



EMDC 2 (2816) CD2

ICS: 13.040.30

DRAFT TANZANIA STANDARD

Determination of bromine in workplace atmospheres

For stakeholders comments

Determination of bromine in workplace atmospheres

0 Foreword

At ambient temperature, bromine is a brownish-red liquid. It has a similarly colored vapour with an offensive and suffocating odor. It is a non-metallic element that is liquid under ordinary conditions; it evaporates easily in a red vapor at standard temperature and pressures. It has a red vapour with disagreeable odor resembling that of chlorine. Bromine is less active chemically than chlorine and fluorine but it is more active than iodine; its compounds are similar to those of the other halogens. Bromine is soluble in organic solvents and in water.

Bromine is used in the following operations (5.5).

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

Bromine is a naturally occurring element that can be found in many inorganic substances. Humans however, have many years ago started the introduction of organic bromines in the environment. These are all compounds that are not natural and can cause serious harm to human health and the environment.

Bromine is corrosive to human tissue in a liquid state and its vapors irritate eyes and throat. Bromine vapors are very toxic with inhalation. The most important health effects that can be caused by bromine-containing organic contaminants are malfunctioning of the nervous system and disturbances in genetic materials.

In the preparation of this Tanzania Standard, assistance was derived from:

Occupational Safety and Health Authority (OSHA) analytical method ID-108

1 Scope

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). The qualitative detection limit of the analytical method is $0.003 \mu\text{g}$ of Br^- per $200 \mu\text{L}$ sample injection or $0.17 \mu\text{g}$ Br^- in a 10-mL sample volume. The quantitative limit is $0.015 \mu\text{g}$ Br^- per $200 \mu\text{L}$ injection or $0.75 \mu\text{g}$ Br^- in a 10-mL sample volume. The working range is 0.015 ppm to 0.31 ppm (30 L air sample)

2. Normative references

There are no normative references in this document

3. Terms and definitions

No terms and definitions are listed in this document

4 Sampling

4.1 Equipment

4.1.1 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.

4.1.2 Personal sampling pumps capable of sampling within $\pm 5\%$ of the recommended flow rate of 0.5 L/min are used.

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

4.1.4 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.

4.1.5 A stopwatch and bubble tube or metre are used to calibrate pumps.

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

4.2 Sampling procedure

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

4.2.2 Place 10 mL 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.

4.2.3 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.

4.2.4 Transfer the collection solution into a 20-mL glass scintillation vial. Rinse the bubbler with 2 mL to 3 mL of unused collection solution and transfer the rinsings 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).

4.2.5 Prepare a blank solution by taking 10 mL to 15 mL of the unused collection solution and transfer to a 20-mL glass vial. Seal the vial as mentioned in clause 2.2.4.

4.2.6 Request bromine analysis on the OSHA 91A form.

4.2.7 Ship the samples to the laboratory using appropriate packaging 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.

5 Analysis

5.1 Precautions

5.1.1 Refer to instrument and standard operating procedure (5.7) manuals for proper operation.

5.1.2 Observe laboratory safety regulations and practices.

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

5.2 Equipment

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

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

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

5.2.4 Micromembrane suppressor (model no. AMMS-1, Dionex or equivalent).

5.2.5. 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).

5.2.6 Disposable syringes (1 mL).

5.2.7 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.

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

5.2.9 Analytical balance (0.01 mg).

5.3 Reagents

All chemicals should be at least reagent grade.

5.3.1 Deionized water (DI H_2O) with a specific conductance of less than 10 microsiemens.

5.3.2 Sodium carbonate.

5.3.3 Sodium bicarbonate.

5.3.4 Sodium hydroxide (for alternate eluent).

5.3.5 Eluent [0.0015 M sodium carbonate (Na₂CO₃) / 0.0015 M sodium bicarbonate (NaHCO₃)]:

Dissolve 0.636 g Na₂CO₃ and 0.504 g NaHCO₃ in 4.0 L of DI H₂O.

5.3.6 Alternate eluent: An alternate eluent is used if interferences are unresolvable. For a gradient pump, use a mixture of: 97 % DI H₂O / 3 % of 0.1 M NaOH. If a gradient pump is not available, this is equivalent to 0.003 M NaOH.

5.3.7. Collection solution (0.003 M NaHCO₃ / 0.0024 M Na₂CO₃): See clause 2.1.1 for instructions.

5.3.8. Sulfuric acid (H₂SO₄), concentrated (98 %).

5.3.9. Regeneration solution (0.02 N H₂SO₄): Carefully add 1.14 mL concentrated H₂SO₄ into a 2-L volumetric flask which contains about 500 mL DI H₂O. Dilute to volume with DI H₂O.

5.3.10. Standard stock solution, Br⁻ (1,000 µg/mL as bromide): Dissolve and dilute 1.4893 g potassium bromide (KBr) to 1 L with DI H₂O.

5.3.11. Standard stock solution, BrO₃⁻ (1,000 µg/mL as bromate): Dissolve and dilute 1.3057 g of potassium bromate (KBrO₃) to 1 L with DI H₂O.

5.4 Standard preparation

Standards (10 and 1 µg/mL as Br⁻ or BrO₃⁻): Make appropriate serial dilutions of Br⁻ and BrO₃⁻ stock solutions with the collection solution. Take aliquots of these standards and prepare the working standards in the range of 0.1 µg/mL to 5 µg/mL using the collection solution as the diluent.

5.5. Sample preparation

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

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

5.6 Analytical Preparation

5.6.1 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.

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

5.7 Analytical procedure

Set up the ion chromatograph and analyze the samples and standards in accordance with the standard operating procedure (5.7). 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 mL/min 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:

Alternat : Conditions	
Ion chromatograph	
Eluent:	97% DI H ₂ O / 3 % 0.1 M NaOH
Separator Column:	AS5
Column temperature:	ambient
Regenerant flow:	1 mL/min to 3 mL/min
Pump	
Pump pressure:	approximately 800 - 1,000 psi
Flow rate:	1 mL/min
Chromatogram	
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.

6 Calculations

6.1 Hard copies of chromatograms containing peak area and height data can be obtained from a printer. A typical chromatogram of Br⁻ and BrO₃⁻ 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 BrO₃⁻, ClO₂⁻, and Br⁻ using suggested alternate conditions (clause 3.7) is shown in figure 3.

6.2 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:

$$\mu\text{gCanalyte} = (S)(SV) - (BL)(BLV)$$

where:

µgCanalyte = Corrected amount (µg) in the sample solution.

S = µg/mL sample (from curve)

SV = Sample solution volume, mL (from clause 3.5.1)

BL = µg/mL blank (from curve)

BLV = Blank solution volume, mL (from clause 3.5.1)

6.3 The concentration of Br₂ in each air sample is expressed in ppm and is calculated as:

$$\text{ppm Br}_2 = \frac{MV \times \mu\text{gCanalyte} \times \text{conversion}}{\text{formula weight} \times \text{air volume}}$$

where:

MV (Molar Volume)	=	24.45 (25 °C and 760 mmHg)
µgCanalyte	=	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:

$$\text{ppm Br}_2 = \frac{0.184 \times \mu\text{gC Br}^-}{\text{air volume}} \text{ (for Br}^- \text{ as analyte)}$$

or:

$$\text{ppm Br}_2 = \frac{0.574 \mu\text{gC BrO}_3^-}{\text{air volume}} \text{ (confirmation using BrO}_3^- \text{)}$$

6.4 Reporting results

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

For stakeholders comments

Annex A
(informative)

A.1 Some physical properties of Br₂ are listed below:

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 ₂ O

For stakeholders comments

Annex B (normative)

B.1 Principle

Bromine is collected in a midjet-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; (6.4)



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 .

B.1.1 Advantages and disadvantages

B.1.1.1 This method has adequate sensitivity for measuring workplace atmosphere concentrations of Br_2 .

B.1.1.2 This method is less affected by interferences found in other methods (i.e. ion specific electrode, volhard titration, and colorimetric determinations).

B.1.1.3 The analytical method can be fully automated. Use of an automatic sampler can improve analytical precision.

B.1.1.4 The amount of Br_2 may be simultaneously confirmed from the bromate anion formed during disproportionation.

B.1.1.5 High humidity does not affect the sampling procedure.

B.1.1.6 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 laboratory.

B.2 Method Performance

Advances in ion chromatographic and sampling instruments should enable users to obtain similar or better results as those mentioned below.

B.2.1 The CV for the overall sampling and analytical method ($\text{CV}_T[\text{pooled}]$) in the range of 0.052 ppm to 0.205 ppm was 0.067.

B.2.2 In validation experiments, this method was capable of measurements within $\pm 25\%$ of the true value over the validation range (95 % confidence level). Bias was -0.056 and overall error was $\pm 19\%$.

B.2.3 Collection efficiency was 100 % for the buffer collection solution.

B.2.4 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).

B.2.5 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 %.

B.3 Interferences

B.3.1 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.

B.3.2 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 clause 3.7) 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.

B.3.3 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.

For stakeholders comments

Figures

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

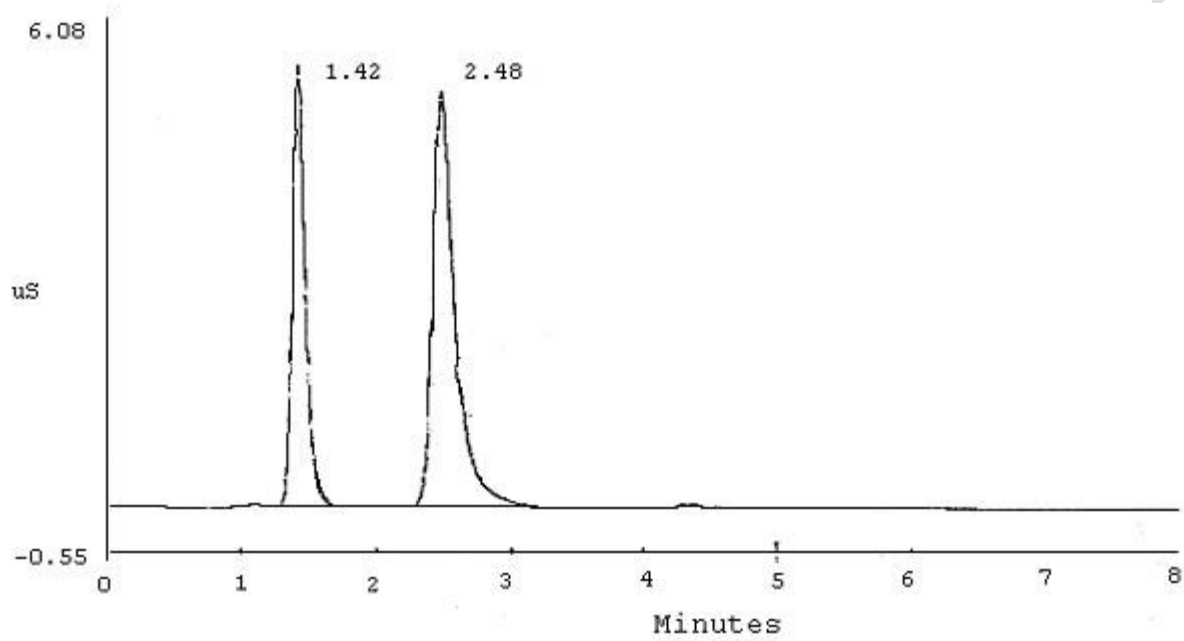


Figure 1

For stakeholder

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

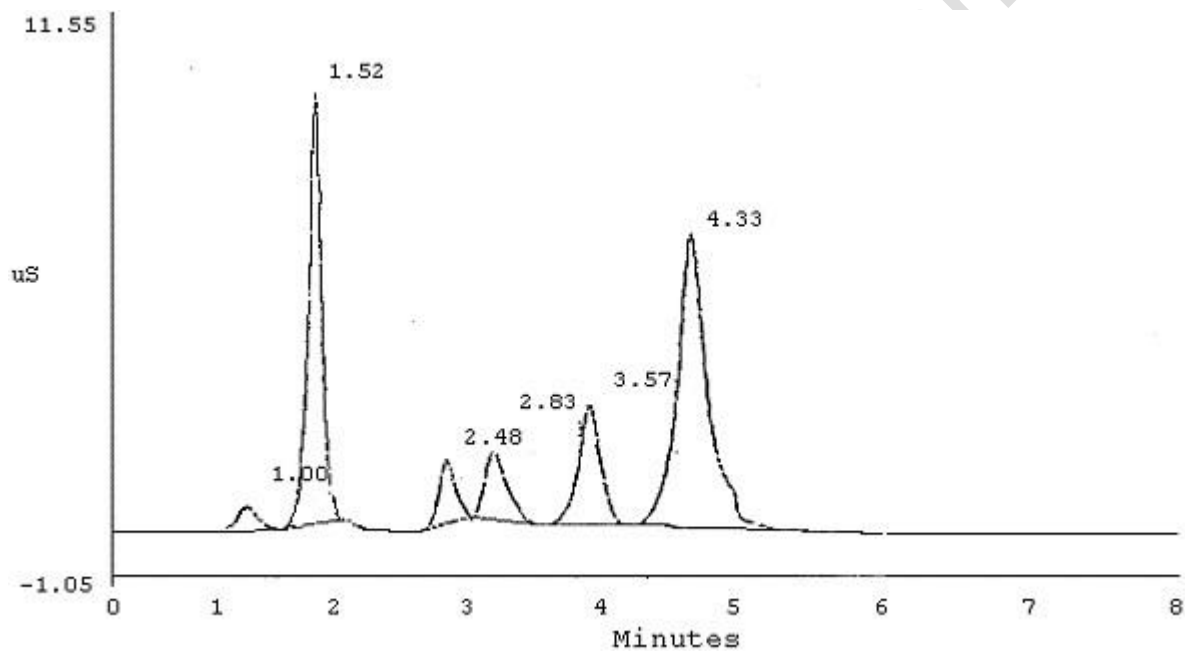


Figure 2

Chromatogram of mixture of chlorite, bromate, chloride, and bromine

(AS5 separator column, gradient pump, and 97 % DI H₂O / 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		5.348e+007	6711421
6	4.25	Chlorite	6.865e+007	6814401
7	4.80	Bromate	2.031e+008	18500982
8	5.80	Chloride	6.541e+005	52785
9	7.35		2.443e+006	35239
10	9.17		5.396e+005	14843
11	10.88		2.231e+008	5722599
12	13.13	Bromide	3.520e+006	40073

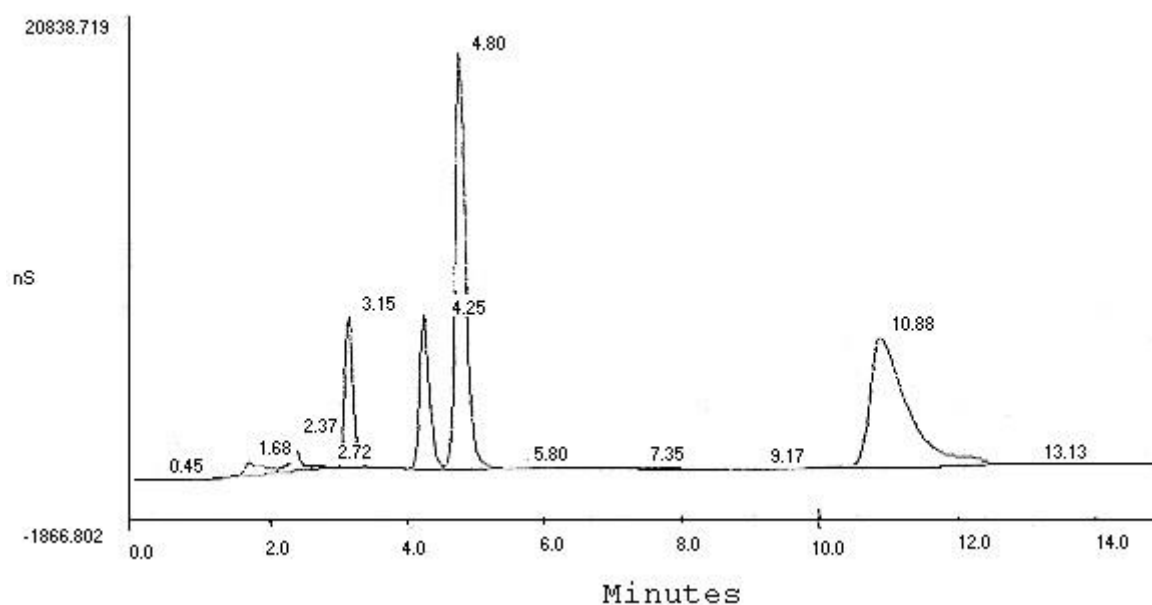


Figure 3

5 Bibliography

5.1 Occupational Safety and Health Administration Technical Center: Bromine Backup Data Report (ID108) by J. Ku. Salt Lake City, UT. Revised 1990.

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

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

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

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

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

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

For Stakeholders Comments

For Stakeholders comments