IS 3025-51 (2001): Methods of Sampling and Tests (Physical and Chemical) for Water and Waste Water, Part 51: Carbonate and Bicarbonate [CHD 32: Environmental Protection and Waste Management]

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भारतीय मानक

जल और अपशिष्ट जल के लिये नमूने लेने और परीक्षण (भौतिक और रसायन) की पद्धतियाँ

भाग 51 कार्बोनेट और बाइकार्बोनेट

(पहला पुनरीक्षण)

Indian Standard

METHODS OF SAMPLING AND TESTS (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER

PART 51 CARBONATE AND BICARBONATE

(First Revision)

ICS 13.060.50; 13.060.60

BUREAU OF INDIAN STANDARDS
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NEW DELHI 110002

April 2001

Price Group 3

Water Environment Protection Sectional Committee, CHD 12

FOREWORD

This Indian standard (Part 51) (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by Water Environment Protection Sectional Committee had been approved by the Chemical Division Council.

Alkalinity of water is its acid neutralizing capacity. It is the sum of all the titratable bases. Alkalinity is significant in many uses and treatments of natural water and wastewater. The alkalinity of many surface water is primarily a function of carbonate, bicarbonate and hydroxide content. It is taken as an indicator of the concentration of these constituents. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes.

The technical committee responsible for formulation of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' had decided to revise the standard and publish it in separate parts. This standard supersedes **44** of IS 3025 : 1964 and is one among the different parts being published under IS 3025 series of standards.

Considerable assistance has been derived from the following documents:

- Standard methods for the examination of water and waste water, 17th edition. American Public Health Association; American Water Works Association; and Water Pollution Control Federation, U.S.A.
- ISO 3196:1975 Sodium hydroxide for industrial use — Determination of carbonates content — Titrimetric method.
- ASTM D 513-88.

The composition of the committee responsible for the preparation of this standard is given in Annex A.

In reporting the result of a test or analysis made in accordance with this standard if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard
METHODS OF SAMPLING AND TESTS (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER
PART 51 CARBONATE AND BICARBONATE
(First Revision)

1 SCOPE

This standard prescribes two methods for the determination of carbonate and bicarbonate in water and wastewater:

a) Titrimetric method, and
b) Calculation method.

2 REFERENCES

The following Indian Standards contain provisions which through reference in this text, constitute provision of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents, Part 1
7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents, Part 2

3 TERMINOLOGY

For the purpose of this standard, the definitions given in IS 7022 (Part 1) and 7022 (Part 2) shall apply.

4 GENERAL

Carbonate, bicarbonate and hydroxide contribute to the alkalinity of water. When the total alkalinity of a water is due almost entirely to hydroxides, carbonates or bicarbonates, and the total dissolved solids is not greater than 500 mg/l, the carbonate and bicarbonate concentrations as $CaCO_3$ may be calculated from the sample *p*H and total alkalinity.

5 SAMPLING AND STORAGE

Collect samples in polyethylene or borosilicate glass bottles and store at a low temperature. Fill bottles completely and cap tightly. Because waste samples may be subjected to microbial action and to loss or gain of carbon dioxide or other gases when exposed to air, analyse samples without delay, preferably within one day. If biological activity is suspected, analyse within six hours. Avoid sample agitation and prolonged exposure to air.

6 INTERFERENCES

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

7 TITRIMETRIC METHOD

7.1 Principle

The titration may be performed potentiometrically or with phenolphthalein indicator. The total OH^-, CO_3^{2-} and HCO_3^- content is first determined by titration with standard acid using methyl orange/bromocresol green indicator. Another equal portion of the sample is titrated against the same acid using phenolphthalein/metacresol purple indicator.

7.2 Apparatus

7.2.1 *Electrometric Titrator*

Use any commercial *p*H meter or electrically operated titrator that uses a glass electrode and may be read to 0.05 *p*H unit. Standardize and calibrate according to manufacturer's instructions. Pay special attention to temperature compensation and electrode care, if automatic temperature compensation is not provided, titrate at 25 ± 5°C.

7.2.2 *Titration Vessel*

For conventional sized electrodes, use a 200 ml, tall-form Berzelius beaker without a spout. Fit beaker with a stopper having three holes, to accommodate the two electrodes and the burette.

7.2.3 *Magnetic Stirrer*

7.2.4 *Pipettes, Volumetric*

7.2.5 *Flasks, Volumetric*

7.2.6 *Burettes, Borosilicate Glass*

7.2.7 *Polyolefin Bottles*

7.3 Reagents

7.3.1 *Sodium Carbonate Solution — Approximately* 0.05 N

Dry 5 g primary standard sodium carbonate, at 250°C for 4 hours and cool in a desicator. Weigh 2.5 ± 0.2 g, transfer to 1 litre volumetric flask, dissolve in distilled water and make up the volume. Do not store for longer than one week.

7.3.2 *Standard Hydrochloric Acid* — 0.1N

Prepare acid solution of approximate normality by diluting 8.3 ml of concentrated hydrochloric acid to 1 litre. Standardize against 40 ml of 0.05N sodium carbonate solution, with about 60 ml of water, in a beaker, by titrating potentiometrically to *p*H 5. Lift out electrodes, rinse into the same beaker and boil gently for 3 to 5 minutes under a water glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to *p*H inflection point. Calculate normality as follows:

$$\text{Normality, } N = \frac{A \times B}{53} \times C$$

where

A = Sodium carbonate in g weighed in 1l flask;

B = Sodium carbonate solution, in ml, for titration; and

C = Acid, in ml, used.

7.3.3 *Standard Hydrochloric Acid* — 0.02 N

Dilute 200 ml of 0.100 0 N standard acid to 1 000 ml with distilled or deionised water. Standardize by potentiometric titration against 15 ml 0.05N sodium carbonate as per procedure in **7.3.2**.

7.3.4 *Methyl Orange/ Boromocresol Green Indicator Solution*

Dissolve 100 mg of methyl orange/bromocresol green, in 100 ml distilled water.

7.3.5 *Metacresol Purple Indicator Solution*

Dissolve 100 mg of metacresol purple in 100 ml water (*p*H 8.3 indicator).

7.3.6 *Phenolphthalein Solution*

Dissolve 1 g of phenophthalein in 100 ml of ethanol and add 100 ml of distilled water with constant stirring. Filter, if precipitate forms, then add 0.02 N NaOH drop-wise until a faint purple colour appears.

7.3.7 *Sodium Thiosulphate* — 0.1 M

Dissolve 25 g sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in water and dilute to 1 000 ml with distilled water.

8 PROCEDURE

8.1 Sample Size

The range of carbonate and bicarbonate concentrations found in wastewater is so large that a single sample size and normality of titrant can not be specified. For alkalinities less than 1 000 mg as $CaCO_3$/l, take 20 ml of sample and titrate with 0.02 N hydrochloric acid; while for alkalinities more than 1 000 mg, as $CaCO_3$/l, take 5 ml of the sample and titrate with 0.1 N hydrochloric acid.

8.2 The end point may be determined by any of the following:

a) By colour change, and
b) Potentiometrically.

8.2.1 *Colour Change*

Colour indicators may be used for routine and control titrations in the absence of interfering colour and turbidity and for preliminary titrations to select sample size and strength of titrant. Take sample size and normality of titrant according to **8.1**. If free residual chlorine is present, add 0.05 ml (1 drop) of 0.1 M sodiumthiosulphate solution, or destroy with ultraviolet radiation. Add 5 drops of phenolphthalein indicator solution and titrate over a white surface to persistent colour change, characteristic of the equivalence of indicator used with sample to a buffer solution at the designated *p*H. Repeat the titration using bromocresol green indicator solution. The two titrations represent the phenolphthalein and the total alkalinity respectively.

8.2.2 *Potentiometric Titration*

8.2.2.1 *Potentiometric titration curve*

Rinse electrodes and titration vessel with distilled water and drain. Select sample size and normality of titrant according to criteria of **8.1**.

Measure sample *p*H. Add standard hydrochloric acid in increments of 0.5 ml or less, such that a change of less than 0.2 *p*H units occur per increment. After each addition mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record *p*H when a constant reading is obtained. Continue adding titrant and measure *p*H. Titrate to *p*H 8.3 and record the cumulative milliliters of titrant added. Continue titrating to *p*H 4.5 and again record the total volume of titrant used. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached, before making the next addition.

9 CALCULATION

9.1 Calculate phenolphthalein alkalinity by using the volume of acid used for phenolphthalein end point or titrate potentiometrically to pH 8.3 . Calculate the total alkalinity by using the volume of acid used for bromocresol green end point or titrate potentiometrically to pH 4.5.

$$\text{Alkalinity (CaCO}_3\text{ mg/l)} = \frac{A \times N \times 50}{\text{ml of sample}}$$

where

A = ml of standard acid used, and

N = Normality of acid.

9.2 The results obtained from the phenolphthalein and total alkalinity determinations offer a means for the calculation of carbonate and bicarbonate, concentrations as $CaCO_3$. The method ascribes the entire alkalinity to bicarbonate, carbonate and hydroxide and it assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH greater than 10. According to this scheme,

a) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity;

b) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half of the total alkalinity;

c) Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half of the total alkalinity. These relationships may be calculated by the following scheme, where P is, phenolphthalein alkalinity and T is total alkalinity.

9.3 Select the smaller value of P or (T–P). Then , carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance (T–$2P$) is bicarbobnate. When the smaller value is (T–P) the balance ($2P$–T) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 1 (A modification of Table 1 is desirable when P is greater than T).

Table 1 Alkalinity Relationships

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
(1)	(2)	(3)	(4)
P = O	O	O	T
P < 1/2 T	O	2P	T-2P
P = 1/2 T	O	2P	O
P > 1/2 T	2P-T	2(T-P)	O
P = T	T	O	O

where

P = Phenolphthalein alkalinity, and

T = Total alkalinity.

10 PRECISION AND BIAS

10.1 No general statement may be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainty involved in sampling and sample handling before the analysis.

10.2 In the range of 10 to 500 mg/l when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg/l (as $CaCO_3$) may be achieved.

ANNEX A

(*Foreword*)

COMMITTEE COMPOSITION

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