Method no.:	ID-108
Matrix:	Air
OSHA Permissible Exposure Limits Bromine (Final Rule Limits):	0.1 ppm (Time Weighted Average) 0.3 ppm (Short-Term Exposure Limit)
Bromine (Transitional Limit):	0.1 ppm (Time Weighted Average)
Collection Procedure:	A calibrated personal sampling pump is used to draw a known volume of air through a midget fritted glass bubbler containing a sodium bicarbonate/sodium carbonate buffer solution.
Recommended Sampling Rate:	0.5 L/min
Recommended Air Volumes Short-Term Exposure Limit Samples:	7.5 L
Time Weighted Average Samples:	30 L
Analytical Procedure:	In the buffer collection solution, bromine disproportionates to bromide and bromate ions. Samples are analyzed with minimum sample preparation as these anions by ion chromatography.
Detection Limits Qualitative:	0.001 ppm (30-L air volume)
Quantitative:	0.005 ppm (30-L air volume)
Precision and Accuracy Validation Level:	0.052 to 0.21 ppm
CV_T:	0.067
Bias:	-0.056
Overall Error:	±19%
Method Classification:	Validated Method
Chemist:	James Ku
Date:	1982, Revised April 1990

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OSHA Technical Center
Salt Lake City, Utah

1. Introduction

This method describes the collection of airborne bromine (Br_2) in the breathing zone of personnel in the workplace and the subsequent analysis by ion chromatography (IC).

1.1. History

Previously, Br_2 air samples were collected in 0.01 N NaOH and analyzed as bromide (Br^-) at the OSHA Laboratory by ion specific electrode (ISE) after neutralization with nitric acid. This method had lower recoveries than expected (8.1) and was possibly due to Br^- and bromate (BrO_3^-) reacting with each other and gradually reverting back to Br_2 in an acidic solution. According to the following equation (8.2):

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow Br_2 + 3H_2O$$
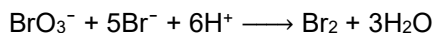
loss of analyte can occur in acidic media. The ISE analysis was further hampered by interferences from other ions such as chloride, iodide, cyanide, or ammonia (8.3). A method for bromine was developed to allow analysis by ion chromatography and to diminish any problems with interferences.

1.2. Principle

Bromine is collected in a midget-fritted glass bubbler (MFGB) containing a weakly basic buffer [sodium carbonate / sodium bicarbonate (Na_2CO_3 / $NaHCO_3$)]. Bromine disproportionates in basic solution to produce Br^- and BrO_3^- according to the following equation (8.4).

$$3Br_2 + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 3H_2O$$

The mole ratio of Br_2 per Br^- formed is 1.2. The amount of Br^- measured by IC is multiplied by this factor to gravimetrically convert Br^- to Br_2. The BrO_3^- formed can also be measured, in principle, with this method. Because the BrO_3^- peak may overlap with peaks of chloride or iodate, measurement of BrO_3^- is normally only used to confirm the presence of Br_2.

1.3. Advantages and Disadvantages

1.3.1. This method has adequate sensitivity for measuring workplace atmosphere concentrations of Br_2.

1.3.2. This method is less affected by interferences found in other methods (i.e. ion specific electrode, Volhard titration, and colorimetric determinations).

1.3.3. The analytical method can be fully automated. Use of an automatic sampler can improve analytical precision.

1.3.4. The amount of Br_2 may be simultaneously confirmed from the bromate anion formed during disproportionation.

1.3.5. High humidity does not affect the sampling procedure.

1.3.6. A disadvantage is the sampling device. Use of bubbler collection techniques may impose certain inconveniences. Spillage can occur during sampling, handling, and during transportation to the lab.

1.4. Uses

Bromine is used in the following operations (8.5):

- the manufacture of ethylene dibromide (anti-knock gasoline)
- organic synthesis reactions
- bleaching agents
- fumigants, as an intermediate (methyl bromide)
- fire-retardants for plastics, dyes, and photography
- water purification
- shrink-proofing wool

1.5. Physical Properties

Bromine (CAS No. 7726-95-6) is a fuming liquid with a pungent odor. Some physical properties of Br_2 are listed below (8.5, 8.6):

Atomic Number:	35
Atomic Symbol:	Br
Molecular Weight(Br_2):	159.89
Melting Point:	-7.2 °C
Boiling Point:	59.4 °C
Vapor Pressure:	22.9 kPa (172 mmHg) at 20 °C
Color (liquid):	Reddish-brown
Flammability:	Nonflammable
Classification:	Corrosive, strong oxidizer
Solubility:	Slightly soluble in H_2O

2. Range and Detection Limit (8.1)

The analytical portion of the evaluation was conducted using a model 10 ion chromatograph (Dionex, Sunnyvale CA) with a 3 × 500-mm separator and 6 × 250-mm suppressor columns. The following results were obtained using this equipment:

2.1.1. The working range was 0.015 to 0.31 ppm (30-L air sample).

2.1.2. The sensitivity of the method was 1.96 µS/cm/µg as Br⁻. The ion chromatograph was set on a range of 30 µS.

2.1.3. The qualitative detection limit of the analytical method was 0.003 µg of Br^- per 200-µL sample injection or 0.17 µg Br^- in a 10-mL sample volume.

2.1.4. The quantitative limit was 0.015 µg Br^- per 200-µL injection or 0.75 µg Br^- in a 10-mL sample volume. The CV of replicate determinations of standards at this level was about 0.11.

3. Method Performance (8.1)

This method was evaluated in 1982 using commercial analytical equipment mentioned in Section 2. Advances in ion chromatographic and sampling instruments should enable users to obtain similar or better results as those mentioned below.

3.1. The CV for the overall sampling and analytical method (CV_T[pooled]) in the range of 0.052 to 0.205 ppm was 0.067.

3.2. In validation experiments, this method was capable of measurements within ± 25% of the true value over the validation range (95% confidence level). Bias was -0.056 and overall error was ±19%.

3.3. Collection efficiency was 100% for the buffer collection solution.

3.4. A breakthrough test, conducted at a concentration of 0.21 ppm, indicated breakthrough of 2.4% occurred after sampling for 240 min at a sampling rate of 0.5 L/min. This amount of breakthrough is within acceptable limits (<5% breakthrough).

3.5. In storage stability studies, the mean of samples analyzed after 15 days was within 1% of the mean of samples analyzed immediately after collection. After 30 days the mean was within 10%.

4. Interferences

4.1. Any substance that has the same retention time as BrO_3^- or Br^- using the operating conditions as described in this method is an interference.

4.2. Nitrate is a potential interference if present in concentrations greater than Br^-. Anions such as chloride (Cl^-), chlorate (ClO_3^-) and iodate (IO_3^-) may interfere with bromate analysis. These interferences may be minimized by changing the eluent strength, eluent pump flow rate, or separator column. A gradient pump system and an alternate eluent (as specified in Section 6.7) displayed excellent separation of ClO_2^-, Cl^-, and BrO_3^-. This alternate eluent is recommended when Cl^- or other anions prevent positive identification of the presence of bromine with the bromate peak.

4.3. Bromide collected with Br_2 in air is an interference; however, differentiation of these two species can be accomplished by determining the amount of BrO_3^- in the sample.

5. Sampling

5.1. Equipment

5.1.1. Collection solution, 0.003 M sodium bicarbonate ($NaHCO_3$)/0.0024 M sodium carbonate (Na_2CO_3): Dissolve 0.25 g each $NaHCO_3$ and Na_2CO_3 in approximately 250 mL of DI H_2O and then dilute to 1 L with DI H_2O. Prepare a new solution every month.

5.1.2. Personal sampling pumps capable of sampling within ± 5% of the recommended flow rate of 0.5 L/min are used.

5.1.3. Midget fritted glass bubblers (MFGBs) (25-mL, part no. 7532, Ace Glass Co., Vineland, NJ).

5.1.4. Shipping vials, glass or plastic: Scintillation vials, 20-mL (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners. Tin or other metal cap liners should not be used.

5.1.5. A stopwatch and bubble tube or meter are used to calibrate pumps.

5.1.6. Various lengths of polyvinyl chloride (PVC) tubing are used to connect bubblers to the pumps.

5.2. Sampling Procedure

5.2.1. Calibrate each sampling pump with a calibration sampling device in-line. The calibration device is a MFGB containing about 10 mL of collection solution.

5.2.2. Place 10 to 15 mL of fresh collection solution in each MFGB. Connect a MFGB to a calibrated sampling pump and then place the sampling device in the breathing zone of the employee.

5.2.3. Sample at a flow rate of 0.5 L/min. For STEL determinations, sample for at least 15 min. For measurements of TWA exposures, sample up to 240 min. Take enough samples to cover the shift worked.

5.2.4. Transfer the collection solution into a 20-mL glass scintillation vial. Rinse the bubbler with 2 to 3 mL of unused collection solution and transfer the rinse into the sample vial. Place the Teflon-lined cap tightly on each vial and seal with vinyl or waterproof tape around the caps to prevent leakage during shipment. Wrap the vial end-to-end with a sample seal (OSHA 21 or equivalent).

5.2.5. Prepare a blank solution by taking 10 to 15 mL of the unused collection solution and transfer to a 20-mL glass vial. Seal the vial as mentioned in Section 5.2.4.

5.2.6. Request bromine analysis on the OSHA 91A form.

5.2.7. Ship the samples to the laboratory using appropriate packing materials to prevent breakage. The identities of any substances known or suspected to be present in the sampled air should be transmitted with the sample.

6. Analysis

6.1. Precautions

6.1.1. Refer to instrument and Standard Operating Procedure (8.7) manuals for proper operation.

6.1.2. Observe laboratory safety regulations and practices.

6.1.3. Sulfuric acid (H_2SO_4) can cause severe burns. Wear protective eyewear, gloves, and labcoat when using concentrated H_2SO_4.

6.2. Equipment

6.2.1. Ion chromatograph (model no. 2010i or 4500, Dionex, Sunnyvale, CA) equipped with a conductivity detector.

6.2.2. Automatic sampler (model no. AS-1, Dionex) and 0.5 mL sample vials.

6.2.3. Laboratory automation system: Ion chromatograph interfaced to a data reduction and control system (AutoIon 450, Dionex).

6.2.4. Micromembrane suppressor (model no. AMMS-1, Dionex).

6.2.5. Anion separator column (model no. HPIC-AS4A, Dionex) with pre-column (model no. HPIC-AG4A, Dionex). An alternative separator column to use when unresolvable interferences occur is model no. HPIC-AS5 (Dionex).

6.2.6. Disposable syringes (1 mL).

6.2.7. Syringe pre-filters, 0.5-µm pore size (part no. SLSR 025 NS Millipore Corp., Bedford, MA).

(Note: Some syringe pre-filters are not cation- or anion-free. Tests should be done with blank solutions first to determine suitability for the analyte being determined).

6.2.8. Miscellaneous volumetric glassware: micropipettes, volumetric flasks, graduated cylinders, and beakers.

6.2.9. Analytical balance (0.01 mg).

6.3. Reagents - All chemicals should be at least reagent grade.

6.3.1. Deionized water (DI H_2O) with a specific conductance of less than 10 µS.

6.3.2. Sodium carbonate.

6.3.3. Sodium bicarbonate.

6.3.4. Sodium hydroxide (for alternate eluent).

6.3.5. Eluent [0.0015 M sodium carbonate (Na_2CO_3) / 0.0015 M sodium bicarbonate ($NaHCO_3$)]: Dissolve 0.636 g Na_2CO_3 and 0.504 g $NaHCO_3$ in 4.0 L of DI H_2O.

6.3.6. alternate eluent: An alternate eluent is used if interferences are unresolvable. For a gradient pump, use a mixture of: 97% DI H_2O / 3% of 0.1 M NaOH. If a gradient pump is not available, this is equivalent to 0.003 M NaOH.

6.3.7. Collection solution (0.003 M $NaHCO_3$ / 0.0024 M Na_2CO_3): See Section 5.1.1 for instructions.

6.3.8. Sulfuric acid (H_2SO_4), concentrated (98%).

6.3.9. Regeneration solution (0.02 N H_2SO_4): Carefully add 1.14 mL concentrated H_2SO_4 into a 2-L volumetric flask which contains about 500 mL DI H_2O. Dilute to volume with DI H_2O.

6.3.10. Standard stock solution, Br^- (1,000 µg/mL as bromide): Dissolve and dilute 1.4893 g potassium bromide (KBr) to 1 L with DI H_2O.

6.3.11. Standard stock solution, BrO_3^- (1,000 µg/mL as bromate): Dissolve and dilute 1.3057 g of potassium bromate ($KBrO_3$) to 1 L with DI H_2O.

6.4. Standard Preparation

Standards (10 and 1 µg/mL as Br$^-$ or BrO$_3^-$): Make appropriate serial dilutions of Br$^-$ and BrO$_3^-$ stock solutions with the collection solution. Take aliquots of these standards and prepare the working standards in the range of 0.1 to 5 µg/mL using the collection solution as the diluent.

6.5. Sample Preparation

6.5.1. Measure and record the total volume of each sample with a graduated cylinder.

6.5.2. If the sample solutions contain suspended particulate, remove the particles using a pre-filter and syringe.

6.6. Analytical Preparation

6.6.1. Fill the 0.5-mL automatic sampler vials with sample, working standard, or blank solutions and push a filtercap into each vial. Label the vials.

6.6.2. Load the automatic sampler with labeled samples, standards and blanks.

6.7. Analytical Procedure

Set up the ion chromatograph and analyze the samples and standards in accordance with the Standard Operating Procedure (8.7). Typical operating conditions for a Dionex 2010i with a data reduction system are listed below.

Standard Conditions:

Ion chromatograph

Eluent:	0.0015 M Na$_2$CO$_3$ / 0.0015 M NaHCO$_3$
Separator column:	AS4A
Column temperature:	ambient
Regenerant flow:	1 to 3 mL/min

Pump

Pump pressure:	approximately 1,000 psi
Flow rate:	2 mL/min

Chromatogram

Run time:	6 min
Sample injection loop:	50 µL
Average retention time:	
Br$^-$	approximately 2.5 min
BrO$_3^-$	approximately 1.5 min

Alternate conditions are available if interference from other anions pose insufficient resolution. Operating conditions with a model 4500 gradient pump system (Dionex) are:

Alternate Conditions:

<u>Ion chromatograph</u>

Eluent:	97% DI H_2O / 3% 0.1 M NaOH
Separator column:	AS5
Column temperature:	ambient
Regenerant flow:	1 to 3 mL/min

<u>Pump</u>

Pump pressure:	approximately 800-1,000 psi
Flow rate:	1 mL/min

<u>Chromatogram</u>

Run time:	14 min
Sample injection loop:	50 µL
Average retention time:	
Br^-	approximately 10.9 min
BrO_3^-	approximately 4.3 min

The alternate conditions should be used when nitrate, chloride, or other anions interfere and make positive identification of bromide and bromate peaks difficult.

7. Calculations

   7.1. Hard copies of chromatograms containing peak area and height data can be obtained from a printer. A typical chromatogram of Br^- and BrO_3^- is shown in Figure 1 and one with interference from chloride on the bromate peak is shown in Figure 2. A chromatogram of 10 µg/mL standards of BrO_3^-, ClO_2^-, and Br^- using suggested alternate conditions (Section 6.7) is shown in Figure 3.

   7.2. Prepare a concentration-response curve by plotting the concentration of the standards in µg/mL (or µg/sample if the same volumes are used for samples and standards) versus peak areas or peak heights. Assuming a constant sample injection volume was used for all samples and standards, calculate sample concentrations (total µg) from the curve. Blank correct all samples as shown:

$$ugC\ Analyte = (S)(SV) - (BL)(BLV)$$

where:

$ugC\ Analyte$ = Corrected amount (µg) in the sample solution.

S = µg/mL sample (from curve)

$$SV \quad = \quad \text{Sample solution volume, mL (from Section 6.5.1)}$$

$$BL \quad = \quad \text{µg/mL blank (from curve)}$$

$$BLV \quad = \quad \text{Blank solution volume, mL (from Section 6.5.1)}$$

7.3. The concentration of Br_2 in each air sample is expressed in ppm and is calculated as:

$$ppm\ Br_2 = \frac{ugC\ Analyte\ \times MV \times conversion}{formula\ weight\ \times air\ volume}$$

where:

MV (Molar Volume)	=	24.45 (25 °C and 760 mmHg)
µgC Analyte	=	blank corrected sample result
conversion (Br^- to Br_2)	=	1.2
conversion (BrO_3^- to Br_2)	=	3.75
formula weight (Br_2)	=	159.8
air volume	=	Air sample taken (in L)

This equation reduces to:

$$ppm\ Br_2 = \frac{0.184 \times ugC\ Br^-}{air\ volume} \quad \text{(for } Br^- \text{ as analyte)}$$

or:

$$ppm\ Br_2 = \frac{0.574 \times ugC\ BrO_3^-}{air\ volume} \quad \text{(confirmation } BrO_3^-\text{)}$$

7.4. Reporting Results

Results are reported to the industrial hygienist as ppm bromine. The numerical result is determined from the bromide analysis.

8. References

8.1. **Occupational Safety and Health Administration Technical Center:** *Bromine Backup Data Report (ID-108)* by J. Ku. Salt Lake City, UT. Revised 1990.

8.2. **Blaedel, W.J. and V.W. Meloche:** *Elemental Quantitative Analysis -- Theory and Practice*. 2nd ed. New York: Harper and Row, Publishers, 1963. p. 854.

8.3. **Orion Research Incorporated:** *Instruction Manual, Halide Electrodes, Model 94-35, Model 94-53*. Cambridge, MA: Orion Research Incorporated, 1982.

8.4. **Cotton, F.A. and G. Wilkinson:** *Advanced Inorganic Chemistry -- A Comprehensive Text*. 2nd rev. ed. New York: Interscience Publishers, 1966. pp. 569-570.

8.5. **Hawley, G.G.:** *The Condensed Chemical Dictionary*. 11th ed. New York: Van Nostrand Reinhold Co., 1987.

8.6. **National Oceanic and Atmospheric Administration (NOAA):** *CAMEO* [Computer Software]. NOAA, 1988.

8.7. **Occupational Safety and Health Administration Technical Center:** *Ion Chromatography Standard Operating Procedure*. Salt Lake City, UT. In progress (unpublished).

Chromatogram of Br^- and BrO_3^- (AS4A Column)

PEAK NUM	RET TIME	PEAK NAME	AREA	height
1	1.42	BROMATE	3.675e+004	5264
2	2.48	BROMIDE	5.881e+004	5212
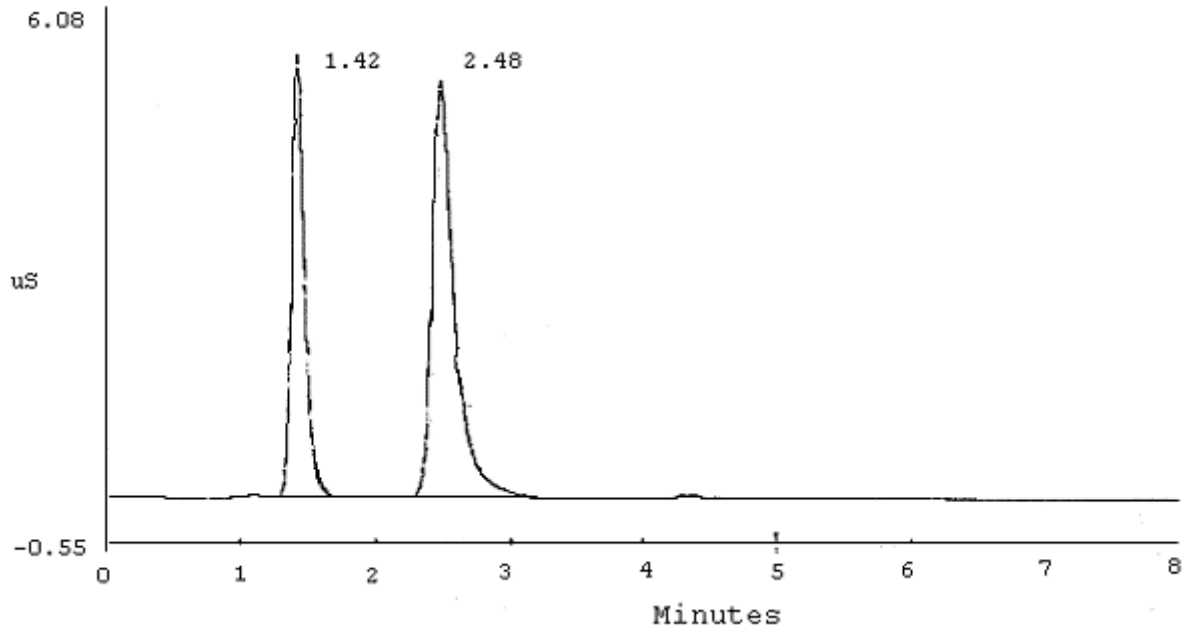
Figure 1.

Chromatogram - Mixture of BrO_3^-, Cl^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-} (AS4A Column).

PEAK NUM	RET TIME	PEAK NAME	AREA	HEIGHT
1	1.00		5.088e+003	572
2	1.52	CHLORIDE	7.232e+004	10323
3	2.48	BROMIDE	1.256e+004	1485
4	2.83	NITRATE	1.801e+004	1680
5	3.57	PHOSPHATE	3.381e+004	2864
6	4.33	SULFATE	1.132e+005	7023
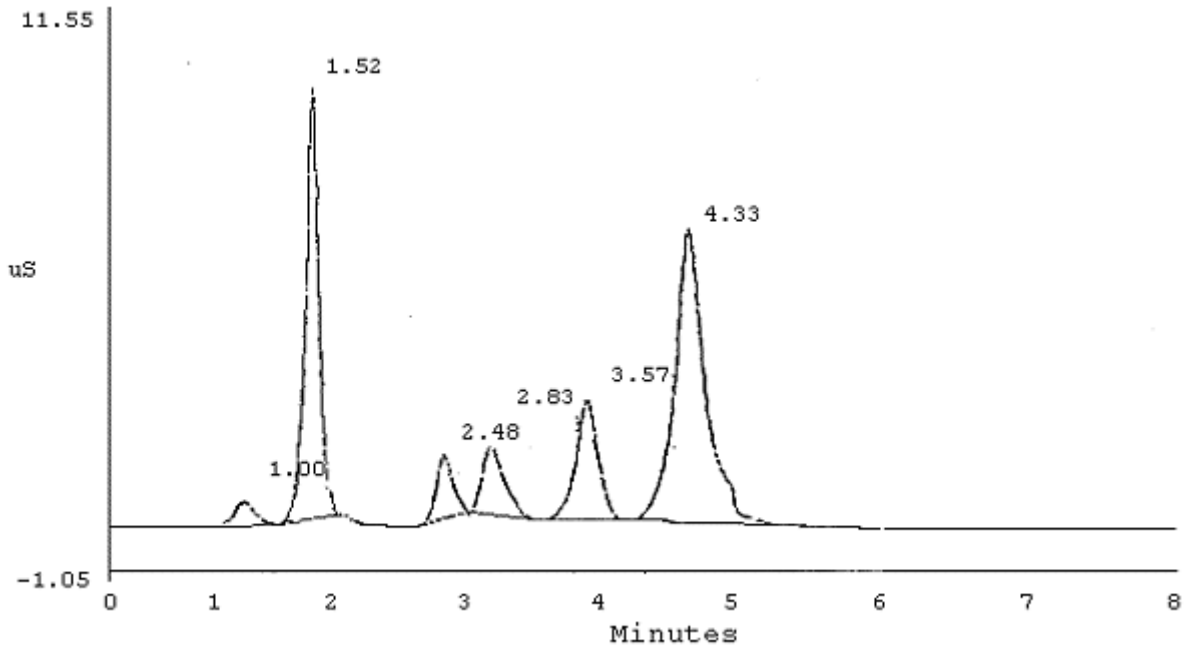
Figure 2.

Chromatogram of Mixture of Chlorite, Bromate, Chloride, and Bromide
(AS5 separator column, gradient pump, and 97% DI H_2O / 3% 0.1 M NaOH eluent).

PEAK NUM	RET TIME	PEAK NAME	AREA	HEIGHT
1	0.45		4.794e+005	21724
2	1.68		1.181e+007	559853
3	2.37		1.283e+007	1040749
4	2.72		8.283e+005	100649
5	3.15	CHLORITE	5.348e+007	6711421
6	4.25	BROMATE	6.865e+007	6814401
7	4.80	CHLORIDE	2.031e+008	18500982
8	5.80		6.541e+005	52785
9	7.35		2.443e+006	35239
10	9.17	BROMIDE	5.396e+005	14843
11	10.88		2.231e+008	5722599
12	13.13		3.520e+006	40073
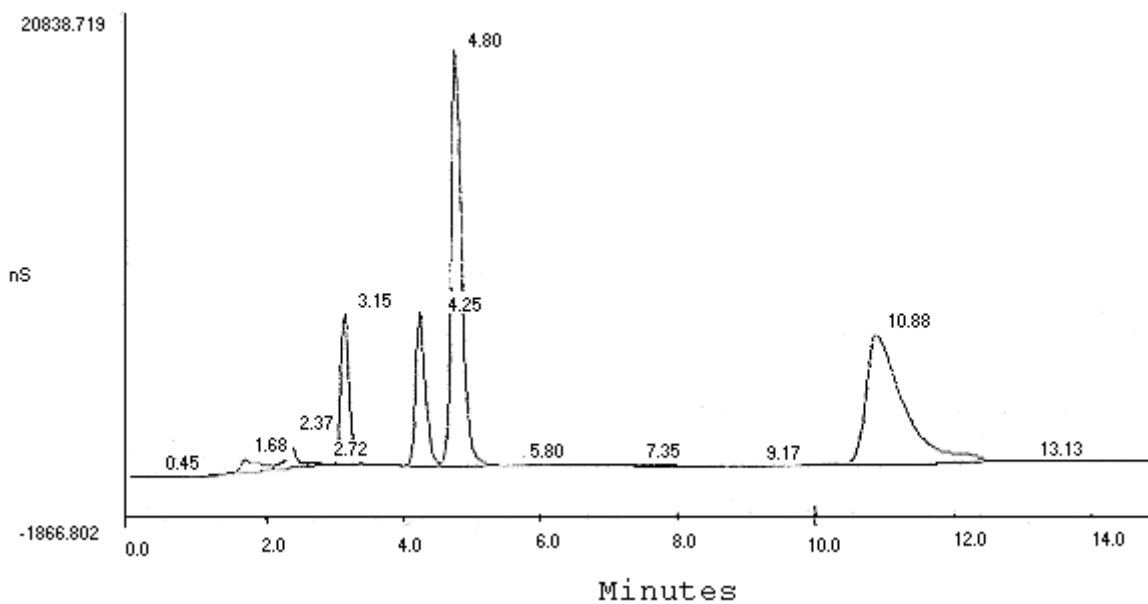
Figure 3

Backup Report

Introduction

The general procedure for collection and analysis of bromine (Br_2) air samples is described in OSHA method no. ID-108 (10.1). Briefly, Br_2 is collected in a midget fritted glass bubbler (MFGB) containing a buffer (0.0030 M $NaHCO_3$ / 0.0024 M Na_2CO_3) collection solution. In this basic solution, Br_2 disproportionates to produce bromide (Br^-) and bromate (BrO_3^-) (10.2) which can be determined by ion chromatography (IC). This method has been evaluated using 30-L, 60-min samples. The concentrations tested were near the OSHA Time Weighted Average (TWA) Permissible Exposure Limit (PEL) of 0.1 ppm.

1. Experimental Protocol

   The evaluation consisted of the following experiments or discussions:

    1. Analysis of a total of 18 spiked samples.

    2. Analysis of a set of 18 samples which were taken from dynamically generated test atmospheres.

    3. Determination of the collection efficiency and the breakthrough when using MFGB.

    4. Storage stability tests for six samples collected at the PEL.

    5. Determination of the detection limit of the method.

    6. Comparison of methods.

    7. Assessment of the precision and accuracy of the method.

    8. Conclusions - including a discussion of changes in the PEL since this evaluation was performed.

2. Analysis

    Samples (six samples at each of three test levels) were prepared by spiking appropriate amounts of standardized Br_2 into collection solutions. The spiked samples were prepared and analyzed to determine analytical precision and accuracy.

    Procedure: Samples were prepared by adding known amounts of a standardized stock Br_2 solution to 10 mL of collection solution. The spikes consisted of 17.8, 35.5, and 71.1 μg of Br_2, which corresponded to about 0.5, 1, and 2 times the PEL if sampling at 0.5 L/min for 60 min.

    2.1. Standardization of Br_2 stock solution:

        A Br_2 stock solution was prepared from a Br_2 permeation tube by bubbling the Br_2 vapor through a collection solution for a given period of time. This stock solution was then analyzed by IC. The concentration of the stock solution was 35.57 μg/mL as Br_2 (29.64 μg/mL as Br^-).

    2.2. Three sets of spiked samples were prepared by adding 0.5, 1.0, and 2.0 mL, respectively, of the Br_2 stock solution into 10-mL volumetric flasks and diluted to volume with collection solution. Each set consisted of 6 samples.

    2.3. The analytical procedure described in OSHA method no. ID-108 (10.1) was followed.

    Results: The results of the analytical experiment are presented in Table 1. The overall analytical recovery was 98.3% which does not indicate a need for an analytical correction factor.

3. Sampling and Analysis

Procedure: A standard generator [Model 350, Analytical Instrument Development Inc. (AID), Avondale, PA] containing Br_2 permeation tubes (from AID) was used as the source for generating dynamic test atmospheres of Br_2. A sampling manifold, constructed from glass and Teflon, was attached to the generator. Samples (6 samples at each of the three test levels) were collected from the manifold using concentrations of 0.5, 1, and 2 times the OSHA TWA PEL (0.1 ppm).

3.1. The permeation rate of the Br_2 permeation tubes was determined by measuring their respective weight loss at a constant temperature of 30 °C ± 0.1 °C over a given period of time. The permeation rates are shown in Table 2. Two different sizes of permeation tubes were used.

3.2. The flow rates of the diluent air and saturated gas stream of bromine from the generator were measured with a soap bubble flow meter to determine the concentration of the generated gas.

3.3. Three sets of six samples were collected individually at about 0.05, 0.1, and 0.2 ppm Br_2. Samples were collected using personal sampling pumps at a sample flow rate of about 0.5 L/min for 60 min.

Results: The results of sampling and analysis are shown in Table 3. Known (Taken) concentrations listed were calculated from the permeation tube weight loss and flows of Br_2 gas and diluent air.

4. Collection Efficiency (CE) and Breakthrough

Procedure - CE: Two MFGBs containing 10 mL of collection solution were connected in series. Six of these series samples were collected at a concentration of 0.2 ppm for 60 min at 0.5 L/min. The amount of Br_2 vapor collected in each MFGB was then measured.

Results: The CE of the first MFGB was calculated by dividing the amount of Br_2 collected in the first MFGB by the total amount of Br_2 collected in the first and second MFGB. The results are reported in Table 4. The CE was 100%.

Procedure - Breakthrough: Two MFGBs in series, as mentioned above, were prepared. Three of these series samples were taken at 0.2 ppm. A flow rate of 0.5 L/min and sampling times of 60, 120, and 240 min were used.

Results: Breakthrough was calculated by dividing the amount of Br_2 collected in the second MFGB by the total amount of Br_2 collected in the first and second MFGBs. The results are given in Table 5. The breakthrough was 2.4% after 240 min.

5. Storage Stability

A study was conducted to assess the storage stability of collected Br_2 in the collection solution.

Procedure: Six samples were generated as described in Section 3. The samples were transferred into 10-mL volumetric flasks. These flasks were then tightly closed and stored on top of a lab bench at normal laboratory temperatures. The samples were analyzed after 1, 5, 15, and 30 day storage periods.

Results: The results of the storage stability study are shown in Table 6. These results indicate that samples may be stored under normal laboratory conditions for a period of at least 30 days.

6. Detection Limit

Procedure: Samples containing small amounts of Br^- were prepared in the collection solution and then analyzed by IC. The Rank Sum Test was used for the determination of the qualitative detection limit.

The test is a non-parametric or a distribution-free test. The quantitative limit was determined by examining the variation (CVs) in results of these samples.

Results: The results of the Rank Sum Test are shown in Table 7. As shown, the qualitative detection limit as Br_2 is 0.02 µg/mL (99% confidence level). The quantitative limit is 0.09 µg/mL as Br_2, or 0.9 µg in a 10 mL sample volume. This corresponds to 0.005 ppm Br_2 for a 30-L air volume. The CV at this level was about 0.11.

7. Analytical Method Comparison

The previous ion specific electrode (ISE) procedure (10.3) used by OSHA was chosen as the reference analytical method to which the results of the IC method were compared.

   7.1. Analytical procedure for ISE (10.3)

       7.1.1. A low level ionic strength adjuster (ISA) was prepared by diluting 20 mL ISA (5 M sodium nitrate) to 100 mL with deionized water.

       7.1.2. Three sets of spiked samples were prepared by adding 5, 10, and 20 mL, respectively, of Br_2 stock solution, 1 mL of ISA, and 50 µL of concentrated nitric acid into 100-mL volumetric flasks and then diluting to volume with collection solution. These samples corresponded to 1.78, 3.56, and 7.11 µg/mL Br^- and were compared to those samples prepared in Section 2.2.

       7.1.3. Two different concentrations of Br^- standards were prepared from potassium bromide to check the slope (-58.0 mV) of the ISE.

       7.1.4. Samples were analyzed using an Orion model 94-35A specific ion electrode and an Orion Model 901 millivolt meter.

   7.2. **Results:** The comparison data of the ISE reference and IC methods are shown in Table 8.

   7.3. **Discussion:** In basic solution, Br_2 disproportionates to produce Br^- and BrO_3^- according to the following equation (10.2):

$$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O \text{ (basic solution)}$$

   The mole ratio of Br_2 per Br^- is 1.2. As the pH is lowered, Br^- and BrO_3^- may react with each other to gradually convert back to Br_2 according to the following equation (10.4):

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O \text{ (acidic solution)}$$

   Results of Br_2 concentration obtained from the ISE were much lower than that from the IC, which was likely due to the change in pH after nitric acid is added. Therefore, results obtained from IC analysis are more accurate and reliable than ISE results.

8. Precision and Accuracy

The data, based on the NIOSH statistical protocol (10.5), are presented in Tables 1 and 3. The pooled coefficients of variation for spiked (CV_1 [pooled]) and generated (CV_2 [pooled]) samples and the overall CV_T (pooled) are:

  CV_1 (pooled) = 0.040, CV_2 (pooled) = 0.065, CV_T (pooled) = 0.067

The bias was -0.056 and overall error was ±19%. Overall error was calculated as:

$OE_i = \pm [|\text{mean bias}_i| + 2CV_i] \times 100\%$ where i is the respective sample pool being examined.

9. Conclusions

The analytical, sampling and analytical, collection efficiency, breakthrough, storage stability, and detection limit experiments displayed acceptable data. A negative bias was noted for the sampling and analysis experiment conducted at two times the TWA PEL; however, the collection efficiency experiment at this concentration indicated no Br_2 was passing into the next bubbler.

The MFGB sampling and IC analytical method for Br_2 has shown to be an acceptable alternative to determining compliance with the OSHA PEL of 0.1 ppm (TWA). The ability of the method to determine compliance to the STEL of 0.3 ppm Br_2 is dependent on the detection limit and potential breakthrough at this concentration. A detection limit of 0.9 µg or 0.018 ppm Br_2 (15-min sample, 7.5-L total air volume) is more than adequate for STEL measurements. Breakthrough was not evident at 60 to 120 min and was only 2.4% at a 240-min sampling time (0.2 ppm concentration). Breakthrough is not expected to occur at 0.3 ppm for a 15-min sampling time. Therefore, it is recommended to sample for TWA or STEL samples at 0.5 L/min as demonstrated in this method.

10. References

10.1. Occupational Safety and Health Administration Technical Center: Bromine in Workplace Atmospheres by J. Ku (USDOL/OSHA-SLTC Method No. ID-108). Salt Lake City, UT. Revised 1990.

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10.3. Orion Research Incorporated: Instruction Manual, Halide Electrodes, Model 94-35. Cambridge, MA: Orion Research Incorporated, 1982.

10.4. Blaedel, W.J. and V.W. Meloche: Elemental Quantitative Analysis -- Theory and Practice. 2nd ed. New York: Harper and Row, Publishers, 1963. p. 854.

10.5. National Institute for Occupational Safety and Health: Documentation of the NIOSH Validation Tests by D. Taylor, R. Kupel and J. Bryant (DHEW/NIOSH Pub. No. 77-185). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977.

Table 1
Analysis - Bromine

-------- 0.5 x PEL[*] --------			--------- 1 x PEL[*] ---------			--------- 2 x PEL[*] ---------		
μg[**]Taken	μg Found	AMR	μg[**]Taken	μg Found	AMR	μg[**]Taken	μg Found	AMR
17.8	18.9	1.062	35.5	34.2	0.963	71.1	73.4	1.032
17.8	19.3	1.084	35.5	33.6	0.946	71.1	72.5	1.020
17.8	17.2	0.966	35.5	33.0	0.930	71.1	72.5	1.020
17.8	17.0	0.955	35.5	33.8	0.952	71.1	69.8	0.982
17.8	16.6	0.933	35.5	34.5	0.972	71.1	69.8	0.982
17.8	17.0	0.955	35.5	33.8	0.952	71.1	69.6	0.979
N		6			6			6
Mean		0.993			0.953			1.003
Std Dev		0.064			0.014			0.024
CV_1		0.064			0.015			0.024

CV_1 (pooled) = 0.040
[*]TWA PEL of 0.1 ppm
[**]μg Found and Taken are reported as Br_2
AMR = Analytical Method Recovery = μg Found/μg Taken

Table 2
Permeation Rates for Bromine Tubes at 30 °C

Tube Size	Time Elapsed (min)	Weight Loss (μg)	Permeation Rate (μg/min)
Large	20,080	36,080	1.797
Large	13,260	24,150	1.821
Large	44,643	79,940	1.793
Small	44,644	38,980	0.873

The average large-size tube permeation rate for Br_2 was 1.803 μg/min.
The small-size tube permeation rate for Br_2 was 0.873 μg/min.

Table 3
Sampling and Analysis - Bromine

| Test Level | ------------------------ Found ---------------------- | | | | Taken | |
	µg	L Air	mg/m³	ppm	ppm	Recovery (%)
0.5 x PEL	6.2	20.6	0.301	0.046	0.052	88.5
	11.9	41.8	0.285	0.044	0.052	84.6
	15.5	42.4	0.366	0.056	0.052	107.7
	13.1	36.4	0.360	0.055	0.052	105.8
	12.5	37.7	0.332	0.051	0.052	98.1
	11.5	35.8	0.321	0.049	0.052	94.2
			N	6		
			Mean	0.050		96.5
			Std Dev	0.005		
			CV$_2$	0.100		
1 X PEL	18.5	27.9	0.663	0.101	0.107	94.4
	18.9	27.2	0.695	0.106	0.107	99.1
	21.7	30.4	0.714	0.109	0.107	101.9
	22.2	28.6	0.776	0.119	0.107	111.2
	20.8	28.6	0.727	0.111	0.107	103.7
	20.8	29.5	0.705	0.108	0.107	100.9
			N	6		
			Mean	0.109		101.6
			Std Dev	0.006		
			CV$_2$	0.055		
2 x PEL	51.1	45.8	1.116	0.171	0.205	83.4
	51.1	46.2	1.106	0.169	0.205	82.4
	51.1	45.5	1.173	0.179	0.205	87.3
	51.1	46.2	1.106	0.169	0.205	82.4
	53.4	46.2	1.156	0.177	0.205	86.3
	50.2	43.4	1.157	0.177	0.205	86.3

N		6	
Mean		0.172	84.7
Std Dev		0.004	
CV_2		0.023	

Results are reported as Br_2

CV_2 (pooled)	=	0.065	CV_T (pooled)	= 0.067
Bias	=	-0.056		
Overall Error	=	±19%		

Table 4
Collection Efficiency - Bromine

Sample No.	ppm found 1st Bubbler	ppm found 2nd bubbler	Collection Efficiency (%)
1	0.171	ND	100.0
2	0.169	ND	100.0
3	0.172	ND	100.0
4	0.169	ND	100.0
5	0.177	ND	100.0
6	0.175	ND	100.0
7	0.177	ND	100.0
		Meam	100.0%

ND = 0.02 µg/mL or 0.001 ppm (30 L air volume)

Table 5
Breakthrough - Bromine

Sampling Time, min	µg found 1st bubbler	µg found 2nd bubbler	% Breakthrough
60	39.4	ND	0
120	76.2	ND	0
240	140	3.3	2.4

ND = 0.02 µg/mL

Table 6
Stability Test - Bromine

| Sample No. | ---------------------- Found --------------------- | | | | Taken | |
	µg	L Air	mg/m^3	ppm	ppm	% Recovery
1 Day						
1	18.500	27.900	0.663	0.101	0.107	94.4
2	18.900	27.200	0.695	0.106	0.107	99.1
3	21.700	30.400	0.714	0.109	0.107	101.9
4	22.200	28.600	0.776	0.119	0.107	111.2
5	20.800	28.600	0.727	0.111	0.107	103.7
6	20.800	29.500	0.705	0.108	0.107	100.9
			N	6		
			Mean	0.109		101.9
			Std Dev	0.006		
			CV	0.055		
5 Days						
1	18.800	27.900	0.674	0.103	0.107	96.3
2	19.300	27.200	0.710	0.109	0.107	101.9
3	21.600	30.400	0.711	0.109	0.107	101.9
4	22.100	28.600	0.773	0.118	0.107	110.3
5	22.100	28.600	0.77	0.118	0.107	110.3
6	21.600	29.500	0.732	0.112	0.107	104.7
			N	6		
			Mean	0.112		104.2
			Std Dev	0.006		
			CV	0.054		

15 Days

1	18.100	27.900	0.649	0.099	0.107	92.5
2	18.500	27.200	0.680	0.104	0.107	97.2
3	20.500	30.400	0.674	0.103	0.107	96.3
4	22.100	28.600	0.773	0.118	0.107	110.3
5	20.900	28.600	0.731	0.112	0.107	104.7
6	21.300	29.500	0.722	0.110	0.107	102.9
			N	6		
			Mean	0.108		100.7
			Std Dev	0.007		
			CV	0.065		

30 Days

1	15.300	27.900	0.548	0.084	0.107	78.5
2	15,700	27.200	0.577	0.088	0.107	82.2
3	17.400	30.400	0.572	0.088	0.107	82.2
4	19.800	28.600	0.692	0.106	0.107	99.1
5	19.100	28.600	0.668	0.102	0.107	95.3
6	19.900	29.500	0.675	0.103	0.107	96.3
			N	6		
			Mean	0.095		88.9
			Std Dev	0.010		
			CV	0.105		

All results are reported as Br_2

Table 7
Bromine Detection Limit - Rank Sum Test
($N_{standard} = N_{blank} = 6$)

Rank	0.02 µg/mL[*]
1	RB1
2	RB1
3	RB1
4	RB1
5	RB1
6	RB1
7	33552 Std
8	39064 Std
9	41328 Std
10	49403 Std
11	52619 Std
12	84583 Std

[*] Measured by peak areas

RB1 = Reagent Blank

Std = Standard, 0.02 µg/mL (as Br_2)

Standards having a concentration of 0.01 µg/mL (as Br_2) gave no response.

Table 8
Comparison of Analytical Methods for Bromine
- Ion Specific Electrode vs. Ion Chromatography -

µg taken	Ion Specific Electrode		Ion Chromatography	
	µg found	AMR	µg found	AMR
0.5 x PEL*				
17.8	16.4	0.921	18.9	1.062
17.8	16.6	0.933	19.3	1.084
17.8	16.4	0.921	17.2	0.966
17.8	16.9	0.949	17.0	0.955
17.8	16.8	0.944	16.6	0.933
17.8	17.4	0.978	17.0	0.955
	N	6		6
	Mean	0.941		0.993
	Std Dev	0.021		0.064
	CV	0.023		0.064
1 x PEL*				
35.5	32.0	0.901	34.2	0.963
35.5	31.8	0.896	33.6	0.946
35.5	31.9	0.899	33.0	0.930
35.5	29.5	0.831	33.8	0.952
35.5	28.4	0.800	34.5	0.972
35.5	30.0	0.845	33.8	0.952
	N	6		6
	Mean	0.862		0.953
	Std Dev	0.043		0.014
	CV	0.050		0.015
2 x PEL*				
71.1	58.3	0.820	73.4	1.032
71.1	57.8	0.813	72.5	1.020
71.1	57.8	0.813	72.5	1.020
71.1	57.7	0.812	69.8	0.982
71.1	57.6	0.810	69.8	0.982
71.1	57.7	0.812	69.6	0.979

N	6	6
Mean	0.813	1.003
Std Dev	0.003	0.024
CV	0.004	0.024

All results are reported as Br_2
AMR = Analytical Method Recovery = µg taken/µg found
* TWA PEL of 0.1 ppm