**BROMINE and CHLORINE** 6011

**Formula:** 1) Br₂  
2) Cl₂  
**MW:** 1) 159.82  
2) 70.91  
**CAS:** 1) 7726-95-6  
2) 7782-50-5  
**RTECS:** 1) EF9100000  
2) FO2100000

**METHOD:** 6011, Issue 3  
**EVALUATION:** FULL  
**Issue 1:** 15 August 1989  
**Issue 3:** 18 February 2022

**OSHA:**  
1) 0.1 ppm  
2) C 1 ppm  
**NIOSH:**  
1) 0.1 ppm; STEL 0.3 ppm  
2) C 0.5 ppm; 15 min ceiling  
**Other OELs:** [1-3]

**PROPERTIES:**  
1) liquid; d₃ 3.1028 g/mL @ 20 °C; BP 58.8 °C; VP 28.2 kPa (212 mm Hg) @ 25 °C; vapor density (air=1) 5.5; 1 ppm=6.53 mg/m³  
2) gas; d₂ 2.898 g/L at 20 °C; BP -34.0 °C; vapor density (air=1) 2.5; 1 ppm=2.90 mg/m³ @ NTP [4]

**SYNONYMS:** none

### SAMPLING

| SAMPLER: | PREFILTER + FILTER  
| (PTFE, 0.5-µm + silver membrane, 25-mm, 0.45-µm) |
| FLOW RATE: | 0.3 to 1 L/min |
| VOL-MIN: | 1) 8 L @ 0.1 ppm  
| 2) 2 L @ 0.5 ppm |
| -MAX: | 1) 360 L  
| 2) 45 L |
| SHIPMENT: | routine, protect from light |
| SAMPLE STABILITY: | ≥30 days at 25 °C [5,6] |
| BLANKS: | 2 to 10 field blanks per set |

**ACCURACY** [5,6]

| RANGE STUDIED: | 1) 0.07 to 1.42 mg/m³ (72-L samples)  
| 2) 0.35 to 6.77 mg/m³ (15-L samples) |
| BIAS: | 1) -1.2%  
| 2) -1.4% |
| OVERALL PRECISION (\(\bar{S}_P\)): | 1) 0.069  
| 2) 0.075 |
| ACCURACY: | 1) ± 13.6%  
| 2) ± 14.8% |

**TECHNIQUE:** ION CHROMATOGRAPHY, CONDUCTIVITY

**ANALYTE:** bromide ion (Br⁻) or chloride ion (Cl⁻)

**EXTRACTION:** 3 mL 6 mM Na₂S₂O₃, 10 min

**INJECTION VOLUME:** 50 µL

**COLUMN:** polystyrene/divinylbenzene substrate agglomerated with anion exchange latex guard and analytical columns, metal-free precolumn, anion micromembrane suppressor

**DETECTOR SETTING:** 10 µS full scale

**ELUENT:** 0.25 mM NaHCO₃/4 mM Na₂CO₃/0.78 mM p-cyanophenol, 2 mL/min

**CALIBRATION:** standard solutions of Br⁻ or Cl⁻ in deionized water

**RANGE:** 5 to 150 µg Br⁻ per sample  
2 to 50 µg Cl⁻ per sample [5,6]

**ESTIMATED LOD:** 1.6 µg Br⁻ per sample  
0.6 µg Cl⁻ per sample [5,6]

**PRECISION (\(\bar{S}_P\)):** 0.045 @ 5 to 100 µg Br⁻ per sample  
0.067 @ 5.3 to 100 µg Cl⁻ per sample [5,6]

**APPLICABILITY:** The working ranges are: for Br₂ 0.002 to 0.1 ppm (0.015 to 0.658 mg/m³) for a 360-L air sample; for Cl₂ 0.015 to 1 ppm (0.04 to 2.9 mg/m³) for a 45-L air sample. The method has sufficient sensitivity for STEL samples.

**INTERFERENCES:** Hydrogen sulfide gives a negative interference. HCl gives a positive interference up to a maximum of 15 µg per sample. HBr gives a positive interference as it is sampled continuously. [5,6]

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 \((\text{NaHCO}_3)\), reagent grade.
4. Sodium carbonate \((\text{Na}_2\text{CO}_3)\), reagent grade.
5. Sulfuric acid \((\text{H}_2\text{SO}_4)\), conc., reagent grade.
6. Potassium bromide \((\text{KBr})\), reagent grade.
7. Potassium chloride \((\text{KCl})\), reagent grade.
8. Nitric acid \((\text{HNO}_3)\), 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 \(\text{NaHCO}_3\)/4 mM \(\text{Na}_2\text{CO}_3\)/0.78 mM \(p\)-cyanophenol. Dissolve 0.042 g \(\text{NaHCO}_3\), 0.848 g \(\text{Na}_2\text{CO}_3\) and 0.186 g \(p\)-cyanophenol in 2 L filtered deionized water.
12. Suppressor regenerant, 0.025 N \(\text{H}_2\text{SO}_4\). Dilute 2.8 mL conc. \(\text{H}_2\text{SO}_4\) to 4 L with deionized water.*
13. Calibration stock solutions, 1 mg/mL (as anion).
   1. Dissolve 0.149 g \(\text{KBr}\) in 100 mL deionized water.
   2. Dissolve 0.21 g \(\text{KCl}\) in 100 mL deionized water.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Silver membrane filter,* 25-mm, 0.45-µm, with porous plastic support pad; prefiler, 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 prefiler. 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.
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 90 L for chlorine.
   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 Na₂S₂O₃ 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 Ag(S₂O₃)₂⁻ 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/m³), of Br₂ or Cl₂ in the air volume sampled, V (L):
\[ C = \frac{W - B}{V}, \text{mg/m}^3 \]

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

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of \( \text{Br}_2 \) and \( \text{Cl}_2 \) 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/m\(^3\) for \( \text{Br}_2 \) and 0.354 to 6.77 mg/m\(^3\) for \( \text{Cl}_2 \). 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, HPIC-AG4A, HPIC-AS4A columns and AMMS anion micromembrane suppressor were used. Overall recovery for \( \text{Br}_2 \) was 98.8% with total overall precision, \( S_{tr} \), of 6.8%. Overall recovery for \( \text{Cl}_2 \) was 98.6% with a total overall precision, \( S_{tr} \), of 6.7%. Samples for \( \text{Cl}_2 \) were stable at least 30 days at 25 °C (103 ± 4% recovery) and up to 60 days at 5 °C (101 ± 3% recovery). The \( \text{Br}_2 \) 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.

REFERENCES:


METHOD WRITTEN BY:
Mary Ellen Cassinelli, NIOSH

METHOD UPDATED BY:
Dawn Farwick, NIOSH/HELD

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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 Na₂S₂O₃.
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 at 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 HNO₃ to remove contaminants;
c. 30 mL 0.1 M Na₂CO₃ to remove the NO₃⁻;
d. Eluent to equilibrate.
Reconditioning is recommended after 100 to 150 analyses.
Figure 1. Silver Filter Sampler