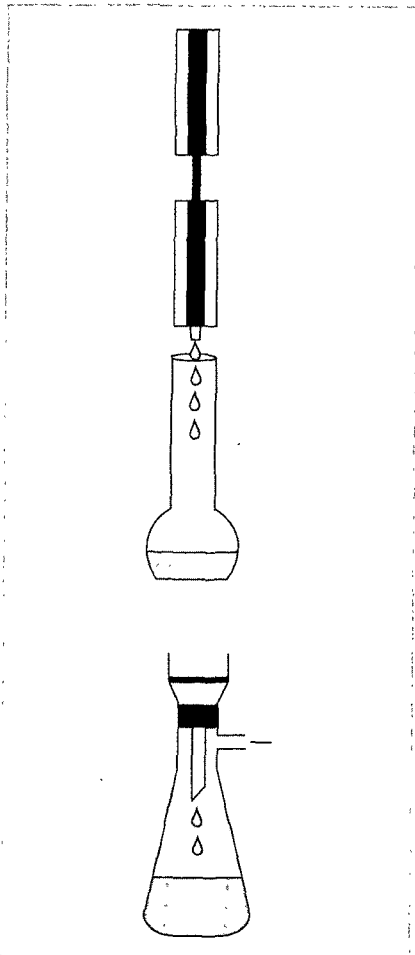


# Environmental Protection Series



Reference Method for the  
Determination of Adsorbable  
Organic Halogens (AOX) in  
Waters and Wastewaters

Reference Method EPS 1/RM/16  
January 1992

Canada



Environment  
Canada

Environnement  
Canada

# **Reference Method for the Determination of Adsorbable Organic Halogens (AOX) in Waters and Wastewaters**

Wastewater Technology Centre  
Conservation and Protection  
Environment Canada

and

Pulp and Paper Research  
Institute of Canada (PAPRICAN)

Reference Method EPS 1/RM/16  
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## Readers' Comments

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Inquiries pertaining to the use of this reference method should be directed to:

Jim Fraser  
Wastewater Technology Centre  
Conservation and Protection  
Environment Canada  
Burlington, Ontario  
L7R 4L7

Additional copies of this document can be obtained from:

Environmental Protection Publications  
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Conservation and Protection  
Environment Canada  
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## Foreword

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*This method for the analysis of Adsorbable Organic Halogens (AOX) in aqueous solutions was developed jointly by Environment Canada's Wastewater Technology Centre and the Pulp and Paper Research Institute of Canada (PAPRICAN). It focuses primarily on process streams and effluents from the pulp and paper industry, although it is applicable to all aqueous media. Two methods for analyzing such samples, namely the column method and the shaker method, are described in detail.*

*Although there are other methods in use, this reference method was developed to provide a standard for comparison across Canada.*



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## Section 1

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### Introduction

In this method, halogenated organic material in an acidified effluent sample is adsorbed on granular activated carbon (GAC). Inorganic halogens that also adsorb on the carbon are removed by washing with a nitrate solution. The GAC with adsorbed organic material is then pyrolyzed in a combustion furnace and the resulting halogens, including chloride, bromide and iodide, are determined by microcoulometric titration and reported as chloride. Fluorinated organics are not detectable.

The adsorption can be carried out either in GAC-packed columns (column method) or by shaking the sample with GAC for a specified time (shaker method). Both adsorption procedures are described in this method. The

results of two interlaboratory studies with kraft mill bleachery effluents (Bethge *et al.*, 1989; Fraser and Reeve, 1989) have shown that, in most cases, there is a good agreement between the two procedures. In final effluents, treated or untreated, results of these studies have shown that both methods agreed within 5%. With chlorination-stage effluent or samples high in suspended solids, however, some laboratories have reported that the column and shaker methods can yield significantly different AOX results. Therefore, the same adsorption procedure must be adopted when comparing AOX results on such samples. For regulatory purposes on final effluents, either method may be applied since they both agree within 5%.

## Section 2

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### Scope

This method is applicable to all types of waters and wastewaters. Organic halides determined by this method are referred to as Adsorbable Organic Halogens (AOX) and include organically-bound halogens present in dissolved or suspended form. Other methods for determining organic halogens, such as TOCl methods (Sjöström *et al.*, 1982) or APHA Standard Method 5320 (see Appendix), produce results that may differ from those obtained by the AOX method.

In general, most halogenated organic compounds are recovered by adsorption on activated carbon. However, some volatile

material, such as chloroform, is only partially recovered. In addition, certain compounds, such as chloroethanol, are poorly adsorbed on the activated carbon. Other compounds, such as chloroacetic acid, can be desorbed by the nitrate wash and are therefore incompletely recovered. As the concentration of these compounds in waters and wastewaters is relatively low, the AOX provides a good estimate of total organically-bound halogens in a sample. In pulp mill effluents, the amount of organically-bound bromine and iodine is negligible. Accordingly, the AOX in these samples consists almost entirely of organically-bound chlorine.

## Section 3

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### Apparatus

Items a., b., and f. to i. are required for the column method, and items c. to h. for the shaker method.

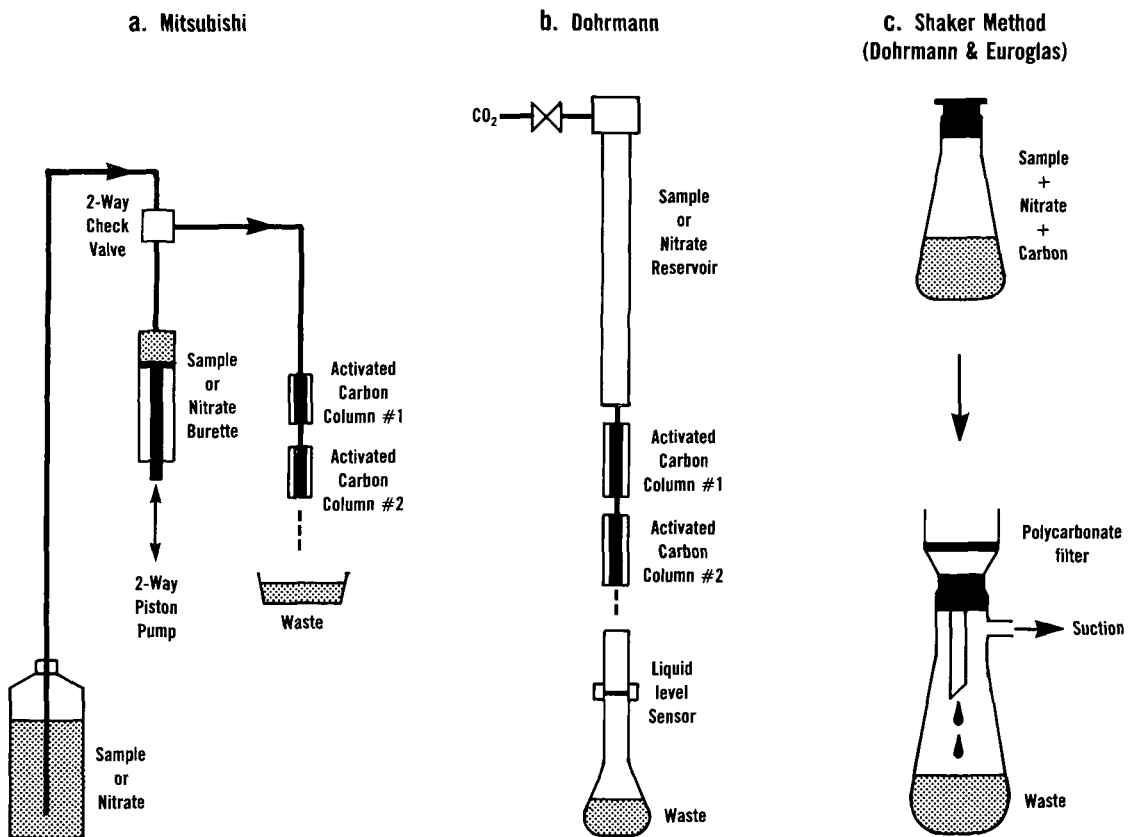
- a. Adsorption module -- Depending on the manufacturer of AOX analyzers, adsorption modules are supplied with either pressurized sample reservoirs or automatic burettes. Samples are delivered at a constant flow rate to two GAC-packed glass columns connected in series, and each column is contained in a column housing (Figure 1(a) or (b)).
- b. Volumetric flasks -- 50 and 100 mL.
- c. Mixing apparatus -- capable of thoroughly mixing the sample and activated carbon. This can either be an orbital-type shaker with adjustable power or a wrist-arm shaker.
- d. Erlenmeyer flasks -- 250 mL, graduated, with glass stoppers or PTFE-lined screw caps. To be used with an orbital-type shaker.
- e. Culture tubes -- 50 mL or larger glass tubes with tightly fitting PTFE-lined screw caps. To be used with a wrist-arm shaker.
- f. Filtering unit for vacuum filtration (Figure 1(c)) -- available, for example, from Millipore.
- g. Polycarbonate membrane filters -- 25-mm diameter, 0.4- $\mu$ m pore diameter, available from Nuclepore. The chloride content per filter should not exceed 0.2  $\mu$ g.
- h. AOX analyzer module -- The analyzer module consists of a multizone combustion chamber and a microcoulometer titration cell. The GAC with adsorbed organic material (and polycarbonate filter, in the case of the shaker method) is placed inside a quartz boat which is then inserted into a sample inlet port.\* The boat is first moved into a prepyrolysis zone where water and other volatiles are evaporated, and then into the combustion zone maintained at a temperature of at least 800°C (Figure 2). All the organic material in the boat (including the volatiles) is combusted in a flow of oxygen and the evolved gases are transported with a carrier gas into the microcoulometer titration cell. Figure 3 illustrates the different designs of titration cells commercially available. Silver ions, from a generator silver electrode, precipitate halogen ions to produce silver halides. The current required to replace the depleted silver ions is integrated and is then reported as an equivalent amount of chloride in micrograms or nanograms. Monitoring of the cell EMF, integration and conversion to concentration units, is accomplished electronically within the instrument.

AOX analyzers are available from the following manufacturers:

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\* If the shaker adsorption method is used, a larger quartz boat and pyrolysis tube are required to accommodate the polycarbonate filter.

- Mitsubishi Chemical Industries Ltd., Tokyo, Japan;
  - Rosemount Analytical, Dohrmann Division, Santa Clara, California;
  - Euroglas BV, Delft, Netherlands (shaker adsorption only).
- i. Integrator -- In commercially-available instruments, the integrator is incorporated into the AOX analyzer. A strip chart recorder is also recommended to diagnose various operating problems, such as detector malfunction.



**Figure 1** Adsorption Onto Carbon (Odendahl *et al.*, 1990)  
 a. and b. Column Adsorption Method  
 c. Shaker Method

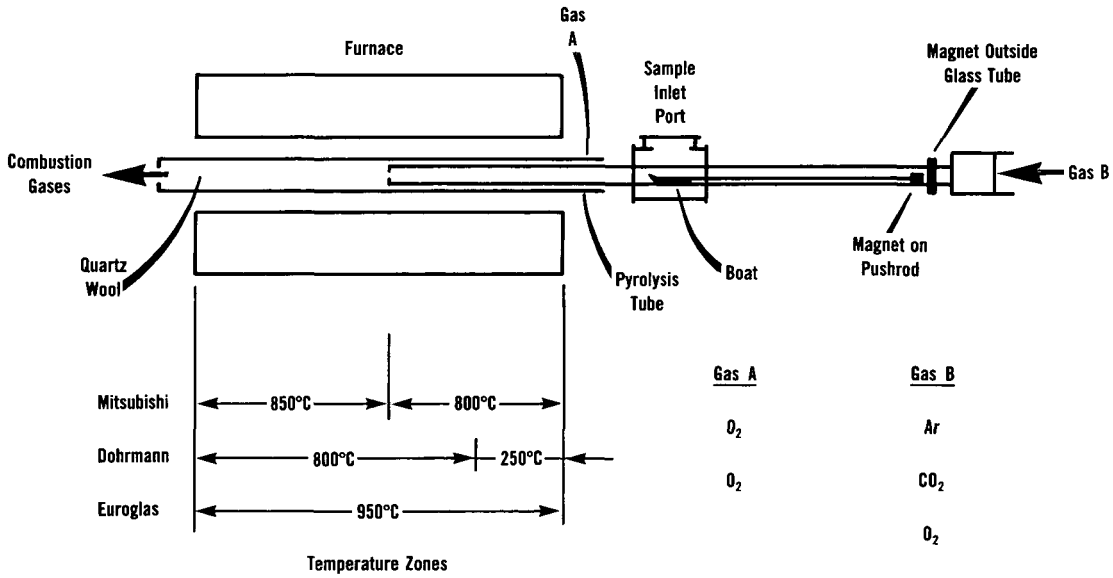


Figure 2 Combustion Section of AOX Analyzers (Odendahl *et al.*, 1990)

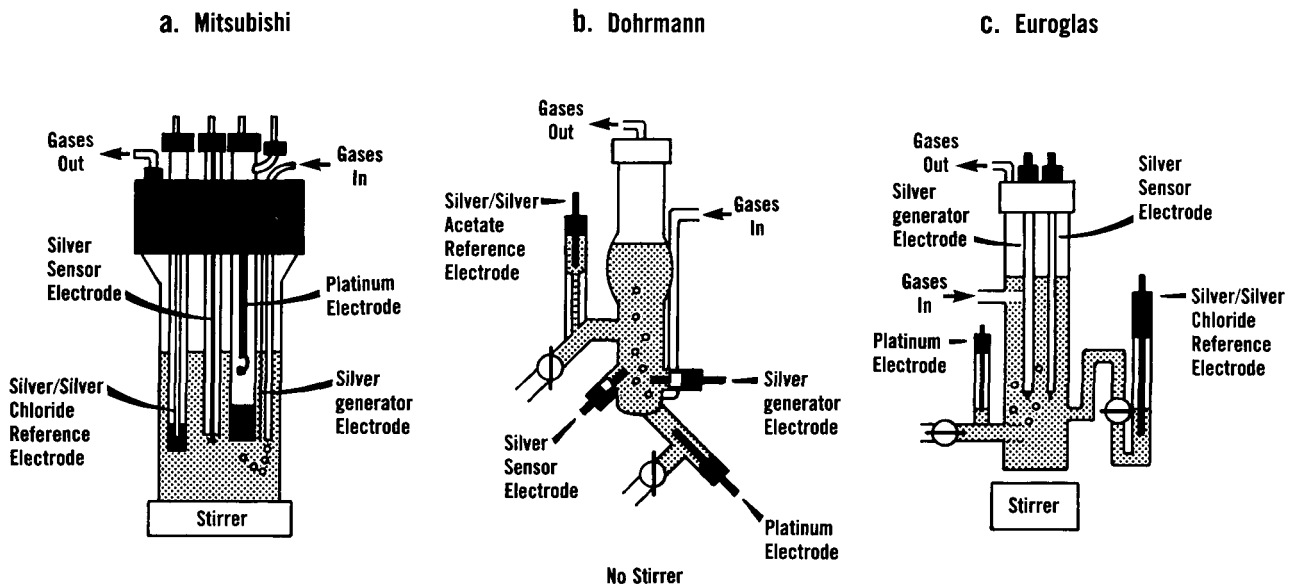


Figure 3 Microcoulometric Titration Cells (Odendahl *et al.*, 1990)

## Section 4

# Reagents and Materials

Water used in preparing various solutions shall be reagent water Type II or better.\* Also, it should not contain more than 2 µg/L of organically-bound chlorine.

**ALL CHEMICALS MUST BE OF ANALYTICAL GRADE UNLESS OTHERWISE INDICATED.**

- a. Granular activated carbon (GAC), screened to 150/75 µm standard sieve (100/200 mesh, Tyler equivalent), and with a chlorine content below 25 µg/g. This can be obtained from suppliers of AOX analyzers.\*\* Activated carbon must have minimal exposure to the laboratory atmosphere and under no circumstances should it be used or stored, in or adjacent to, laboratories that use halogenated compounds, such as chlorinated solvents or hydrochloric acid.
- b. Noncombustible insulating material, such as cerafelt, available from manufacturers of AOX analyzers. This is formed into plugs to hold GAC in the prepared columns.
- c. Carbon dioxide, nitrogen, or argon, purity 99.99%. Carbon dioxide or nitrogen is used in the adsorption module. Argon or carbon dioxide is used as carrier gas in the combustion chamber (Figure 2). Follow the manufacturer's recommendations.
- d. Oxygen, purity 99.99%, used for combustion.
- e. Aqueous acetic acid, 70 to 80%, as recommended by the manufacturer.
- f. Nitric acid, HNO<sub>3</sub>, concentrated.
- g. Sodium sulphite (anhydrous), Na<sub>2</sub>SO<sub>3</sub>, crystals.
- h. Sodium chloride standard, NaCl. Dissolve 0.1648 g NaCl and dilute to 100 mL with water; 1 µL = 1 µg Cl<sup>-</sup>.
- i. Ammonium chloride standard, NH<sub>4</sub>Cl. Dissolve 0.1509 g NH<sub>4</sub>Cl and dilute to 100 mL with water; 1 µL = 1 µg Cl<sup>-</sup>.
- j. Nitrate solution, 5.0 g/L as NO<sub>3</sub><sup>-</sup>. Dissolve 8.2 g KNO<sub>3</sub> in water. Adjust to pH 2 with nitric acid and dilute to 1 L.
- k. Trichlorophenol stock solution. Dissolve 1.856 g 2,4,6-trichlorophenol in methanol (HPLC grade) and dilute to 100 mL with methanol; 1 µL = 10 µg Cl<sup>-</sup>.
- l. Trichlorophenol standard solution. Make a 1:20 dilution of the trichlorophenol stock solution with methanol; 1 µL = 0.5 µg Cl<sup>-</sup>.

\* The specifications for Reagent Water are described in ASTM D1193-77. Type II Reagent Water has the following specifications:

Total matter, max: 0.1 mg/L  
 Electrical conductivity, max: 1.0 µS/cm at 25°C  
 Minimum color retention time of potassium permanganate: 60 min  
 Maximum soluble silica: not detectable

\*\* Activated carbon is also supplied in powdered form by some manufacturers of AOX analyzers. Differences in adsorption affinity between granular and powdered carbon have not been established.

## Section 5

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### Sampling

The sampling location must be chosen carefully to ensure that there is sufficient agitation and that the sample is representative of the effluent stream under study.

Collect composite samples over an appropriate time period and store in amber glass bottles with PTFE-lined caps. If amber bottles are not available, polyethylene bottles can be used, but these must be stored in the dark.

Acidify samples taken downstream of a biological treatment plant to pH 1.5 to 2.0 with nitric acid. Completely fill the bottles with sample, and seal.

For bleach plant effluents containing residual chlorine, add sodium sulphite crystals.\*

If samples cannot be analyzed promptly, refrigerate at 4°C with minimal exposure to light.\*\* Storage time and temperature must be reported in all cases.

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\* Sodium sulphite must be added to reduce any residual chlorine which could otherwise react with organic material in the sample to form organically-bound chlorine. To test for residual chlorine, transfer 5 to 10 mL of sample to a test tube. Dissolve a few crystals of potassium iodide in the sample, then add 3 to 5 drops of a 1% starch solution. A blue colour indicates that residual chlorine is present. Other oxidants may give the same reaction.

It may be necessary to adjust the amount of sodium sulphite added to the sample depending on the result of the starch test. Adding too much sulphite must be avoided because it could give misleadingly low results. Start with 5 mg/L and add more if necessary, until the blue colour disappears. The test for residual chlorine and addition of sodium sulphite, if necessary, must be carried out at the time of sampling.

\*\* No statistically significant changes have been observed in the AOX concentration of final kraft mill effluent over a 12-week storage period under these conditions. However, other kraft mill process streams, including C-stage and E-stage, have displayed instability within two days of sampling and therefore should be analyzed promptly.

Samples should not be stored frozen. Immediate freezing of C- and E-stage effluents showed no significant improvement in stability over those that were refrigerated. In fact, repeated freezing and thawing produced gross instability in all sample types studied.



## Section 6

### Procedure

It is essential that all steps of the procedure be conducted in a halogen-free atmosphere. In order to avoid possible halogen contamination, always use appropriate equipment, such as measuring spoon, forceps, or tweezers, when manipulating various materials (e.g., GAC, polycarbonate filter, quartz boat) used in this test.

#### 6.1 Column Adsorption Method

Shake the sample bottle vigorously before taking an aliquot to ensure homogeneity. Use of a stirring bar and a magnetic stirrer can facilitate mixing. If the sample contains a high level of suspended solids, it must be mixed continuously during sampling. A wide-bored pipette is convenient for such samples. Any material adhering to the walls of the pipette must be rinsed off.

In most cases, samples must be diluted to bring their AOX concentration within the linear range of the instrument. This range may vary with the type of instrument used and must be determined from a working range curve. Examples of dilution factors for various types of mill effluents are given in Table 1. Other types of waters and wastewaters may require considerably less dilution, or none at all. The final pH after

dilution must be 1.5 to 2.0. The pH is adjusted with nitric acid using a pH meter or pH probe.

If the diluted sample contains little or no suspended solids, proceed as described under Case 1 - Samples not requiring pre-filtration. If the adsorption column becomes plugged, however, the sample must first be filtered, as described under Case 2 - Samples requiring pre-filtration. Plugging is not likely with most samples since the level of suspended solids is usually negligibly low after dilution.

#### Case 1 - Samples not requiring pre-filtration

Using the measuring spoon provided with the instrument, pack two adsorption glass columns with approximately 40 mg of GAC each, and with plugs of cerafelt at both ends. Insert each column in its housing, connect the columns in series, and attach them to the adsorption module.

Deliver a measured aliquot of sample, diluted if necessary, (up to 100 mL, typically 25 to 50 mL) into the sample container of the adsorption module and start the flow of sample through the columns. Depending on the type of adsorption module used, the flow

**Table 1** Examples of Dilution Factors for Various Types of Mill Effluents

Effluent	Dilution Factor
Chlorination	500 to 1000
Extraction	500 to 1000
Combined (untreated)	100
Combined (treated)	50

rate is either pre-set at 3 mL/min or can be adjusted as required.

After the sample has passed through the columns, stop the flow, rinse the reservoir of the adsorption module with about 10 to 20 mL of water, and then wash the columns with 4 mL of nitrate solution at a flow rate of 1 to 3 mL/min or as recommended by the manufacturer.

Remove the top column from its housing, and using a clean ejector rod (supplied by the manufacturer), eject the GAC and cerafelt plugs into the sample boat.

Pyrolyze the GAC and determine the halogen content. Repeat for the bottom column. The microcoulometric titration is carried out by the instrument and an absolute value of halide content in  $\mu\text{g}$  or  $\text{ng}$  is obtained on the readout of the instrument. A strip-chart recorder may be used to monitor the titration cell.

Of the total organic halogen measured on both columns, 90% or more should be adsorbed on the top column and 10% or less on the bottom one. If more than 10% is adsorbed on the bottom column, repeat the analysis with a more diluted sample. Reducing the sample flow rate may also improve recovery on the top column.

Run the determination at two levels of dilution. If there is more than a 10% discrepancy between duplicate values, repeat the determination at a different dilution.

### **Case 2 - Samples requiring pre-filtration**

Filter the required amount of sample, diluted if necessary, through a polycarbonate membrane filter using the filtering unit. Perform a separate AOX analysis on the filtrate as described in Case 1. Replace the flask in the filtering unit with a clean one and wash the filter with 4 mL of nitrate solution (Section 4j.). Combust the filter and solids and determine the halogen content as described previously. The AOX content of

the solids must be added to that of the filtrate to give the total AOX of the sample.

Run the determination at two levels of dilution. If there is more than a 10% discrepancy between duplicate values, repeat the determination at a higher dilution.

### **6.2 Shaker Adsorption Method**

Follow the same guidelines for sample dilution and acidification as given for the column method.

Pipet an appropriate volume of the acidified sample into a 250-mL Erlenmeyer flask or a 50-mL culture tube. Add 40 mg of GAC (dispensed with the measuring spoon), 5 mL of nitrate solution, and stopper the flask. Shake for 1 hour on the mixing apparatus to ensure that the sample and GAC are thoroughly mixed.

At the end of this period, filter through the polycarbonate membrane filter using the filtering apparatus. Rinse the flask and the sides of the filtering funnel with small portions of nitrate solution, about 25 mL in all. After disconnecting the filtering unit, rinse the upper portion of the filter tube with a minimal amount of nitrate solution (2 to 5 mL) to completely transfer any remaining GAC onto the polycarbonate filter.

Transfer the filter with GAC onto the quartz boat and pyrolyze the filter and GAC to determine the halogen content.

Run the determination at two levels of dilution. If there is more than a 10% discrepancy between duplicate values, repeat the determination at a higher dilution.

### **6.3 Blanks**

Method blank - Repeat the entire procedure outlined for either the column or shaker adsorption method substituting water for the sample. The amount of GAC used for sample and blank must be the same. The use of the measuring spoon is recommended to ensure

that a constant amount of GAC is always delivered to the boat. The blank value should be less than 2 µg for 100 mL of water passed through the column. Duplicate method blank determinations must be performed each day that samples are analyzed.

**GAC blank** - Directly pyrolyze a sample of GAC ensuring that the amount used for blank and sample is the same. Use the measuring spoon for this purpose. Duplicate blank determinations must be performed each day that samples are analyzed. The GAC should not have a blank value greater than 25 µg/g.

**Polycarbonate filter blank** - This is used only for samples requiring pre-filtration, column method. Directly pyrolyze a polycarbonate membrane filter and determine its halogen content. Duplicate blank determinations must be performed on each batch of filters.

#### 6.4 Instrument Working Range

Determine the linear range of the instrument by analyzing several aliquots of 2,4,6-trichlorophenol standard solution. A typical range is 0.5 to 50 µL but higher volumes may be used. Directly inject onto the GAC and determine the chloride content, corrected for the GAC blank, after pyrolysis.

Plot the readout in µg against the expected chloride content. This curve is used to establish the linear working range of the instrument, based on which, optimum sample dilutions can be determined. The working range must be determined initially and should then be checked occasionally or after major servicing to the instrument.

Although the method provides linearity for up to 50 µg of chloride, it is not recommended that samples containing more than 25 µg of chloride be run as this would considerably lengthen the cell recovery time.

#### 6.5 Quality Control

a. **Sodium chloride standard** - This is used to check the function of the titration cell

and microcoulometer. Directly inject 10 µL of this standard into the acetic acid solution of the titration cell. Avoid contact with the electrodes. The amount of chloride detected should be within 5% of the expected value. This standard check must be performed each day that samples are analyzed.

- b. **Standard reference solution** - Each day that samples are analyzed, inject aliquots of trichlorophenol standard solution directly onto the GAC in the quartz boat. Make at least two injections of different volumes and within the linear range of the instrument. The AOX value must be corrected for the GAC blank. Recovery should be within 95 to 105% of the expected value. If it is too low, use the ammonium chloride standard to check for possible loss of hydrogen halide in the pyrolysis furnace and at the entrance of the titration cell.
- c. **Ammonium chloride standard** - To check for possible loss of hydrogen halide, directly inject 10 µL of this standard onto the quartz boat. Recovery should be at least 95%. It is preferable to use a quartz boat reserved for this purpose, since an encrusted boat can reduce the recovery significantly. This is not a routine test and should be performed only when loss of halide due to leakage is suspected.
- d. **Spike recovery** - It is recommended that spike addition measurements be made with trichlorophenol on a daily basis. This is particularly advisable for samples that are being analyzed for the first time or for those types of samples not frequently analyzed. A recovery of at least 90% of the added standard should be obtained. Low recovery could be due to matrix effects, such as the presence of a high level of organic material. Analyzing the sample at several levels of dilution can also help pinpoint such problems.

## Section 7

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### Calculations

Calculate the AOX value of the sample, as chloride, from one of the following equations.

#### 7.1 Column Method

##### Case 1: Samples not requiring pre-filtration

$$[\text{AOX}] \text{ mg/L} = \frac{(C_1 + C_2 - C_3) \times d}{1000 \times V} \quad (1)$$

where  $C_1$  = AOX in the top GAC column,  $\mu\text{g}$

$C_2$  = AOX in the bottom column,  $\mu\text{g}$

$C_3$  = mean of AOX values from duplicate method blanks,  $\mu\text{g}$ .  
Each method blank is the sum of the AOX in both columns.

$d$  = dilution factor

$V$  = volume of sample adsorbed, L

The factor of 1000 converts from  $\mu\text{g/L}$  to  $\text{mg/L}$ .

##### Case 2: Samples requiring pre-filtration

$$[\text{AOX of solids}] \text{ mg/L} = \frac{(C_4 - C_5) \times d}{1000 \times V} \quad (2)$$

where  $C_4$  = AOX of solids and polycarbonate filter,  $\mu\text{g}$

$C_5$  = mean of AOX values from duplicate polycarbonate filter blanks,  $\mu\text{g}$

$d$  = dilution factor

$V$  = volume of sample filtered, L

Total AOX of sample,  $\text{mg/L}$  = AOX of filtrate (from Equation 1) + AOX of solids (from Equation 2).

#### 7.2 Shaker Method

$$[\text{AOX}] \text{ mg/L} = \frac{(C_1 - C_2) \times d}{1000 \times V} \quad (3)$$

where  $C_1$  = AOX on GAC and polycarbonate filter,  $\mu\text{g}$

$C_2$  = mean of AOX values from duplicate method blanks,  $\mu\text{g}$

$d$  = dilution factor

$V$  = volume of sample adsorbed, L

The factor of 1000 converts from  $\mu\text{g/L}$  to  $\text{mg/L}$ .

*Section 8*

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**Report**

Report the mean of duplicate determinations to three significant figures for AOX values above 10 mg/L and to two significant figures for values below 10 mg/L. Specify the storage time and temperature of each sample. State any departure from the standard procedure.

In the case of pulp mill effluents, AOX results are generally expressed in terms of kg/tonne of pulp. Conversion from mg/L to kg/tonne is accomplished from measurements of effluent flows and production rates.

## Section 9

## Precision

- (a) Within-lab variation - The test precision was determined using the data from 171 duplicate AOX determinations on various types of mill effluent. As indicated in Table 2, the precision was not directly proportional to the AOX level, but was best represented by splitting the data into three ranges and calculating the precision for each of the ranges.
- (b) Interlaboratory variation - An interlaboratory study was conducted on six kraft mill effluent samples with 21 laboratories using either the column or shaker method (Fraser and Reeve, 1989). The results are shown in Table 3.

**Table 2 Precision of AOX Results**

Test Range AOX (mg/L)	Number of Duplicates	Standard Deviation	Coefficient of Variation (%)	Repeatability (based on average of duplicates) (%)
0 to 10	29	0.52	9.12	18.7
10.1 to 50	80	1.10	3.79	7.5
50.1 to 350	62	3.69	2.84	5.7

**Table 3 AOX Interlaboratory Study**

Sample	Mean of 21 laboratories AOX, mg/L	Standard deviation mg/L	Coefficient of variation %
1	216	23.2	11
2	5.9	1.1	19
3	2.9	0.6	21
4	32.8	4.3	13
5	7.4	0.6	8
6	3.8	0.6	16

**The samples listed in Table 3 are identified as follows:**

- 1 -- chlorination stage effluent
- 2 -- biologically treated final effluent
- 3 -- sample No. 2 diluted twice
- 4 -- extraction stage effluent
- 5 -- untreated combined effluent
- 6 -- sample No. 5 diluted twice

## Section 10

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### Cleaning Procedures

The titrimetric cell, complete with electrodes, should be flushed at least once each day that samples are analyzed. Flushing may be required more often depending on the sample matrices and concentrations being analyzed or overall cell performance. The flushing procedure is as follows:

- drain the cell;
- rinse with distilled or deionized water;
- rinse with acetone;
- rinse three times with distilled or deionized water;
- rinse twice with electrolyte; and
- recharge the cell with electrolyte and allow it to stabilize before using.

If a visible film of material remains on the walls of the titration vessel after cleaning, the cell must be cleaned more thoroughly using chromic acid. For this purpose, the cell must be detached from the combustion unit, all electrodes except the reference electrode must be removed and their ports plugged with solid septa. Extreme care must be taken to prevent chromic acid from coming in contact with either the reference cell or the side arm

leading to it. A strong detergent and a bottle brush may also be used. With continuous use, electrodes should last at least five to six months.

The combustion tube should also be cleaned regularly, depending on use. To do this, the furnace is switched off and the tube removed.

**CAUTION:** The combustion tube remains hot for some time and therefore should be handled only at the cool end. After cooling, the tube may be cleaned with chromic acid. Sintering of the quartz will eventually cause poor performance, generally reflected as low spike recoveries and tailing of peaks. With continuous use, combustion tubes should generally last at least three to four months.

The sample reservoirs on the adsorption unit should be washed at least once a month with hot water and detergent and a bottle brush. They must then be thoroughly rinsed with hot tap water, distilled water and nitrate washing solution.

All 'O' rings at the various interfaces should be routinely checked for wear or cracking.

These cleaning procedures may vary according to manufacturer's recommendations.

## References

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- Bethge, P.O., Y. Frisk, and H.L. Hardell, "Determination of Chlorinated Organics in Pulp Mill Effluents", STFI Report No. 63 from the SSVL Project "Environment 90" (October, 1989).
- Fraser, J.L. and D.W. Reeve, "Adsorbable Organic Halogen, Interlaboratory Comparison Study", CPPA Technical Section Preprints, *Pacific Coast and Western Branches Conference*, Whistler, B.C. (May 24-27, 1989).
- Odendahl, S.M., K.M. Weishar, and D.W. Reeve, "Chlorinated Organic Matter in Bleached Chemical Pulp Production. Part II: A Review of Measurement Techniques for Effluents", *Pulp Paper Can.*, 91(4), T136 (1990).
- Sjöström, L., R. Radeström, and K. Lindström, "Determination of Total Organic Chlorine in Spent Bleach Liquors", *Svensk Papperstid.*, 85(3), R7 (1982).

## Bibliography

---

- Dressman, R.C. and A.A. Stevens, "The Analysis of Organohalides in Water - An Evaluation Update", *J. Am. Water Works Assoc.*, 75(8), 431 (1983).
- Stevens, A.A., R.C. Dressman, R.K. Sorrell, and H.J. Brass, "Organic Halogen Measurements: Current Uses and Future Prospects", *J. Am. Water Works Assoc.*, 77(4), 146 (1985).
- Takahashi, Y., R.T. Moore, and R.J. Joyce, "Measurement of Total Organic Halides (TOX) and Purgeable Organic Halides (POX) in Water Using Carbon Adsorption and Microcoulometric Determination", in: *Chemistry in Water Reuse*, Vol. 2, W.J. Cooper (ed.), Ann Arbor, Mi, Ann Arbor Science Publishers, Chapter 7, pp. 127-146 (1981).

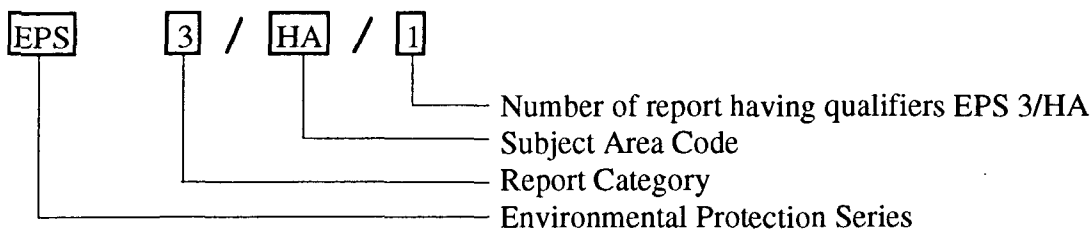


**Related Methods**

1. APHA Standard Method 5320. Standard Methods for the Examination of Water and Wastewater, Published by APHA, AWWA and WPCF, 17th Edition, 1989.
2. German Standard DIN 38409.
3. SCAN-W 9:89.
4. U.S. EPA Method 9020.

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