METHOD #: 377.1 Approved for NPDES (Editorial Revision 1978)

TITLE: Sulfite (Titrimetric)

ANALYTE: Sulfite, SO_3

INSTRUMENTATION: Titration

STORET No. 00740

1.0 Scope and Application

1.1 This method is applicable to drinking and surface waters, sewage and industrial wastes. The primary application has been to cooling,process and distribution water systems and boiler feedwaters to which sulfide is added in order to reduce dissolved oxygen and eliminate corrosion.

1.2 The minimum detectable limit is 2-3 mg/L SO_3.

2.0 Summary of Method

2.1 An acidified sample containing a starch indicator is titrated with a standard potassium iodide-iodate titrant to a faint permanent blue end point which appears when the reducing power of the sample has been completely exhausted.

3.0 Interferences

3.1 The temperature of the sample must be below 50°C.

3.2 Care must be taken to allow as little contact with air as possible. For example, do not filter the sample. Keep the buret tip below the surface of the sample.

3.3 Other oxidizable substances, such as organic compounds, ferrous iron and sulfide are positive interferences. Sulfide may be removed by adding 0.5 g of zinc acetate and analyzing the supernatant of the settled sample.

3.4 Nitrite gives a negative interference by oxidizing sulfite when the sample is acidified; this is corrected by either using a proprietary indicator which eliminates nitrite or by adding sulfamic acid.

3.5 Copper and possibly other heavy metals catalyze the oxidation of sulfite; EDTA is used to complex metals.

3.6 A blank must be run to correct for interferences present in the reagents.

4.0 Apparatus

4.1 Standard laboratory glassware is used.

5.0 Reagents

5.1 Sulfuric acid, H_2SO_4, 1 + 1.

5.2 Starch indicator: Amylose, Mallinckrodt Chemical Works; Thyodene, Magnus Chemical Co. or equivalent.

5.3 Dual-Purpose Sulfite Indicator Powder: a proprietary formulation containing sulfamic acid to destroy nitrite.

5.4 Standard potassium iodide-iodate titrant, 0.0125N: Dissolve 445.8 mg anhydrous potassium iodate, KIO_3 (primary standard grade dried for several hours at 120°C), 4.25 g KI and 310 mg $NaHCO_3$ in distilled water and dilute to 1 liter. This titrant is equivalent to 500 μg SO_3/1.00 mL.

5.5 Sulfamic Acid: Crystalline

5.6 EDTA Reagent Dissolve 2.5 g EDTA in 100 mL distilled water.

6.0 Procedure

6.1 Sampling Contact with air must be minimized. If the sample temperature is greater than 50°C, it must be cooled in a special apparatus described elswhere (see Bibliography). Immediately add 1 mL of EDTA Solution (5.6) per 100 mL of sample.

6.2 Starch Indicator

6.2.1 Place 1 mL H_2SO_4 (5.1) in titration vessel.

6.2.2 Add 0.1 g sulfamic acid crystals (5.5).

6.2.3 Add 50 mL sample.

6.2.4 Add approximately 0.1 g starch indicator (5.2).

6.2.5 Titrate with potassium iodide-iodate titrant (5.4) until a faint permanent blue color develops. Keep the pipet tip below the surface of the sample. View the color change against a white background. Record the mL titrant.

6.2.6 Run a reagent blank using distilled water instead of sample (6.2.3).

6.3 Dual Purpose Sulfite Indicator Powder.

6.3.1 Place 50 mL sample in a titration vessel.

6.3.2 Add 3-4 drops phenolphthalein indicator.

6.3.3 Add sufficient scoops (1 g) of indicator (5.3) to discharge the red color.

6.3.4 Titrate with potassium iodide-iodate titrant (5.4) until a faint permanent blue color develops. View the color change against a white background. Record the mL titrant.

6.3.5 Run a reagent blank using distilled water instead of sample (6.3.1).

7.0 Calculations

7.1 Use the formula:

$$\text{mg/L } SO_3 = \frac{A \times N \times 40{,}000}{\text{mL sample}}$$

where:

A = mL titrant (6.2.5 or 6.3.4) B = mL
B = mL titrant for the blank (6.2.6 or 6.3.5) and
N = normality of KI-KIO_3 titrant (5.4)

7.2 To calculate as Na_2SO_3
mg/L Na_2SO_3 = mg/L SO_3 x 1.57

8.0 Precision and Accuracy

8.1 Precision and accuracy data are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1339-72, Method C, p 440 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 508, Method 429, (1975).