

METHOD #:	320.1	Approved for NPDES (Issued 1974)
TITLE:		Bromide (Titrimetric)
ANALYTE:		CAS # Br Bromide 7726-95-6
INSTRUMENTATION:		Titration
STORET No.		71870

1.0 Scope and Application

- 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial waste effluents.
- 1.2 The concentration range for this method is 2-20 mg bromide/L.

2.0 Summary of Method

- 2.1 After pretreatment to remove interferences, the sample is divided into two aliquots. One aliquot is analyzed for iodide by converting the iodide to iodate with bromine water and titrating iodometrically with phenylarsine oxide (PAO) or sodium thiosulfate. The other aliquot is analyzed for iodide plus bromide by converting these halides to iodate and bromate with calcium hypochlorite and titrating iodometrically with PAO or sodium thiosulfate. Bromide is then calculated by difference.

3.0 Sample Handling and Preservation

- 3.1 Store at 4°C and analyze as soon as possible.

4.0 Interferences

- 4.1 Iron, manganese and organic matter can interfere; however, the calcium boxide pretreatment removes or reduces these to insignificant concentrations
- 4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of oxidant and oxidant-quencher.

5.0 Reagents

- 5.1 Acetic Acid Solution (1:8): Mix 100 mL of glacial acetic acid with 800 mL of distilled water
- 5.2 Bromine Water: In a fume hood, add 0.2 mL bromine to 500 mL distilled water. Stir with a magnetic stirrer and a Teflon - coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered, colored bottle
- 5.3 Calcium Carbonate (CaCO_3): Powdered
- 5.4 Calcium Hypochlorite Solution (Ca(OCl)_2): Add 35 g of Ca(OCl)_2 to

- approximately 800 mL of distilled water in a 1 liter volumetric flask. Stir on a magnetic stirrer for approximately 30 minutes. Dilute to 1 liter and filter. Store in a glass-stoppered, colored flask
- 5.5 Calcium Oxide (CaO): Anhydrous, powdered
 - 5.6 Hydrochloric Acid Solution (1:4): Mix 100 mL of HCl (sp. gr. 1.19) with 400 mL of distilled water.
 - 5.7 Potassium Iodide (KI): Crystals, ACS Reagent Grade.
 - 5.8 Sodium Acetate Solution (275 g/L): Dissolve 275 g sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in distilled water. Dilute to 1 liter and filter
 - 5.9 Sodium Chloride (NaCl): Crystals, ACS Reagent Grade
 - 5.10 Sodium Formate Solution (500 g/L): Dissolve 50 g sodium formate (NaCHO_2) in hot distilled water and dilute to 100 mL
 - 5.11 Sodium Molybdate Solution (10 g/L): Dissolve 1 g sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in distilled water and dilute to 100 mL
 - 5.12 Sulfuric Acid Solution (1:4): Slowly add 200 mL H_2SO_4 (sp. gr. 1.84) to 800 mL of distilled water
 - 5.13 Phenylarsine Oxide (0.0375N): Hach Chemical Co., or equivalent. Standardize with 0.0375 N potassium biiodate (5.19, 5.23)
 - 5.14 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 mL of commercially available 0.0375 N phenylarsine oxide (5.13) to a 500 mL volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.
 - 5.15 Commercially available starch indicator such as thyodene or equivalent may be used
 - 5.16 Sodium Thiosulfate, Stock Solution, (0.75 N): Dissolve 186.14 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 mL chloroform.
 - 5.17 Sodium Thiosulfate Standard Titrant, (0.0375 N): Prepare by diluting 50.0 mL of stock solution (5.16) to 1.0 liter. Preserve by adding 5 mL of chloroform. Standardize with 0.0375 N potassium biiodate (5.19, 5.23)
 - 5.18 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 mL of sodium thiosulfate standard titrant (5.17) to a 500 mL volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily
 - 5.19 Potassium Biiodate Standard, (0.0375 N): Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 mL to 1.0 liter for 0.0375 N biiodate solution
 - 5.20 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 mL per liter of chloroform and storage in a 10°C refrigerator. Commercially available dry, powdered starch indicators may be used in place of starch solution
 - 5.21 Nitrogen Gas: Cylinder
 - 5.22 Potassium Fluoride ($\text{KF} \cdot 2\text{H}_2\text{O}$): ACS Reagent Grade
 - 5.23 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N Sodium Thiosulfate: Dissolve approximately 2 g (± 1.0 g) KI (5.7) in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.12) followed by 20 mL standard potassium biiodate solution (5.19). Place in dark for 5 minutes, dilute to 300 mL and titrate with the phenylarsine oxide (5.13) or sodium thiosulfate (5.17) to a pale straw color. Add a small scoop of indicator (5.15). Wait until

homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ± 0.05 mL.

6.0 Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.5) to 400 mL of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 mL.

6.2 Iodine Determination

6.2.1 Place 100 mL of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 mL beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.12)

6.2.2 Transfer the sample to a 250 mL widemouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask. A 250 mL iodine flask would increase accuracy and recision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.4.1)

6.2.3 Add 15 mL sodium acetate solution (5.8) and 5 mL acetic acid solution (5.1). Mix well. Add 40 mL bromine water solution (5.2); mix well. Wait 5 minutes

6.2.4 Add 2 mL sodium formate solution (5.10); mix well. Wait 5 minutes.

6.2.5 Purge space above sample with gentle stream of nitrogen (5.21) for approximately 30 seconds to remove bromine fumes

6.2.6 If a precipitate forms (iron), add 0.5 g $\text{KF} \cdot 2\text{H}_2\text{O}$ (5.22)

6.2.7 A distilled water blank must be run with each set of sample a because of iodide in reagents. If the blank is consistently shown to be zero for a particular "lot" of chemicals, it can be ignored.

6.2.8 Titrate as described in 6.4

6.3 Bromide Plus Iodide Determination

6.3.1 Place 100 mL of pretreated sample (6.1) or a fraction thereof diluted to that volume, in a 150 mL beaker. Add 5 g NaCl and stir to dissolve. Neutralize by dropwise addition of HCl solution (5.6) as in (6.2.1). Transfer as in (6.2.2)

6.3.2 Add 20 mL of calcium hypochlorite solution (5.4). Add 1 mL of HCl solution (5.6) and add approximately 0.2 g calcium carbonate (5.3).

6.3.3 Heat to boiling on a hot plate; maintain boiling for 8 minutes.

6.3.4 Remove from hot plate and carefully add 4 mL sodium formate solution (5.10).

Caution: TOO RAPID ADDITION MAY CAUSE FOAMING. Wash down sides with distilled water

6.3.5 Return to hot plate and maintain boiling conditions for an additional 8 minutes. Occasionally wash down sides with distilled water if residue is deposited from boiling action.

6.3.6 Remove from hot plate. Wash down sides and allow to cool

6.3.7 If a precipitate forms (iron), add 0.5 g $\text{KF} \cdot 2\text{H}_2\text{O}$ (5.22)

6.3.8 Add 3 drops sodium molybdate solution (5.11)

- 6.3.9 A distilled water blank must be run with each set of samples because of iodide, iodate, bromide, and/or bromate in reagents.
- 6.3.10 Titrate as described in 6.4
- 6.4. Titration
 - 6.4.1 Dissolve approximately 1 g potassium iodide (5.7) in sample from (6.2.8 or 6.3.10) Add 10 mL of H₂SO₄ solution (5.12) and place in dark for 5 minutes.
 - 6.4.2 Titrate with standardized phenylarsine oxide working standard (5.14) or sodium thiosulfate working standard (5.18), adding indicator (5.15 or 5.20) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7.0 Calculations

- 7.1 Principle: Iodide is determined by the titration of the sample as oxidized in (6.2); bromide plus iodide is determined by the titration of the sample as oxidized in (6.3). The amount of bromide is then determined by difference. The number of equivalents of iodine produced a constant of 13,320 as shown in the equation in (7.2). Experimental data is entered in the appropriate place and the equation is solved for mg/L bromide

7.2 Equation

$$\text{Br (mg/L)} = 13,320 \left[\left(\frac{A \times B}{C} \right) - \left(\frac{D \times E}{F} \right) \right]$$

where:

- A = the number of mL of PAO needed to titrate the sample for bromide plus iodide (with the number of mL of PAO needed to titrate the blank subtracted)
- B = the normality of the PAO needed to titrate the sample for bromide plus iodide
- C = the volume of sample taken (100 mL or a fraction thereof) to be titrated for bromide plus iodide
- D = the number of mL of PAO needed to titrate the sample for iodide (with the number of mL of PAO needed to titrate the blank subtracted).The blank for the iodide titration is often zero
- E = the normality of the PAO used to titrate the sample for iodide
- F = the volume of sample taken (100 mL or a fraction thereof) to be titrated for iodide.

8.0 Precision and Accuracy

- 8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 0.3, 2.8, 5.3, 10.3 and 20.3 mg/L of bromide, the standard deviations were ±0.13, ±0.37, ±0.38, ± 0.44 and ±0.42 mg/L, respectively
- 8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 2.8, 5.3, 10.3 and 20.3 mg/L of bromide, recoveries were 96, 83, 97 and 99%, respectively

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1246-68, Method C, p 328 (1976).
2. Bender, D. F., "Modification of the Iodimetric Titration Methods for the Determination of Bromide and its application to Mixed Domestic-Industrial Waste Effluents", Analyst (London), 100, p 400-404 (June 1975).