METHOD #: 376.1	Approved for NPDES (Editorial Revision 1978)
TITLE:	Sulfide (Titrimetric, Iodine)
ANALYTE:	Sulfide
INSTRUMENTATION:	Titration
STORET No.	Total 00745 Dissolved 00746

- 1.0 Scope and Application
 - 1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).
 - 1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/L.
- 2.0 Summary of Method
 - 2.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate or phenylarsine oxide.
- 3.0 Comments
 - 3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.
 - 3.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.
 - 3.3 If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.
- 4.0 Apparatus: Ordinary laboratory glassware.
- 5.0 Reagents
 - 5.1 Hydrochloric acid, HCl, 6 N
 - 5.2 Standard iodine solution, 0.0250 N: Dissolve 20 to 25 g KI in a little water in a litter volumetric and add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.0250 N sodium thiosulfate or phenylarsine oxide using a starch indicator.

- 5.3 Phenylarsine oxide 0.0250 N: commercially available.
- 5.4 Starch indicator: commercially available.
- 5.5 Procedure for standardization (see Residual Chlorine-iodometric titration Method 330.3, section 5.15).
- 6.0 Procedure
 - 6.1 Unprecipitated sample
 - 6.1.1 Place a known amount of standard iodine solution (5.2) into a 500 mL flask. The amount should be estimated to be in excess of the amount of sulfide expected.
 - 6.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 mL
 - 6.1.3 Add 2 mL of 6 N HCl (5.1).
 - 6.1.4 Pipet 200 mL of sample into the flask, keeping the tip of the pipet below the surface of the sample.
 - 6.1.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used in performing steps 6.1.1 and 6.1.5.
 - 6.1.6 Titrate with the reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution (5.3)) using a starch indicator (5.4) until the blue color disappears. Record the number of milliliters used.
 - 6.2 Precipitated samples
 - 6.2.1 Add the reagents to the sample in the original bottle. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3 Dewatered samples

- 6.3.1 Return the glass fibre filter paper which contains the sample to the original bottle. Add 200 mL distilled water. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.
- 6.3.2 The calculations (7) should be based on the volume of original sample put through the filter.

7.0 Calculations

- 7.1 One mL of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.
- 7.2 Use the formula

mg/L sulfide =
$$\frac{400(A - B)}{mL \text{ sample}}$$

where:

- A = mL of 0.0250 N standard iodine solution (5.2)
- B = mL of 0.0250 N standard reducing sodium thiosulfate or phenylarsine oxide) solution (5.3).
- 8.0 Precision and Accuracy

8.1 Precision and accuracy for this method have not been determined.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 505, Method 428D, (1975).