Bromide, titrimetric, hypochlorite oxidation

Parameter and Code:

Bromide, dissolved, I-1125-85 (mg/L as Br): 71870

1. Application

This method may be used to analyze any natural or treated water or brine containing at least 1.0 mg/L of bromide. Highly concentrated brines may require dilution.

2. Summary of method

2.1 The determination of bromide involves the determination of bromide and iodide collectively, and then the determination of iodide alone; bromide is calculated by difference. Bromide and iodide are oxidized to bromate and iodate, respectively, by hypochlorite, and the excess hypochlorite is subsequently decomposed with sodium formate (Kolthoff and others, 1969).

$$3OCl^{-1} + Br^{-1} \rightarrow BrO_3^{-1} + 3Cl^{-1}$$

$$3OCl^{-1} + I^{-1} \rightarrow IO_3^{-1} + 3Cl^{-1}$$

Iodine equivalent to the combined iodate and bromate is then liberated by addition of potassium iodide to an acid solution.

$$BrO_3^{-1} + 6I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O + Br^{-1}$$

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O$$

The liberated iodine is titrated with standard thiosulfate with use of starch as the indicator.

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}$$

2.2 Iodide alone is determined by oxidation to iodate with bromine in a buffered solution. Iodine equivalent to the iodate is then liberated from added potassium iodide and titrated with thiosulfate as in the combined determination.

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Iodine flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2*M*: Mix 125 mL glacial $HC_2H_3O_2$ (sp gr 1.069) with demineralized water and dilute to 1 L.

5.2 *Bromine water*, saturated: Add to approx 250 mL demineralized water slightly more liquid Br_2 than will dissolve when mixed. Store in a glass-stoppered, actinic-glass bottle.

5.3 *Calcium carbonate*, powder, $CaCO_3$.

5.4 *Calcium oxide*, anhydrous powder, CaO.

5.5 *Hydrochloric acid*, 6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

5.6 *Methyl red indicator solution*, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

5.7 *Potassium fluoride*, crystals, $KF \cdot 2H_2O$.

5.8 *Potassium hypochlorite solution*, 4.4 g/L: Dissolve 6.2 g KOH in 100 mL demineralized water; then saturate the solution with bromine-free Cl_2 while continually cooling and stirring. Store in a glass-stoppered, actinic-glass bottle. Prepare fresh daily.

5.9 *Potassium iodide*, crystals, IO_3^{-1}-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.10 *Sodium acetate solution*, 165 g/L: Dissolve 273 g $NaC_2H_3O_2 \cdot 3H_2O$ in demineralized water and dilute to 1 L.

5.11 *Sodium chloride*, crystals: Free from I^{-1}, IO_3^{-1}, Br^{-1}, and BrO_3^{-1}. The NaCl can be tested for IO_3^{-1} and BrO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates presence of IO_3^{-1} or BrO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.12 *Sodium formate solution*, 50 g/100 mL: Dissolve 50 g $NaHCO_2$ in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.13 *Sodium molybdate solution*, 1.0 g/100 mL: Dissolve 1.2 g $Na_2MoO_4 \cdot 2H_2O$ in demineralized water and dilute to 100 mL.

5.14 *Sodium thiosulfate solution*, 0.10*N*: Dissolve 25.0 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free, demineralized water; add 1 g Na_2CO_3 and dilute to 1 L.

5.15 *Sodium thiosulfate standard solution*, 0.010*N*: Dilute 100.0 mL 0.10*N* $Na_2S_2O_3$ solution to 950 mL with carbon dioxide-free, demineralized water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Cool and dissolve 0.3567 g in demineralized water, and dilute to 1,000 mL. Pipet 25.00 mL of the KIO_3 solution into a 250-mL iodine flask; then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6*M* H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, and then titrate with standard $Na_2S_2O_3$ solution, adding 2 mL starch indicator solution as the end point is approached (light straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

5.16 *Starch indicator solution*, stable or "thyodene," powdered (Fisher No. T138 or equivalent).

5.17 *Sulfuric acid*, 3.6*M*: CAUTIOUSLY add 200 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approx 400 mL sample; mix, let stand about 1 h, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 For the combined Br^{-1} and I^{-1} determination, pipet a volume of the filtrate containing less than 5.0 mg Br^{-1} and I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure along with the sample.

6.4 Add sufficient NaCl to produce a 3.0 g Cl^{-1} content.

6.5 Add a drop of methyl red indicator solution, and make the solution just acidic with 6*M* HCl.

6.6 Add 10 mL KClO solution, 0.5 mL 6*M* HCl, and sufficient $CaCO_3$ to produce an excess of approx 0.1 g.

6.7 Heat the solution to boiling and maintain this temperature for about 8 min.

6.8 Reduce the excess KClO by adding 2 mL $NaHCO_2$ solution, taking precaution to wash down the sides of the flask with a small amount of hot water. Keep the solution hot for an additional 8 min.

6.9 Cool and add several drops of Na_2MoO_4 solution. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.

6.10 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.11 Titrate the liberated I_2 with 0.01*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached. Disregard a return of the blue color after the end point has been reached.

6.12 For the I^{-1} determination, pipet a volume of filtrate (step 6.1) containing less than 5.0 mg I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.13 Prepare a blank of 100.0 mL demineralized water and carry through the procedure along with the sample.

6.14 Add a drop of methyl red indicator solution, and make the solution just acidic with 3.6*M* H_2SO_4.

6.15 Add 15.0 mL $NaC_2H_3O_2$ solution, 5.0 mL 2.2*M* $HC_2H_3O_2$, and sufficient bromine water to produce a light-yellow color; mix and allow to stand 5 min.

6.16 Reduce the excess Br_2 by adding $NaHCO_2$ solution drop by drop until the yellow tinge in the sample disappears; then add an excess of 1 mL.

6.17 Wash the sides of the flask with a small amount of water, and blow out Br_2 vapors with a syringe and a glass tube inserted into the mouth of the flask. If any iron precipitates at this point, add 0.5 g $KI \cdot 2H_2O$.

6.18 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.19 Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color). Disregard a return of the blue color after the end point has been reached.

7. Calculations

7.1 Determine $Br^{-1}+I^{-1}$ in epL as follows:

$$Br^{-1}+I^{-1}(\text{epL})= \frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times (\text{mL}_t - \text{mL}_b)$$

7.2 Determine I^{-1} in epL as follows:

$$I^{-1}(\text{epL})=\frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times (\text{mL}_i - \text{mL}_b).$$

7.3 Determine Br^{-1} in mg/L as follows:

$$Br^{-1}(\text{mg/L})=79.91\times[\text{epL }(I^{-1}+ Br^{-1})-\text{epL } I^{-1}]$$

where

epL= equivalents per liter,

mL_b= titrant volume for blank determination,

mL_t= titrant volume for combined determination,

and

mL_i= titrant volume for I^{-1} determination.

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Single-operator precision of this method (American Society for Testing and Materials, 1984) may be expressed as follows:

$$S_o = 0.0044X$$

where

S_o= single-operator precision, milligrams per liter,

and

X= concentration of bromide, milligrams per liter.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 482-90.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis (4th ed.): New York, Macmillan, 1199 p.