METHOD #: 375.3 Approved for NPDES (Editorial Revision 1978)

TITLE: Sulfate (Gravimetric)

ANALYTE: Sulfate, SO_4

INSTRUMENTATION: Drying Oven

STORET No. Total 00945

1.0 Scope and Application

1.1 This method is applicable to drinking, surface and saline water, domestic and industrial wastes.

1.2 This method is the most accurate method for sulfate concentrations above 10 mg/L. Therefore, it should be used whenever results of the greatest accuracy are required.

2.0 Summary of Method

2.1 Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as $BaSO_4$.

2.2 Preserve by refrigeration at 4°C.

3.0 Interferences

3.1 High results may be obtained for samples that contain suspended matter, nitrate, sulfite and silica.

3.2 Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Occlusion of alkali sulfate with barium sulfate causes the substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfate of alkali metal acts similarly and decomposes when heated. Heavy metals such as chromium and iron, cause low results by interfering with complete precipitation and by formation of heavy metal sulfates.

4.0 Apparatus

4.1 Steam bath

4.2 Drying oven, equipped with thermostatic control.

4.3 Muffle furnace with heat indicator.

4.4 Desiccator

4.5 Analytical balance, capable of weighing to 0.1 mg.

4.6 Filter paper, acid-washed, ashless hard-finish filter paper sufficiently retentive for fine precipitates.

5.0 Reagents

5.1 Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water in a 100 mL volumetric flask and dilute to the mark with distilled water.

5.2 Hydrochloric acid, HCl, 1 + 1

5.3 Barium chloride solution: Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 liter of distilled water. Filter through a membrane filter or hard-finish filter paper. One mL of this reagent is capable of precipitating approximately 40 mg SO_4.

5.4 Silver nitrate-nitric acid reagent: Dissolve 8.5 g $AgNO_3$ and 0.5 mL conc. HNO_3 in 500 mL distilled water.

6.0 Procedure

6.1 Removal of silica: If silica concentration is greater than 25 mg/L

6.1.1 Evaporate sample nearly to dryness in a platinum dish on a steam bath.

6.1.2 Add 1 mL HCl solution (5.2), tilt dish and rotate until acid contacts all of the residue.

6.1.3 Continue evaporation to dryness.

6.1.4 Complete drying in an oven at 180°C.

6.1.5 If organic matter present, char over a flame.

6.1.6 Moisten with 2 mL distilled water and 1 mL HCl solution (5.2).

6.1.7 Evaporate to dryness on a steam bath.

6.1.8 Add 2 mL HCl solution (5.2).

6.1.9 Take up soluble residue in hot distilled water and filter.

6.1.10 Wash the insoluble silica with several small portions of hot distilled water.

6.1.11 Combine filtrate and washings.

6.2 Precipitation of barium sulfate

6.2.1 If necessary, treat clarified sample to remove interfering agents.

6.2.2 Adjust to contain approximately 50 mg SO_4 ion in a 250 mL volume.

6.2.3 Adjust acidity with HCl solution (5.2) to pH 4.5 to 5.0, using pH meter or orange color of methyl red indicator (5.1).

6.2.4 Add an additional 1 to 2 mL HCl solution (5.2).

6.2.5 For lower concentrations of sulfate ion fix the total volume at 150 mL.

6.2.6 Heat to boiling and, while stirring gently, add warm $BaCl_2$ solution (5.3) slowly, until precipitation appears to be complete; then add approximately 2 mL in excess.

6.2.7 If amount of precipitate is small, add a total of 5 mL $BaCl_2$ solution (5.3).

6.2.8 Digest the precipitate at 80 to 90°C preferably overnight but for not less than 2 hours.

6.3 Filtration and Weighing

6.3.1 Mix a little ashless filter paper pulp with the $BaSO_4$ and filter at room temperature.

6.3.2 Wash the precipitate with small portions of warm distilled water until the washings are free of chloride as indicated by testing with silver nitrate-nitric acid reagent (5.4).

6.3.3 Dry the filter and precipitate.

6.3.4 Ignite at 800°C for 1 hour. DO NOT LET THE FILTER PAPER FLAME.
6.3.5 Cool in a desiccator and weigh.

7.0 Calculation

$$mg/L\ SO_4 = \frac{mg\ BaSO_4 \times 411.5}{mL\ sample}$$

8.0 Precision and Accuracy

8.1 A synthetic unknown sample containing 259 mg/L sulfate, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 250 μg/L nitrite N, 1.1 mg/L nitrate N and 42.5 mg/L alkalinity (contributed by $NaHCO_3$), was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516-68, Method A, p 429 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 493, Method 427A, (1975).