DETERMINATION OF SULPHIDE IN WATER

This method is applicable in essentially all waters including most industrial waste waters.

Equipment Required

1. pH/mV Analyzer or pH Meter with millivolt scale
2. Sulphide Combination Ion Selective Electrode

Reagents

1. Sodium hydroxide pellets
2. Ascorbic acid
3. Disodium EDTA
4. Sodium sulphide hydrate
5. Lead perchlorate
6. Zinc Acetate

Reagent and Standard Preparation

Sulphide Antioxidant Buffer Preparation (SOAB)

To approximately 600ml of distilled water in a 1000ml volumetric flask, add 80g reagent grade NaOH pellets, 35g of ascorbic acid, and 67g of disodium EDTA stir until everything dissolves. Dilute to the mark with distilled water. Freshly prepared SAOB, when stored in a tightly stoppered bottle, has a shelf llie of approximately two weeks, if opened frequently. When oxidised, the solution turns dark brown and should be discarded. Light brown solutions are still usable.

Sodium Sulphide Standards

Sulphide standardizing solutions are prepared from reagent grade sodium sulphide hydrate, $Na_2S.9H_2O$. All sulphide solution preparation and measurement should be performed in a fume hood, to avoid breathing noxious fumes. Precise standards cannot be prepared by weighing the salt because of the large and variable water of hydration. Instead, prepare saturated Na_2S solution by adding 100g of the $Na_2S.9H_2O$ to 100ml of DI water, shake well, stopper securely, and allow to stand overnight. To prepare a stock sulphide solution, pipette 1ml of the saturated solution described above into 50ml of SAOB and dilute to 100ml using DI water.

Standardization

The concentration of stock sulphide solution must be determined by electrode titration before constructing a calibration curve. Use a titrant of known concentration of 0.1M lead perchlorate. Take 50ml of stock sulphide solution, add this to 25ml SAOB and 25ml H_2O and titrate using the sulphide electrode.

Calculation

The concentration of stock sulphide solution in mg/l (C) is given by: C= (Volume of 0.1M lead solution) x 64. Each day, prepare four calibration standards using 100ml volumetrics as follows:

A - 5.00ml of sulphide stock to 45ml of SAOB and make up to 100ml using DI water.
B - 1.00ml of sulphide stock 50ml of SAOB and make up to 100ml using DI water.

C - 2.00ml of calibration standard A 50ml of SAOB and make up to 100ml using DI water.
D -1.00ml of calibration standard A 50ml of SAOB and make up to 100ml using DI water.

The concentration of the calibrating standard is calculated from the concentration of the sulphide stock, as determined by titration. If the stock concentration is C mg/l, then the calibration standards have the following concentrations:

A= 0.05C
B= 0.01C
C= 0.001C
D= 0.0005C

Sample Preparation

Samples are treated prior to analysis with sulphide antioxidant buffer. Samples should be taken with a minimum of aeration to avoid air oxidation or loss of any volatiles. Samples can be preserved by adding 0.2ml of 2M zinc acetate (equivalent to 128 mg/L S=) and 0.05ml (1 drop) of 6M sodium hydroxide to a 100ml bottle, filling it completely with the sample, and stoppering it with no air bubbles trapped under the stopper. If the concentration of sulphide is greater than approximately 100mg/l, the amounts of both reagents should be increased. SAOB contains EDTA to redissolve the zinc and free the sulphide. The entire sample is used for analysis, and since the results will be given as mg sulphide per litre, the sample volume must be known.

Method

Prepare a calibration curve by immersing the electrode in each of the calibration standards, beginning with the weakest one, and record the stable millivolt potential reading developed by each one. Construct a graph using this data using semi log paper and placing the sulphide concentration scale on the logarithmic scale and the mV reading on the linear scale. Pipette the sample into an equal volume of SAOB, stir thoroughly without vortex and allow to stand for 3-5 minutes. Place the electrodes in the solution, record the stable electrode potential and determine the sulphide concentration of the sample from the calibration curve. Between samples, rinse the electrode with deionised water, blot dry, and immerse them in a "blank" solution of 50ml SAOB plus 50ml deionised water.

Expected Range: Samples containing 0.1 to 3200mg/l of sulphide may be analysed by this method. The concentration range may be extended by dilution of an appropriate aliquot.

Reference

Annual Book of ASTM Standards, Part 31.