UDC 628·1/·3 : 543·363 (First Reprint JULY 1992) IS : 3025 (Part 35) - 1988

Indian Standard (Reaffirmed 1999)

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

PART 35 SILICA

(First Revision)

Water Sectional Committee, CDC 26; Panel for Methods of Test for Water, Wastewaters and Effluents CDC 26 : P1 [Ref : Doc : CDC 26 (9306)]

1. Scope — Prescribes four methods for determination of silica as follows:

a) Gravimetric method,

b) Molybdosilicate method,

c) Heteropoly blue method, and

d) Automated method for molybdate-reactive silica.

1.1 Gravimetric method determines total silica. Other methods determine molybdate reactive silica.

2. Gravimetric Method

2.1 *Principle* — Hydrochloric acid decomposes silicates and dissolved silica, forming silicic acids that are precipitated as partially dehydrated silica during evaporation and baking. Ignition completes dehydration of silica, which is weighed and then volatilized as silicon tetrafluoride, leaving any impurities behind as non-volatile residue. The residue is weighed and silica is determined as loss on volatilization.

2.2 *Interference* — Glassware contributes silica and hence avoid its use as far as possible. Use reagents and distilled water low in silica. Carry out a blank to correct for silica introduced by the reagents and apparatus.

2.3 *Apparatus*

2.3.1 *Platinum crucibles* — With covers.

2.3.2 *Platinum evaporating dishes* — 200 ml capacity. In dehydration steps, acid-leached glazed porcelain evaporating dishes free from etching may be substituted for platinum, but for greatest accuracy, platinum is preferred.

2.4 *Reagents*

2.4.1 *Hydrochloric acid* — 1 : 1 and 1 : 50.

2.4.2 *Sulphuric acid* — 1 : 1.

2.4.3 *Hydrofluoric acid* — 48 percent.

2.4.4 *Perchloric acid* — 72 percent.

2.5 *Procedure* — Before determining silica, test sulphuric acid and hydrofluoric acid for interfering non-volatile matter by carrying out procedure given in **2.5.1.5**. Use an empty clean platinum crucible. If any increase in weight is observed, make a correction in the silica determinations.

2.5.1 *Hydrochloric acid dehydration*

2.5.1.1 *Sample evaporation* — To a clear sample containing at least 10 mg of silica, add 5 ml of 1 : 1 hydrochloric acid. Evaporate to dryness in a 200 ml platinum or acid leached glazed porcelain dish, in several portions if necessary, on a waterbath or over a hot plate. Protect against contamination from atmospheric dust. During evaporation add a total of 15 ml of 1 : 1 hydrochloric acid in several portions. Dry the dish and place it in an oven at 110°C or over a hot plate to bake for 30 minutes.

Adopted 29 February 1988

Gr 3

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

2.5.1.2 *First filtration* — Add 5 ml of 1 : 1 hydrochloric acid, warm and add 50 ml of hot distilled water. While the mixture is hot, filter through an ashless medium textured filter paper, decanting as much liquid as possible. Wash dish and residue with hot 1 : 50 hydrochloric acid and then with a minimum volume of distilled water until washings are chloride-free. Save all washings. Set aside filter paper with its residue.

2.5.1.3 *Second filtration* — Evaporate filtrate and washings from the above operation to dryness in the original platinum dish. Bake residue at 110°C in an oven or over a hot plate for 30 minutes. Repeat steps given in **2.5.1.2**. Use a separate filter paper and rubber policeman to aid in transferring residue from dish to filter. Take special care with porcelain dishes because silica adheres to the dish.

2.5.1.4 *Ignition* — Transfer the two filter papers (one, if dehydrated by **2.5.2**) and residues to a covered platinum crucible, dry at 110°C and ignite at 1 200°C to constant mass. Avoid mechanical loss of residue when first charring and burning off paper by gradual heating at minimum temperature. Too rapid heating may form black silicon carbide. Cool in desiccator, weigh and repeat ignition and weighing until constant mass is attained. Record mass of crucible and contents.

2.5.1.5 *Volatilization with hydrofluoric acid* — Thoroughly moisten weighed residue with distilled water. Add 4 drops of 1 : 1 sulphuric acid, followed by 10 ml of hydrofluoric acid, measuring the latter in a plastic graduated cylinder. Slowly evaporate to dryness over an air bath or hot plate in a hood and avoid loss by splattering. Ignite crucible to constant mass at 1 200°C. Record mass of crucible and contents.

2.5.2 *Perchloric acid dehydration* — Follow procedure as given in **2.5.1.1** until all but 50 ml of sample has been evaporated. Add 5 ml of perchloric acid and evaporate until dense white fumes appear. Continue dehydration for 10 minutes. Cool, add 5 ml of 1 : 1 hydrochloric acid and 50 ml of hot distilled water. Bring to boil and filter through an ashless quantitative filter paper. Wash thoroughly ten times with hot distilled water and proceed as directed in **2.5.1.4** and **2.5.1.5**. For many purposes, the silica precipitate is often sufficiently pure for the purpose intended and may be weighed direct, omitting hydrofluoric acid volatilization.

2.6 *Calculation* — Substract mass of crucible and contents after hydrofluoric acid treatment from the corresponding mass before hydrofluoric acid treatment. The difference (*A*) in milligrams is loss on volatilization and represents silica.

$$\text{Silica (as SiO}_2\text{), mg/l} = \frac{A \times 1\,000}{V}$$

where

V is volume in ml of sample taken for test.

3. Molybdosilicate Method

3.1 *Principle* — Ammonium molybdate at *p*H about 1·2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy molybdophosphoric acid. Even if phosphate is known to be absent, the addition of oxalic acid is must in this method. The intensity of yellow colour produced is proportional to concentration of molybdate reactive silica.

In at least one of its forms, silica does not react with molybdate even though it is capable of passing through the filter paper and not noticeably turbid. It is not known to what extent such unreactive silica occurs in waters. Molybdate unreactive silica can be converted into molybdate reactive form by heating or fusing with alkali.

3.2 *Interference* — Glasswares contribute to silica and avoid using these. Tannin, large amounts of iron, turbidity, colour, sulphide and phosphate interfere.

3.3 *Apparatus*

3.3.1 *Platinum dishes* — 100 ml capacity.

3.3.2 *Spectrophotometer* — for use at 410 nm, providing a light path of 1 cm or longer.

3.3.3 *Nessler tubes* — matched, 50 ml capacity, tall.

3.4 *Reagents*

3.4.1 *Sodium bicarbonate*

3.4.2 *Sulphuric acid* — 1 N.

3.4.3 *Hydrochloric acid* — 1 : 1.

3.4.4 *Ammonium molybdate reagent* — Dissolve 10 g ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in distilled water with stirring and gentle warming, and dilute to 100 ml. Filter, if necessary. Adjust to *p*H 7 to 8 with silica free ammonia or sodium hydroxide and store in polyethylene bottle to stabilize.

3.4.5 *Oxalic acid solution* — Dissolve 7·5 g of oxalic acid in distilled water and dilute to 100 ml.

3.4.6 *Stock silica solution* — Dissolve 4·73 g of sodium metasilicate nonahydrate ($Na_2SiO_3.9H_2O$) in distilled water and dilute to 1000 ml. Analyze 100·0 ml portions by method given in **2** to determine concentration. Store in plastic bottle.

3.4.6.1 *Standard silica solution* Dilute 10·00 ml of stock solution to 1 000 ml with distilled water. 1·00 ml = 10·0 μg of SiO_2.

3.4.7 *Permanent colour solutions*

3.4.7.1 *Potassium chromate solution* — Dissolve 630 mg of potassium chromate in distilled water and diltue to 1 litre.

3.4.7.2 *Borax solution* — Dissolve 10 g of sodium borate decahydrate in distilled water and dilute to 1 litre.

3.5 Procedure

3.5.1 *Colour development* — To 50 ml of sample, add in quick succession 1·0 ml of 1 : 1 hydrachloric acid and 2·0 ml ammonium molybdate reagent. Mix by inverting at least six times and let stand for 5 to 10 minutes. Add 2·0 ml of oxalic acid solution and mix well. Read colour after 2 minutes but before 15 minutes, measuring time from addition of oxalic acid. Measure colour in a spectrophotometer or visually.

3.5.2 To detect the presence of molybdate unreactive silica, digest sample with sodium bicarbonate before colour development. This digestion may not be sufficient to convert all molybdate unreactive silica to the molybdate-reactive form. Complex silicates and higher silica polymers require extended fusion with alkali at higher temperature or digestion under pressure for complete conversion Omit digestion, if all the silica is known to react with molybdate.

Prepare a clear sample by filtration, if necessary. Place 50·0 ml or smaller portion diluted to 50 ml in a 100 ml platinum dish. Add 200 mg of silica-free sodium bicarbonate and digest on steam bath for 1 h. Cool and add slowly, 2·4 ml of 1 N sulphuric acid with stirring. Do not interrupt analysis but proceed at once with remaining steps. Transfer quantitatively to a 50 ml Nessler tube and make up to mark with distilled water.

3.5.3 *Preparation of standards* — If sodium bicarbonate treatment is used, add to the standards 200 mg of sodium bicarbonate and 2·4 ml of 1 N sulphuric acid to compensate both for the slight amount of silica introduced by the reagents and for the effect of the salt on colour intensity. Dilute to 50 ml.

3.5.4 *Correction for colour or turbidity* — Prepare a special blank for every sample that needs such correction. Carry two identical portions of each such sample through the procedure, including sodium bicarbonate treatment, if this is used. To one portion, add all reagent as directed in **3.5.1**. To the other, add hydrochloric acid and oxalic acid but no molybdate. Adjust spectrophotometer to zero absorbance with the blank containing no molybdate before reading absorbance of molybdate treated sample.

3.5.5 *Spectrophotometric measurement* — Prepare a calibration curve from a series of approximately six standards to cover the range given below:

Light Path cm	*Silica in 55 ml Final Volume* μg
1	200—1 300
2	100—700
5	40—250
10	20—130

Follow steps given in **3.5.1** on suitable portions of standard silica solutions diluted to 50·0 ml in Nessler tubes. Set spectrophotometer at zero absorbance with distilled water and read all standards including reagent blank, against distilled water. Plot migrogram silica in the final (55 ml) developed solution against spectrophotometer readings. Run a reagent blank and at least one standard with each group of samples to confirm that the calibration curve previously established has not shifted.

3.5.6 *Visual comparison* — Make a set of permanent artificial colour standards, using potassium chromate and borax solutions. Mix liquid volumes specified below and place them in well stoppered, appropriately labelled 50 ml Nessler tubes. Verify correctness of those permanent artificial standards by comparing them visually against standards prepared by analyzing portions of the standard silica solution. Use permanent artificial colour standards only for visual comparison.

Value in Silica mg	*Potassium Chromate Solution* ml	*Borax Solution* ml	*Water* ml
0·00	0·0	25	30
0·10	1·0	25	29
0·20	2·0	25	28
0·40	4·0	25	26
0·50	5·0	25	25
0·75	7·5	25	22
1·0	10·0	25	20

3.6 *Calculation*

$$\text{Silica (as SiO}_2\text{), mg/l} = \frac{\mu\text{g of SiO}_2\text{ (in 55 ml of final volume)}}{\text{Volume in ml of sample for test}}$$

Also report whether sodium bicarbonate degestion was used.

4. Heteropoly Blue Method

4.1 *Principle* — Ammonium molybdate at *p*H about 1·2 reacts with silica and any phosphate present to produce heteropoly acids. The yellow molybdosilicic acid is reduced by means of aminonaphthol sulphonic acid to heteropoly blue.

4.2 *Interference* — Glassware contributes silica and avoid using glassware. Tannin, large amount of iron, turbidity, sulphide and phosphate interfere.

4.3 *Apparatus*

4.3.1 *Platinum dishes* — 100 ml capacity.

4.3.2 *Spectrophotometer* — for use at 815 nm (may be used at 650 nm with appreciably reduced sensitivity) with a light path of 1 cm or longer.

4.3.3 *Nessler tubes* — matched, 50 ml, tall form.

4.4 *Reagents*

4.4.1 All reagents listed in **3.4** are required.

4.4.2 *Reducing agent* — Dissolve 500 mg of 1 amino-2 naphthol-4 sulphonic acid and 1 g of sodium sulphite in 50 ml of distilled water with gentle warming, if necessary; add this to a solution of 30 g of sodium hyposulphite in 50 ml distilled water. Filter and keep in a plastic bottle.

4.5 *Procedure*

4.5.1 *Colour development* — Proceed as given in **3.5.1** up to and including the words 'add 2·0 ml of oxalic acid solution and mix well'. Measuring time from the moment of adding oxalic acid, wait at least 2 minutes but not more than 15 minutes, add 2·0 ml of reducing agent and mix thoroughly. After 5 minutes, measure the blue colour spectrophotometerically or visually. If sodium bicarbonate pre-treatment is used follow **3.5.2**.

4.5.2 *Spectrophotometric measurement* — Prepare a calibration curve from a series of approximately six standards to cover the optimum range indicated below. Carry out the steps described in **4.5.1** on suitable portions of standard silica solution diluted to 50·0 ml in Nessler tubes; pre-treat standards, if sodium bicarbonate digestion is used Adjust spectrophotometer to zero absorbance with distilled water and read all standards, including a reagent blank, against distilled water. If necessary to correct for colour or turbidity in a sample, follow steps given in **3.5.4**. To the special blank, add hydrochloric and oxalic acids but no molybdate or reducing agent. Plot mg of silica in the final 55 ml developed soultion against absorbance. Run a reagent blank and at least one standard with each group of samples to check the calibration curve.

Light Path cm	*Silica in 55 ml Final Volume, µg*	
	650 nm Wave Length	815 nm Wave Length
1	40-300	20-100
2	20-150	110-50
5	7-50	4-20
10	4-30	2-10

4.5.3 *Visual comparison* — Prepare a series of not less than 12 standards, covering the range 0 to 120 µg of silica (as SiO_2) by placing the calculated volumes of standard silica solution in 50 ml Nessler tubes, diluting to mark with distilled water and developing colour as prescribed in **4.5.1**.

4.6 *Calculation*

$$\text{Silica (as } SiO_2 \text{), mg/l} = \frac{\mu g \text{ of } SiO_2 \text{ in 55 ml of final volume}}{\text{Volume in ml of sample taken for test}}$$

4.6.1 Report whether sodium bicarbonate digestion was used.

5. Automated Method for Molybdate Reactive Silica

5.1 *Principle* — This method is an adoption of heteropoly blue method utilizing continuous flow analytical instrument.

5.2 *Interference* — Glassware contributes to silica and avoid using these. Tannin, large amounts or iron, turbidity, sulphide and phosphates interfere.

5.3 *Apparatus*

5.3.1 *Automated analytical equipment* — The required continuous-flow analytical instrument consists of interchangeable components shown in Fig. 1.

5.4 *Reagents*

5.4.1 *Sodium dicarbonate* — powder.

5.4.2 *Sulphuric acid* — 1 N.

5.4.3 *Hydrochloric acid* — 1 : 1.

5.4.4 *Ammonium molybdate reagent* — *See* **3.4.4**

5.4.5 *Oxalic acid solution* — *See* **3.4.5**.

5.4.6 *Stock silica solution* — *See* **3.4.6**.

5.4.6.1 *Standard silica solution* — *See* **3.4.6.1**.

5.4.7 *Reducing agent* — Dissolve 120 g of sodium hyposulphite and 4 g of sodium sulphite in 800 ml of warm distilled water. Add 2 g of 1-amino-2-naphthol-4-sulphonic acid, mix well and dilute to 1 litre. Filter and store in plastic bottle. To prepare working reagent, dilute 100 ml of this to 1 litre with distilled water.

5.5 *Procedure* — Set up manifold as shown in Fig. 1 and follow the instructions prescribed by the manufacturer. Determine absorbance at 660 nm.

5.6 *Calculation* — Prepare standard curves by plotting peak heights of standards processed through the manifold against silica (as SiO_2) concentration in standards. Compute samples of SiO_2 concentration by comparing sample peak height with standard curve.

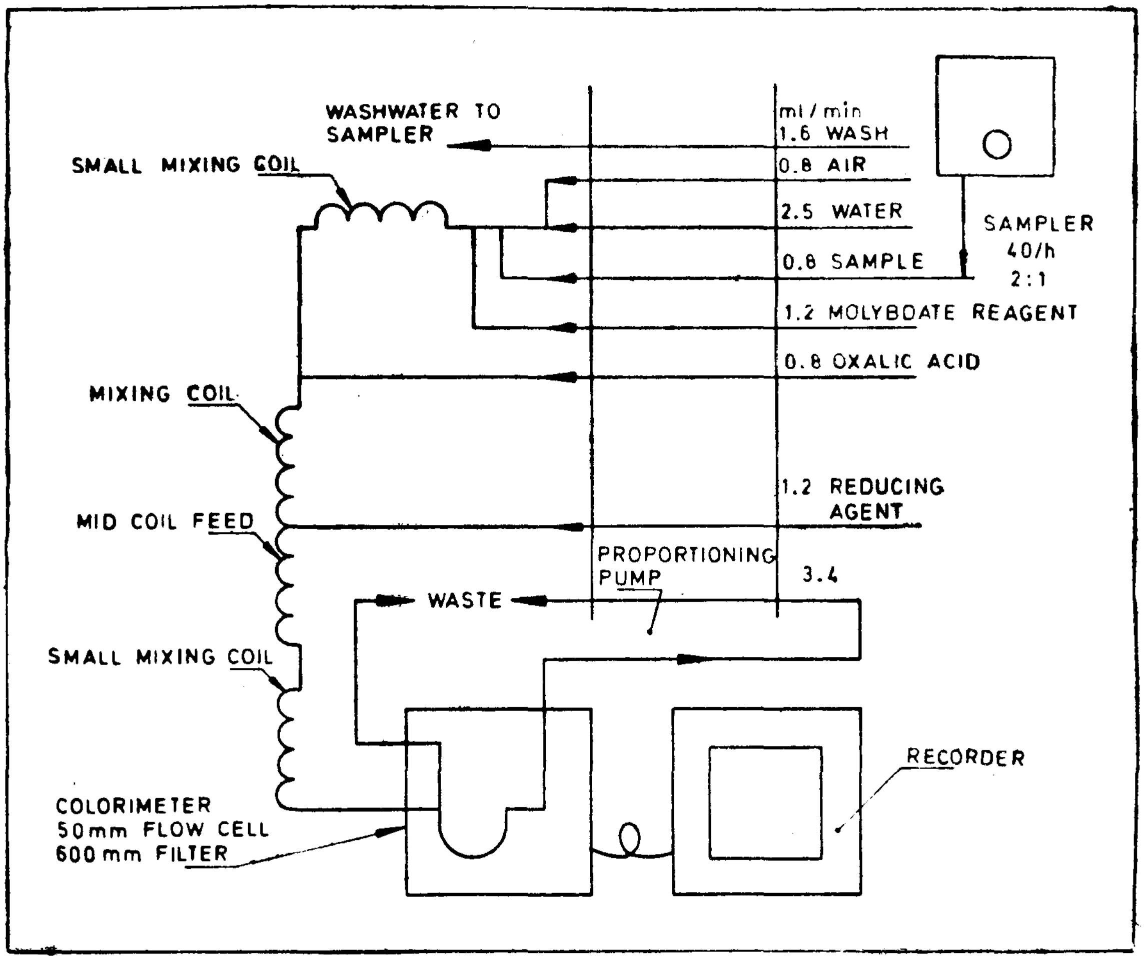

FIG. 1 SILICA MANIFOLD

EXPLANATORY NOTE

Silicon ranks next to oxygen in abundance on earth's crust. The silica content of natural waters is in the range of 1 to 30 mg/l. Silica in water is undesirable for a number of industrial uses because it forms difficult to remove silica and silicate scales in equipment, particularly on high pressure steam turbine blades. It is possible to convert various forms of silica to the molybdate reactive form for determination by methods given in this standard. Gravimetric method determines more than one form of silica. It will determine all dissolved silica and some colloidally dispersed silica. Gravimetric method may be used to standardize sodium silicate solutions used as standards in other methods for determination of silica. Molybdosilicate method is recommended for relatively pure waters having 0·4 to 25 mg of SiO_2 per litre and gravimetric method is not recommended when samples contain less than 20 mg SiO_2/l. The range can be extended by diluting, concentrating or by varying light path. Interferences due to tannin, colour and turbidity are more severe with this method as compared to hetropoly blue method. The yellow colour produced has a limited stability and attention to timing is necessary. The colour developed in molybdosilicate and hetropoly blue methods are affected by high concentrations of salts. Hetropoly blue method is recommended for low range, from 0·04 to 2 mg SiO_2/l. Hetropoly blue method shall be the refree method. This standard supersedes **30** of IS : 3025-1964 'Methods of sampling and test (physical and chemical) for water used in industry'. In the preparation of this standard, considerable assistance has been derived from Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association, Washington, USA, 16th Edition, 1985.

Printed at Dee Kay Printers, New Delhi, India