the percent recovery of the blank-subtracted PAR standard. The percent recovery shall be in the range of 71 - 116 percent.

11.2.3 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 on-going precision and recovery test (Section 11.2), or recalibrate (Section 7.5 - 7.6).

11.2.4 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 11.2), or recalibrate (Section 7.5 - 7.6), and re-analyze the sample set that was analyzed during the eight hour shift.

11.2.5 If the recovery is within the acceptable range at the end of the shift, and samples are to be analyzed during the next 8 hour shift, the end of shift verification may be used as the beginning of shift verification for the subsequent shift provided the next 8 hour shift begins as the first shift ends.

11.3 Add results that pass the specification in 11.2.2 to initial and previous ongoing data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory data quality for each analyte 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 - 105%.

12 Calculations

12.1 Calculate the concentration of chloride (in micrograms) detected in each sample and blank per the following:

$$OX\ (Cl^-\ corrected)\ (ug/g) = d(C - B) / M$$

where

C = Cl^- from micro-coulometer, ug

B = Cl^- from micro-coulometer for the blank (8.4), ug

M = mass of sample adsorbed, g

12.1.1 The replicate results must be averaged and the resulting average used as the sample result.

12.1.2 Calculate the relative standard deviation (RSD).

12.1.3 If the RSD is greater than 20 percent, the analyses must be repeated.

12.1.4 If the RSD remains greater than 20 percent, the result may not be reported for regulatory compliance purposes.

12.2 High concentrations of OX--if the amount of chloride exceeds the calibration range, dilute the sample by a factor of 10 and reanalyze.

12.3 Low concentrations of OX--the final result should be significantly above the level of a blank.

12.3.1 If the instrument response of a sample exceeds the instrument response of the blank by a factor of at least 3, the result is acceptable.

12.3.2 If the instrument response of a sample is less than three times the instrument response of the blank, and the sample has been diluted, analyze a less dilute aliquot of sample.

12.3.3 If the instrument response of an undiluted sample is less than three times the instrument response of 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.

12.4 Report final results that meet all of the specifications in this method as the blank-subtracted value, in ug/L Cl^- (not as 2,4,6-trichlorophenol), to three significant figures.

13 Method performance--the specifications contained in this method are based on single laboratory data (reference 13). These specification will be updated as further data become available.

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