

# BROMINE

6011

See CHLORINE, Method 6011, for procedure

Br<sub>2</sub>

MW: 159.82

CAS: 7726-95-6

RTECS: EF9100000

METHOD: 6011, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

**OSHA :** 0.1 ppm  
**NIOSH:** 0.1 ppm; STEL 0.3 ppm  
**ACGIH:** 0.1 ppm; STEL 0.3 ppm  
 (1 ppm = 6.53 mg/m<sup>3</sup>)

**PROPERTIES:** liquid; d 3.119 g/mL @ 20 °C;  
 BP 58.78 °C; VP 23.3 kPa (175 mm Hg)  
 @ 20 °C vapor density (air=1) 5.5

**SYNONYMS:** None.

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	PREFILTER + FILTER (PTFE, 0.5-µm + silver membrane, 25-mm, 0.45-µm)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY, CONDUCTIVITY
<b>FLOW RATE:</b>	0.3 to 1 L/min	<b>ANALYTE:</b>	bromide ion (Br <sup>-</sup> )
<b>VOL-MIN:</b>	8 L @ 0.1 ppm	<b>EXTRACTION:</b>	3 mL 6 mM Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 10 min
<b>-MAX:</b>	360 L	<b>INJECTION VOLUME:</b>	50 µL
<b>SHIPMENT:</b>	routine, protect from light	<b>COLUMN:</b>	Dionex HPIC-AG4A guard, HPIC-AS4A separator, MFC-1 precolumn, AMMS anion suppressor
<b>SAMPLE STABILITY:</b>	≥30 days at 25 °C [1]	<b>DETECTOR SETTING:</b>	10 µS full scale
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>ELUENT:</b>	0.25 mM NaHCO <sub>3</sub> /4 mM Na <sub>2</sub> CO <sub>3</sub> /0.78 mM p-cyanophenol, 2 mL/min
ACCURACY		<b>CALIBRATION:</b>	standard solutions of Br <sup>-</sup> in deionized water
<b>RANGE STUDIED:</b>	0.07 to 1.42 mg/m <sup>3</sup> (72-L samples)	<b>RANGE:</b>	5 to 150 µg Br <sup>-</sup> per sample [1]
<b>BIAS:</b>	- 1.2%	<b>ESTIMATED LOD:</b>	1.6 µg Br <sup>-</sup> per sample [1]
<b>OVERALL PRECISION (Ŝ<sub>r,T</sub>):</b>	0.069 [1]	<b>PRECISION (Ŝ<sub>r</sub>):</b>	0.045 @ 5 to 100 µg per sample [1]
<b>ACCURACY:</b>	± 13.6%		

**APPLICABILITY:** The working ranges for Br<sub>2</sub> and Cl<sub>2</sub> are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m<sup>3</sup>) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m<sup>3</sup>) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

**INTERFERENCES:** Hydrogen sulfide gives a negative interference. HCl gives a positive interference upon a maximum of 15 µg per sample. HBr gives a positive interference as it is sampled continuously [1].

**OTHER METHODS:** P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

# CHLORINE

6011

Cl<sub>2</sub>

MW: 70.91

CAS: 7782-50-5

RTECS: FO2100000

**METHOD:** 6011, Issue 2

**EVALUATION:** FULL

**Issue 1:** 15 May 1989

**Issue 2:** 15 August 1994

**OSHA :** C 1 ppm  
**NIOSH:** 0.5 ppm; STEL 1 ppm  
**ACGIH:** 0.5 ppm; STEL 1 ppm  
 (1 ppm = 2.90 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** gas; d 3.214 g/L at 0 °C; BP -34.6 °C;  
 vapor density (air = 1) 2.5

**SYNONYMS:** None.

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	PREFILTER + FILTER (PTFE, 0.5-µm + silver membrane, 25-mm, 0.45-µm)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY, CONDUCTIVITY
<b>FLOW RATE:</b>	0.3 to 1 L/min	<b>ANALYTE:</b>	chloride ion (Cl <sup>-</sup> ) or bromide ion (Br <sup>-</sup> )
<b>VOL-MIN:</b>	2 L @ 0.5 ppm	<b>EXTRACTION:</b>	3 mL 6 mM Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 10 min
<b>-MAX:</b>	90 L	<b>INJECTION VOLUME:</b>	50 µL
<b>SHIPMENT:</b>	routine, protect from light	<b>COLUMN:</b>	Dionex HPIC-AG4A guard, HPIC-AS4A separator MFC-1 precolumn, AMMS anion suppressor
<b>SAMPLE STABILITY:</b>	≥30 days at 25 °C [1]	<b>DETECTOR SETTING:</b>	10 µS full scale
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>ELUENT:</b>	0.25 mM NaHCO <sub>3</sub> /4 mM Na <sub>2</sub> CO <sub>3</sub> /0.78 mM p-cyanophenol, 2 mL/min
<b>ACCURACY</b>		<b>CALIBRATION:</b>	standard solutions of Cl <sup>-</sup> in deionized water
<b>RANGE STUDIED:</b>	0.35 to 6.77 mg/m <sup>3</sup> (15-L samples)	<b>RANGE:</b>	2 to 50 µg Cl <sup>-</sup> per sample [1]
<b>BIAS:</b>	- 1.4%	<b>ESTIMATED LOD:</b>	0.6 µg Cl <sup>-</sup> per sample [1]
<b>OVERALL PRECISION (Ŝ<sub>rT</sub>):</b>	0.075 [1]	<b>PRECISION (Ŝ<sub>p</sub>):</b>	0.067 @ 5.3 to 100 µg per sample [1]
<b>ACCURACY:</b>	± 14.8%		

**APPLICABILITY:** The working ranges for Br<sub>2</sub> and Cl<sub>2</sub> are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m<sup>3</sup>) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m<sup>3</sup>) respectively for a 90-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 [1].

**OTHER METHODS:** P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

**REAGENTS:**

1. Sodium thiosulfate, reagent grade.
2. Water, deionized.
3. Extraction solution: 6 m M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Dissolve 0.474 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in 500 mL deionized water.
4. Eluent: 0.25 m M NaHCO<sub>3</sub>/4 m M Na<sub>2</sub>CO<sub>3</sub>/0.78 m M p-cyanophenol. Dissolve 0.041 g NaHCO<sub>3</sub>, 0.848 g Na<sub>2</sub>CO<sub>3</sub> and 0.186 g p-cyanophenol in 2 L filtered deionized water.
5. Suppressor regenerant, 0.025 N H<sub>2</sub>SO<sub>4</sub>. Dilute 2.8 mL conc. H<sub>2</sub>SO<sub>4</sub> to 4 L with deionized water.\*
6. 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, (Costar/Nuclepore, Poretics, or equivalent) with porous plastic support pad (Costar/Nuclepore); prefilter, PTFE with PTFE support, 0.5-µm (Gelman Zefluor, SKC, or equivalent), or polyester, 0.4-µm (Costar/Nuclepore) with porous plastic support pad; three-piece, 25-mm carbon-filled polypropylene cassette (opaque) with 50-mm extension (Costar/Nuclepore or Gelman) (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 Dionex MFC-1, HPIC-AG4A, HPIC-AS4A columns, AMMS anion micromembrane suppressor, conductivity detector and integrator (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-tip.
9. Forceps.

\* 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. Please screen before field use.

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**SPECIAL PRECAUTIONS:** Sulfuric acid is extremely corrosive to skin, eyes, and mucous membranes. Wear protective clothing. Handle in a fume hood.

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**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.
4. Seal ends of sampler with plugs. Pack securely for shipping.

**SAMPLE PREPARATION:**

- NOTE: Silver halides are photosensitive. Protect from light during transfer and desorption.
5. Under very dim or red light, open cassette and transfer the silver filter with forceps to amber bottle. Add 3 mL 6 m M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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.  
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<sup>+</sup> and Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup> deteriorate column performance. Use a metal free column (MFC-1) 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<sup>-</sup> or Cl<sup>-</sup> in each sample, W (µg), and in the average blank, B (µg).
15. Calculate the concentration, C (mg/m<sup>3</sup>), of Br<sub>2</sub> or Cl<sub>2</sub> in the air volume sampled, V (L):

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

**EVALUATION OF METHOD:**

The method was evaluated by sampling generated atmospheres of Br<sub>2</sub> and Cl<sub>2</sub> at both high (80%) and low (20%) relative humidities [1]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m<sup>3</sup> for Br<sub>2</sub> and 0.354 to 6.77 mg/m<sup>3</sup> for Cl<sub>2</sub>. Overall recovery for Br<sub>2</sub> was 98.8% with total overall precision,  $\hat{S}_{RT}$ , of 6.8%. Overall recovery for Cl<sub>2</sub> was 98.6% with total overall precision,  $\hat{S}_{RT}$ , of 6.7%. Samples for Cl<sub>2</sub> were stable at least 30 days at 25 °C (103 ± 4% Recovery) and up to 60 days at 5 °C (101 ± 3% Recovery). The Br<sub>2</sub> samples were stable up to 60 days at 25 °C (99.2 ± 10.1% Recovery).

## REFERENCES:

- [1] Cassinelli, M.E. Development of Solid Sorbent Monitoring Method for Chlorine and Bromine with Determination by Ion Chromatography, Appl. Occup. Environ. Hyg., 6:215-226 (1991).
- [2] NIOSH Manual of Analytical Methods, 2nd ed.; Taylor, D.G., Ed.; V. 1, P&CAM 209; U.S. Department of Health Education and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 77-157, 1977.
- [3] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, Method No. ID-101). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.
- [4] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-108). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

## METHOD WRITTEN BY:

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## APPENDIX A: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

NOTE: Some lots of silver membrane filters contain extremely high chloride background levels. If excessively high this cleaning procedure will not remove all of the chloride, even if repeated several times. Screening is necessary for each lot before being used for this method. Screening may be done by following this procedure at least twice, or by analyzing by XRD.

1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 M  $\text{Na}_2\text{S}_2\text{O}_3$ .
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 at least 8 months.

## 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  $\text{HNO}_3$  to remove contaminants;
- c. 30 mL 0.1 M  $\text{Na}_2\text{CO}_3$  to remove the  $\text{NO}_3^-$ ;
- d. Eluent to equilibrate.

Reconditioning is recommended after 100 to 150 analyses.

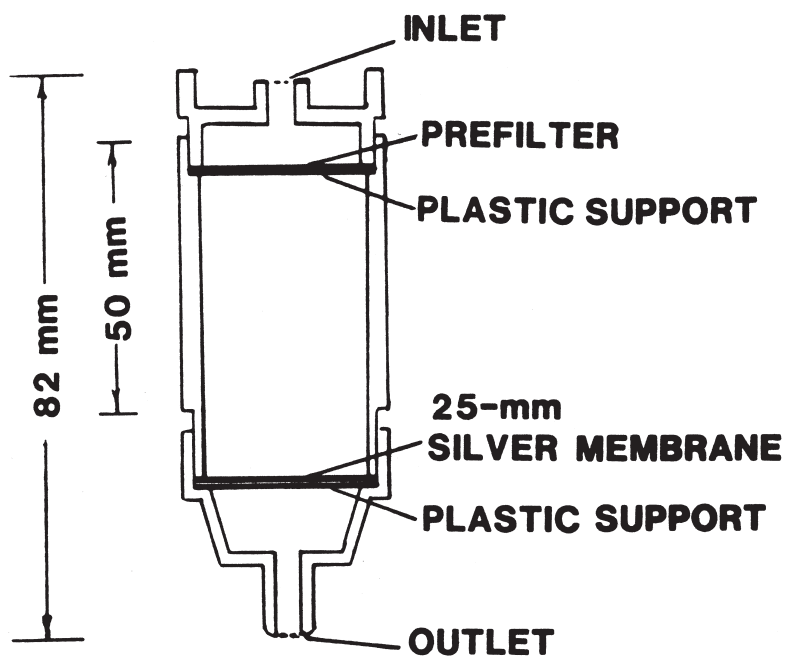


Figure 1. Silver Filter Sampler