Sulfide, titrimetric, iodometric

Parameter and Code:
Sulfide, total, I-3840-85 (mg/L as S): 00745

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing more than 0.5 mg/L of sulfide.

1.2 Water-suspended sediment may be analyzed by this method if sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn.

1.3 Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration and agitation of the sample should, therefore, be avoided. The addition of 2 g of zinc acetate per liter of water will fix the sample for several days. Acidic water must be neutralized before addition of zinc acetate.

2. Summary of method

2.1 This iodometric method does not differentiate the forms of the sulfide ion in solution.

2.2 Sulfide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate, using starch as an indicator (Kolthoff and others, 1969).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

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

A blank is treated exactly the same as the samples. The sulfide concentration is calculated from the difference between the volume of thiosulfate required for the blank and the volume used for the sample.

2.3 This method is similar to that in an article published by the American Public Health Association (1980).

3. Interferences

Reducing substances such as sulfites and heavy-metal ions react with iodine, which contributes to positive errors. Oxygen and other oxidants may react with hydriodic acid to liberate iodine, which contributes to negative errors.

4. Apparatus

4.1 *Buret,* 10-mL capacity.

4.2 *Flasks,* Erlenmeyer, 250-mL capacity.

5. Reagents

5.1 *Hydrochloric acid,* concentrated (sp gr 1.19).

5.2 *Iodine standard solution,* 0.010*N:* Dissolve 6 g iodate-free KI in approx. 25 mL water. Add 1.2690 g resublimed I_2. When solution is complete, dilute to 1 L. Standardize with 0.010*N* $Na_2S_2O_3$, using starch as an indicator.

$$\text{Normality of } I_2 = \frac{0.010 \times \text{mL } Na_2S_2O_3}{\text{mL } I_2}$$

Adjust the normality of the iodine standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or iodine as indicated by the first titration. Confirm the normality by restandardization.

5.3 *Potassium iodide,* crystals, iodate-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL 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 blue color indicates the presence of IO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.4 *Sodium thiosulfate standard solution,* 0.010*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water and dilute 1 L with carbon dioxide-free water. Standardize against KIO_3 as follows: Dry approx. 0.5 g KIO_3 for 2 h at 180 °C. Dissolve 0.3567 g in water and dilute to 1,000 mL. Pipet 25.0 mL KIO_3 solution into a 250-mL Erlenmeyer flask, then add successively 75 mL deionized water and 0.5 g iodate-free KI. After solution is complete, add 10 mL HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ solution, adding starch indicator solution as the end point is approached (light-straw color):

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

Adjust the normality of the thiosulfate standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or sodium thiosulfate as indicated by the first titration. Confirm the normality by restandardization.

5.5 *Starch indicator solution,* stable (NOTE 1).

NOTE 1. A convenient substitute for starch indicator solution is the product thyodene, sold by Fisher Scientific Co. It can be used in its dry form and produces an end point similar to that of starch.

6. Procedure

6.1 Shake the sample vigorously and immediately pipet a volume of sample with ZnS in suspension containing less than 1.5 mg S^{-2} (100.0 mL max) into a 250-mL Erlenmeyer flask, and adjust the volume to approx. 100 mL.

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

6.3 Add 10.0 mL 0.010*N* I_2 and mix.

6.4 Without delay add 10 mL concentrated HCl.

6.5 Immediately titrate the excess 12 with 0.010*N* $Na_2S_2O_3$, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color).

7. Calculations

$$S^{-2}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times 0.1603 \times (\text{mL blank titrant} - \text{mL sample titrant})$$

8. Report

Report sulfide, total (00745), concentrations as follows: 0.5 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Public Health Association, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., p. 448.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative Chemical Analysis (4th ed.): New York, Macmillan, p. 857.