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Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 29 SULPHIDE

(First Revision)

1. Scope — Prescribes two methods for the determination of total and dissolved sulphides in waters and wastewaters by titrimetric iodine method or methylene blue method. Iodometric method is suitable for measurement of sulphide in concentration above 1 mg/l if interferences are absent and loss of hydrogen sulphide is avoided. The methylene blue method is applicable to sulphide concentration up to 20 mg/l.

2. Iodometric Method

2.1 *Principle and Theory* — Sulphides are stripped from the acidified sample with an inert gas and collected in zinc acetate solution. Excess iodine solution added to the zinc sulphide suspension reacts with the sulphide under acidic condition.

Thiosulphate is used to measure unreacted iodine to indicate the quantity of iodine consumed by sulphide. The reaction may be given as follows:

1) $S + I_2 = S_2 + 2\ I$

2) I_2 (excess) $+ 2\ S_2O_3 = S_4O_6 + 2\ i$

2.2 *Interferences*

2.2.1 Reduced sulphur compounds, such as sulphite, thiosulphate and hydrosulphite, which decompose in acid, may yield erractic results.

2.2.2 Volatile iodine consuming substances will give high results.

2.2.3 Eliminate interferences due to sulphite, thiosulphate, iodide and many other soluble substances, but not ferro-cyanide, by first precipitating zinc sulphide, removing the supernatant, and replacing it with distilled water. Use the same procedure, even when not needed for removal of interferences, to concentrate sulphide.

2.2.3.1 *Procedure* — Put required quantity of 2 N zinc acetate solution into 500 ml glass bottle, file with sample and add required quantity of 6 N sodium hydroxide solution. Stopper with no airbubbles under stopper and mix by rotating back and forth vigorously about a transverse axis. Addition of reagents may be varied in volume so that the resulting precipitate is not excessively bulky and settles rapidly. Add enough sodium hydroxide to produce a *p*H above 9. Let the precipitate settle for 30 minutes. Filter the precipitate through glass fibre filter paper and carry out titration immediately.

2.3 *Sampling and Storage*

2.3.1 Sampling and storage shall be done as prescribed in IS : 3025 (Part I)-1986 'Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling (*first revision*)'. Samples must be taken with a minimum of aeration and preserved at low temperature (sulphide may be volatilized by aeration and any oxygen is advertently added to the sample may convert the sulphide to an unmeasurable form).

2.3.2 Preserve the sample with addition of 2 ml/l of zinc acetate. Samples not preserved must be analyzed immediately.

2.4 *Apparatus*

2.4.1 *Reaction flask* — Wide mouth bottle of 1 litre capacity, with a 2 hole stopper, fitted with a fritted gas-diffusion tube (plastic, ceramic or glass and a gas outlet tube).

Water Sectional Committee, CDC 26; Panel for Methods of Test for Water and Effluents, CDC 26 : P1 [Ref : Doc : CDC 26 (9094)]

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2.4.2 *Absorption flasks* — Two 250-ml capacity long necked flask with 2 hole stoppers fitted with glass tubes and suitable connections to pass gas through in series.

2.5 *Reagents*

2.5.1 *Zinc acetate solution (2 N)*— Dissolve 110 g Zn ($C_2H_3O_2$)$_2$.2H_2O in 400 ml distilled water and finally make up to 1 litre.

2.5.2 *Inert gas* — A cylinder of nitrogen [pure grade, *see* IS : 1747-1972 Specification for nitrogen (*first revision*)] or CO_2 or a CO_2 gas generator [Grade 1, *see* IS : 307-1966 Specification for carbon dioxide(*second revision*)].

2.5.3 *Sulphuric acid concentrated*

2.5.4 *Standard iodine solution (0·025 N)* — Dissolve 20-25 g potassium iodide (KI) in a little water and add 3·175 g iodine. After iodine has dissolved, dilute to 1 litre with distilled water, standardize this solution against 0·025 N sodium thiosulphate using starch indicator.

2.5.5 *Hydrochloric acid concentrated*

2.5.6 *Standard thiosulphate solution (0·025 N)* — Dissolve 6·205 g $Na_2S_2O_3.5H_2O$ in 800 ml boiled and cooled distilled water. Add 0·4 g NaOH or 5 ml chloroform as a preservative and finally make up to 1 litre.

2.5.7 *Starch indicator solution* — Add 5·0 g starch to 800 ml boiling distilled water and stir. Dilute to one litre and boil for few minutes and let settle over night. Use the clear supernate. (This solution may be preserved by adding 1·25 g salicyclic acid/litre or by adding a few drops of toluene).

2.5.8 *Aluminium chloride solution (6 N)* — Take the 100 g $AlCl_3.6H_2O$ from a previously unopened reagent bottle and dissolve in 144 ml distilled water.

Note — Because of the hygroscopic and caking tendencies of this chemical, it will be convenient to purchase in small packing.

2.5.9 *Sodium hydroxide (6 N)* — Dissolve 240 g NaOH in distilled water and dilute to 1 litre.

2.6 *Procedure*

2.6.1 *Total sulphide*

2.6.1.1 Take 5 ml zinc acetate solution (**2.5.1**) and 95 ml distilled water into each of the two absorption flasks.

2.6.1.2 Connect the reaction flask and two absorption flasks in series and purge the system with CO_2 or N_2 for 2 minutes. Measure 500 ml well mixed sample into the reaction flask.

2.6.1.3 Acidify the sample with 10 ml concentrated H_2SO_4 and replace the prepared 2 holes stopper tightly; pass N_2 or CO_2 (not air or oxygen) through the sample for 1 hour or until the experiments show no more sulphide coming over.

2.6.1.4 To each of the absorption flasks, then add iodine solution well in excess of the amount necessary to react with the collected sulphide.

2.6.1.5 Add 2·5 ml concentrated HCl acid to each flask, stopper and shake to mix thoroughly.

2.6.1.6 Transfer contents of both flasks and back titrate with 0·025 N sodium thiosulphate solution using starch solution as indicator. Run a blank parallel for accurate results.

2.7 *Dissolved Sulphide*

2.7.1 Remove suspended solids in the sample by flocculation and settling.

2.7.1.1 Fill 1 litre bottle with flowing sample in such a way that the sample, which has had the least possible contact with air. Add 2 ml aluminium chloride solution (**2.5.7**) and 2 ml NaOH solution (**2.5.8**) and stopper with no air bubbles under the stopper. Rotate back and forth about a transverse axis as vigorously as possible for at least 1 minute in order to flocculate the contents thoroughly.

Note — The volume of these chemicals may be varied according to experience, the idea being to get good clarification without using excessively large amounts.

2.7.1.2 Allow to settle for 15 minutes, or until supernatant liquid is reasonably clear. Alternatively remove, suspended matter by centrifugation.

2.7.2 Proceed as for total sulphide after taking 500 ml sample into the reaction flask.

2.8 *Calculation*

$$\text{mg/}l\text{, sulphide} = \frac{(V_1 - V_2) \times 400}{V}$$

where

V_1 = volume in ml of standard iodine solution added,
V_2 = volume in ml of standard thiosulphate solution used, and
V = volume in ml of sample taken.

3. Methylene Blue Method

3.1 *Principle and Theory* — The methylene blue method is based on the reaction of sulphide, ferric chloride and dimethyl-p-phenylenediamine to produce methylene blue. Ammonium phosphate is added after colour development to remove ferric chloride colour. The method is applicable at sulphide concentrations up to 20 mg/l.

3.2 *Apparatus*

3.2.1 *Matched test tubes* — Approximately 125 mm long and 15 mm OD.

3.2.2 *Droppers* — Capable of delivering 20 drops/ml of methylene blue solution.

3.2.3 *Spectrophotometer* — Suitable for use at 664 mm with cells providing light paths of 1 cm and 1 mm or filter photometer with a filter providing maximum transmitance near 600 nm.

3.3 *Reagents*

3.3.1 *Amine sulphuric acid stock solution* — Dissolve 27 g N, N-dimethyl-p-phenylene diamine-oxalate in a cold mixture of 50 ml concentrated sulphuric acid and 20 ml of distilled water. Cool and dilute to 100 ml with distilled water. Use fresh oxalate as old stock may be oxidized and discoloured to a degree that results interfering colours in the test. Store in a dark glass bottle. When this stock solution is diluted and used in the procedure with a sulphide free sample, it will first be pink but then should become colourless within 3 minutes.

3.3.2 *Amine-sulphuric acid reagent solution* — Dilute 25 ml of stock solution (*see* **3.3.1**) with 975 ml 1 : 1 sulphuric acid. Store in a dark glass bottle.

3.3.3 *Ferric chloride solution* — Dissolve 100 g of ferric chloride ($FeCl_3 . 6H_2O$) in 40 ml water.

3.3.4 *Sulphuric acid solution* — 1 : 1.

3.3.5 *Diammonium hydrogen phosphate solution* — Dissolve 400 g of $(NH_4)_2HPO_4$ in 800 ml of distilled water.

3.3.6 *Methylene blue solution I* — Dissolve 1·0 g of dye (should be 84 percent or more) in distilled water and make up to 1 litre. Standardize this against sulphide solutions of known strength and adjust its concentration so that 0·05 ml (1 drop) is equivalent to 1·0 mg of sulphide per litre.

3.3.6.1 *Methylene blue solution II* — Dilute 10·00 ml of adjusted methylene blue solution I to 100 ml.

3.4 *Procedure*

3.4.1 *Colour development* — Transfer 7·5 ml of sample to each of two matched test tubes, using a special wide-tip pipette or filling to marks on test tubes. Add to tube A 0·5 ml of amine-sulphuric acid reagent and 0·15 ml of ferric chloride solution. Mix immediately by inverting slowly, only once (excessive mixing causes low results by loss of hydrogen sulphide as a gas before it has had time to react). To tube B add 0·5 ml of 1 : 1 sulphuric acid and 0·15 ml of ferric chloride solution and mix. The presence of sulphide will be indicated by the appearance of blue colour in tube A. Colour development is generally complete in about 1 minute, but a longer time often is required for fading out of the initial pink colour. Wait 3 to 5 minutes and add 1·6 ml of diammonium hydrogen phosphate solution to each tube. Wait for 3 to 15 minutes and make colour comparisons. If zinc acetate was used, wait at least 10 minutes before making a visual colour comparison,

3.4.2 *Colour determination*

3.4.2.1 *Visual colour estimation* — Add methylene blue solution I or II, depending on sulphide concentration and desired accuracy, dropwise, to the second tube, until colour matches that developed in the first tube. If the concentration exceeds 20 mg/1, repeat test with a portion of sample diluted to one tenth. With methylene blue solution I adjusted so that 0·05 ml (1 drop) is equivalent to 1·0 mg of sulphide per litre when 7·5 ml of sample are used:

mg of sulphide/litre— No. of drops of solution I + 0·1 (No. of drops of solution II)

3.4.2.2 *Photometric method* — A cell with a light path of 1 cm is suitable for measuring sulphide concentration from 0·1 to 2·0 mg/l. Use shorter or longer light paths for higher or lower concentrations. The upper limit of the method is 20 mg/l. Zero instrument with a portion of treated sample from tube B. Prepare calibration curves on the basis of colorimetric tests made on sodium sulphide solutions simultaneously analyzed by the iodometric method, plotting concentration as absorbance. A straight line relationship between concentration and absorbance can be assumed from 0 to 1·0 mg/l. Read sulphide concentration from calibration curve.

EXPLANATORY NOTE

Sulphide is often present in ground water, especially in hot springs. Its common presence in waste waters comes partly from the decomposition of organic matter, sometimes from industrial wastes, but mostly from the bacterial reduction of sulphates. Hydrogen sulphide gas escaping into air from sulphide-containing waste waters cause odour nuisance. Hydrogen sulphipe is a toxic gas. It attacks metals directly or indirectly. From analytical point of view, three categories of sulphides in water and waste water are distinguished, namely, total sulphides, dissolved sulphides and unionized hydrogen sulphide. This method supersedes, **16** of IS : 2488 (Part 1) - 1966 'Methods of sampling and test for industrial effluents: Part I' and **46** of IS : 3025-1964 'Methods of sampling and test (physical and chemicals) for water used in industry'.

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