

REAGENTS:

1. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), reagent grade.
2. p-Cyanophenol ($\text{C}_7\text{H}_5\text{NO}$), reagent grade.
3. Sodium bicarbonate (NaHCO_3), reagent grade.
4. Sodium carbonate (Na_2CO_3), reagent grade.
5. Sulfuric acid (H_2SO_4), conc., reagent grade.
6. Potassium bromide (KBr), reagent grade.
7. Potassium chloride (KCl), reagent grade.
8. Nitric acid (HNO_3), conc., reagent grade.
9. Water, deionized (at least 18 MOhm-cm).
10. Extraction solution: 6 mM $\text{Na}_2\text{S}_2\text{O}_3$. Dissolve 0.474 g $\text{Na}_2\text{S}_2\text{O}_3$ in 500 mL deionized water.
11. Eluent: 0.25 mM NaHCO_3 /4 mM Na_2CO_3 /0.78 mM p-cyanophenol. Dissolve 0.042 g NaHCO_3 , 0.848 g Na_2CO_3 and 0.186 g p-cyanophenol in 2 L filtered deionized water.
12. Suppressor regenerant, 0.025 N H_2SO_4 . Dilute 2.8 mL conc. H_2SO_4 to 4 L with deionized water.*
13. Calibration stock solutions, 1 mg/mL (as anion).
 1. Dissolve 0.149 g KBr in 100 mL deionized water.
 2. Dissolve 0.21 g KCl in 100 mL deionized water.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Silver membrane filter,[†] 25-mm, 0.45- μm , with porous plastic support pad; prefilter, PTFE with PTFE support, 0.5- μm , or polyester, 0.4- μm with porous plastic support pad; three-piece, 25-mm carbon-filled polypropylene cassette (opaque) with 50-mm extension (Fig. 1)
 - a. In the outlet piece of cassette, place porous plastic support pad and cleaned silver filter. Insert 50-mm extension (cowl) securely.
 - b. At the inlet (top) of the extension, place porous plastic support pad and prefilter. Insert inlet cassette piece securely.
 - c. Seal each connection with shrinkable bands or tape.
2. Personal sampling pump, 0.3 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph with metal-free trap pre-column containing chelating resin, analytical and guard ion-exchange columns containing polystyrene/divinylbenzene substrate agglomerated with anion exchange latex, anion micromembrane suppressor, conductivity detector and connected to a data processing unit (page 6011-1).
4. Bottles, 30-mL, wide mouth with screw caps, amber or opaque polyethylene.
5. Micropipettes, with disposable tips.
6. Volumetric flasks, 10- and 100-mL.
7. Repipet reagent dispensers, 0 to 10-mL.
8. Syringes, 10-mL, polyethylene, luer lock style or equivalent.
9. Forceps.
10. Autosampler vials.

[†]Silver membrane filters must be cleaned prior to use (see APPENDIX A).

NOTE: Some lots of silver membrane filters contain excessively high chloride background levels. After cleaning, please screen before field use.

SPECIAL PRECAUTIONS: Wear appropriate personal protective clothing, safety goggles, and gloves. All work should be performed with adequate ventilation. It is imperative that acid be added to water to avoid a violent exothermic reaction. Sulfuric acid is extremely corrosive to skin, eyes, and mucous membranes.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
 2. Attach sampler to personal sampling pump with flexible tubing.
 3. Sample at an accurately known flow rate between 0.3 and 1 L/min for a total sample size of 8 to 360 L for bromine or 2 to 45 L for chlorine.
 4. Seal ends of sample with plugs. Pack securely for shipping.
- NOTE: Silver halides are photosensitive. Protect from light during sampling, transfer, and desorption.

SAMPLE PREPARATION:

5. Under very dim or red light, open cassette and transfer the silver filter with forceps to amber bottle. Add 3 mL 6 mM $\text{Na}_2\text{S}_2\text{O}_3$ and cap.
NOTE: Prefilter may be analyzed for particulate halides or discarded.
6. Allow samples to stand a minimum of 10 min with occasional swirling. Samples may remain in the desorbing solution for up to 24 hours.
NOTE: Once desorbed, samples are no longer photosensitive.
7. Uncap the sample bottles and add 7 mL deionized water for a total solution volume of 10 mL.
8. Pour sample into 10-mL plastic syringe for manual injection or into autosampler vials.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of 0.2 to 15 μg bromide and/or 0.05 to 5 μg chloride per mL of sample.
 - a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark with deionized water.
 - b. Prepare fresh working standards biweekly.
 - c. Analyze working standards together with samples and blanks (steps 11 through 13)
 - d. Prepare a calibration graph (peak height vs. μg of anion per sample)
10. Analyze three quality control spikes, three analyst spikes and media blanks to ensure that calibration graph is in control.

MEASUREMENT:

11. Set ion chromatograph according to manufacturer's instructions and to conditions given on page 6011-1.
NOTE: Excessive amounts of Ag^+ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ deteriorate column performance. Use a metal-free pre-column prior to the chromatographic columns and recondition the column every 100 to 150 analyses (See APPENDIX B).
12. Inject 50- μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from syringe to ensure complete rinse of the sample loop.
13. Measure peak height. If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. From the calibration graph, determine the mass of Br or Cl in each sample, W (μg), and in the average blank, B (μg).
15. Calculate the concentration, C (mg/m^3), of Br_2 or Cl_2 in the air volume sampled, V (L):

$$C = \frac{W-B}{V}, \text{mg/m}^3$$

NOTE: $\mu\text{g/L} = \text{mg/m}^3$

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of Br₂ and Cl₂ at both high (80%) and low (20%) relative humidities [5,6]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m³ for Br₂ and 0.354 to 6.77 mg/m³ for Cl₂. Samples were analyzed using a Dionex 4000i Ion Chromatograph with conductivity detector and AutoRegen accessory (Dionex Corp., Sunnyvale, California), a WISP 710B autosampler (Waters Division of Millipore, Milford, Massachusetts), and interfaced with a Hewlett - Packard 3357 Laboratory Data System (Hewlett - Packard, Avondale, Pennsylvania). Dionex MFC-1, HPLC-AG4A, HPLC-AS4A columns and AMMS anion micromembrane suppressor were used. Overall recovery for Br₂ was 98.8% with total overall precision, S_{rel} , of 6.8%. Overall recovery for Cl₂ was 98.6% with a total overall precision, S_{rel} , of 6.7%. Samples for Cl₂ were stable at least 30 days at 25 °C (103 ± 4% recovery) and up to 60 days at 5 °C (101 ± 3% recovery). The Br₂ samples were stable up to 60 days at 25 °C (99.2 ± 10.1% recovery).

In this updated version of NIOSH 6011, Issue 3, the Chlorine and Bromine methods, found separately in the NMAM 4th edition, were combined. No new evaluation data are reported in this issue; however, the maximum sample volumes were recalculated using original data from the previous issue.

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APPENDIX A: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 mM $\text{Na}_2\text{S}_2\text{O}_3$.
2. Allow to stand for a minimum of 10 min with occasional swirling.
3. Discard solution and rinse thoroughly with deionized water. Allow the filters to stand in last rinse for a few minutes.
4. Remove filters from bottles and dry between layers of absorbent laboratory towels.
5. Store cleaned filters between paper disks in manufacturer's container. Filters are stable for a least 8 months.

NOTE: Some lots of silver membrane filters contain extremely high chloride background levels. If excessively high, this cleaning procedure will not remove all the chloride, even if repeated several times. Screening is necessary for each lot before being used for this method. Screening may be done by analyzing the cleaned filters starting with Step 5 of this method, or by analyzing by XRD. Background levels should be ND to obtain optimal precision and accuracy.

APPENDIX B: COLUMN RECONDITIONING PROCEDURE

In the following order, pump through the analytical columns at 2 mL/min:

- a. 30 mL deionized water to rinse;
- b. 60 mL 1 M HNO_3 to remove contaminants;
- c. 30 mL 0.1 M Na_2CO_3 to remove the NO_3^- ;
- d. Eluent to equilibrate.

Reconditioning is recommended after 100 to 150 analyses.

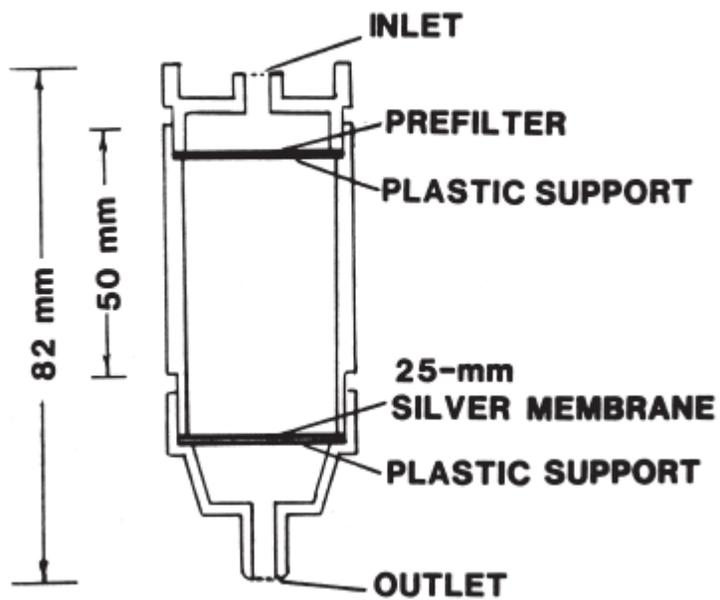


Figure 1. Silver Filter Sampler