IS 3025-11 (1983): Methods of sampling and test (physical and chemical) for water and wastewater, Part 11: pH value [CHD 32: Environmental Protection and Waste Management]

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UDC 628·1/·3 : 543·3 : 543·257·1

(Fourth Reprint SEPTEMBER 1998)

IS : 3025 (Part 11) - 1983

(Reaffirmed 2002)

Indian Standard

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

PART 11 *p*H VALUE

(First Revision)

Water Sectional Committee, CDC 26; Panel for Methods of Test for Water, and Effluents, CDC 26 : P1 [Ref : Doc : CDC 26 (8845)]

1. Scope — Prescribes electrometric and colorimetric methods for the determination of *p*H value. Both methods are applicable to all types of water and waste water.

2. Electrometric Method

2.1 *Principle* — The *p*H value is determined by measurement of the electromotive force of a cell consisting of an indicator electrode (an electrode responsive to hydrogen ions such as a glass electrode) immersed in the test solution and a reference electrode (usually mercury/calomel electrode). Contact between the test solution and the reference electrode is usually achieved by means of a liquid junction, which forms part of the reference electrode. The electromotive force is measured with a *p*H meter, that is, a high impedence voltmeter calibrated in terms of *p*H.

2.1.1 Several types of electrodes have been suggested for electrometric determination of *p*H value. Although the hydrogen gas electrode is recognised as primary standard the glass electrode in combination with calomel electrode is generally used with reference potential provided by saturated calomel electrode. The glass electrode system is based on the fact that a change of 1 *p*H unit produces an electrical change of 59·1 mV at 25°C. The active element of a glass electrode is a membrane of a special glass. The membrane forms a partition between two liquids of differing hydrogen ion concentration and a potential is produced between the two sides of the membrane which is proportional to the difference in *p*H between the liquids.

2.2 *Interference*

2.2.1 Above *p*H value of 10, high sodium concentrations interfere with the measurement. Corrections for the sodium error may be made by consulting the chart supplied by the manufacturer of electrodes being used. Sodium errors at *p*H value levels greater than 10 can be reduced or eliminated by using a low sodium error electrode.

2.2.2 Oil and grease may interfere by coating the *p*H electrode and causing a sluggish response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 percent) may be necessary to remove any remaining film.

2.2.3 Temperature affects the *p*H values in two ways. The first is covered by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of *p*H inherent in the sample at various temperatures. This error is sample-dependent and cannot be controlled. Therefore, the temperature at the time of analysis should be reported.

2.3 *Apparatus*

2.3.1 *p*H *meter* — With glass and reference electrode (saturated calomel), preferably with temperature compensation.

2.3.2 *Magnetic strirrer* — With polytetrafluoroethylene coated stirring bar.

2.3.3 *Thermometer* — With least count of 0·5°C.

2.4 *Reagents* — Standard *p*H buffer solutions from available tablets or powder, or known amount of chemicals may be used for the preparation. Procedures for the preparation of some standard *p*H buffer solutions are given below and Table 1 shows the *p*H value of these buffers at different temperatures.

Adopted 30 December 1983	© August 1985, BIS	Gr 2

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2.4.1 *Borax buffer* — 0·01 M solution, *p*H value 9·18 at 25°C. Dissolve 3·814 g borax. ($Na_2B_4O_7.10 H_2O$) in deionised or distilled water and dilute to 1 litre. Fresh borax may be used or it may be recrystalised but it should not be over dried. For preparation of dilution water freshly boil and cool deionised or distilled water to expel carbon dioxide gas. Specific conductance of dilution water should be less than 2 µS at 25°C and *p*H valve 5·6 to 6·0 for preparation of all standard solutions.

2.4.2 *Phosphate buffer* — 1 : 1 solution, *p*H value 6·865 at 25°C. For Preparing 0·025 M potassium dihydrogen phosphate and 0·025 M disodium hydrogen phosphate, dry potassium dihydrogen phosphate and sodium dihydrogen phosphate, in an oven at 130°C for 2 hours and cool in a desiccator. Dissolve 3·388 g potassium dihydrogen phosphate and 3·533 g sodium dihydrogen phosphate in deionised or distilled water and make up to 1 litre.

2.4.3 *Tartrate buffer* — 0·034 M solution, *p*H value 3·56 at 25°C. Prepare a saturated solution of potassium hydrogen tartrate in deionised or distilled water.

2.4.4 *Phthalate buffer* — 0·05 M solution, *p*H value 4·008 at 25°C. Dissolve 10·12 g potassium hydrogen phthalate in deionised water and dilute to 1 litre.

2.4.5 *Tetraoxalate buffer* — 0·05 M solution, *p*H value 1·68 at 25°C. Dissolve 12·61 g potassium tetetraoxalate dihydrate in deionised water and dilute to 1 litre.

2.4.6 *Calcium hydroxide buffer* — 0·020 3 M solution, *p*H value 12·45 at 25°C. Ignite well-washed calcium carbonate ($CaCO_3$) of low alkali grade in a platinum dish at 1 000°C for 1 hour. Hydrate the cooled calcium oxide by adding slowly, with stirring, distilled or deionised water and heat to boiling. Filter the cooled suspension and collect the solid calcium hydroxide on a fritted glass filter of medium porosity. Dry the collected calcium hydroxide in an oven at 110°C, cool and pulverise to uniformly fine granules. Vigorously shake an excess amount of this product in polyethylene bottle with distilled or demineralised water. Allow the gross excess to settle and filter by suction through a fritted glass funnel. Keep the bottle securely stoppered to prevent ingress of carbon dioxide.

2.4.6.1 The *p*H value of these buffers at different temperature is given in Table 1.

2.5 *Sample Handling and Preservation*

2.5.1 Samples should be analyzed as soon as possible, preferably in the field at the time of sampling.

2.5.2 High purity waters and waters not at equilibrium with the atmosphere (ground waters or lake waters collected at depth) are subject to changes when exposed to the atmosphere. Therefore the sample containers should be filled completely and kept sealed prior to analysis.

TABLE 1 *p*H OF BUFFERS AT DIFFERENT TEMPERATURES

(*Clause* 2.4.6.1)

Temperature (1)	0·05 M Potassium Tetraoxlate (2)	0·034 M Potassium Hydrogen Tartrate (Saturated) (3)	0·05 M Potassium Hydrogen Phthalate (4)	0·025 M Potassium Dihydrogen Phosphate & Disodium Hydrogen Phosphate (5)	0·01 M Sodium Borate Decahydrate (Borax) (6)	0·0203 M Calcium Hydroxide Saturated (7)
°C						
0	1·67	—	4·01	6·98	9·46	13·43
5	1·67	—	4·01	6·95	9·39	13·21
10	1·67	—	4·00	6·92	9·33	13·00
15	1·67	—	4·00	6·90	9·27	12·81
20	1·67	—	4·00	6·88	9·23	12·63
25	1·68	3·56	4·01	6·86	9·18	12·45
30	1·68	3·55	4·02	6·85	9·14	12·30
35	1·69	3·55	4·03	6·84	9·10	12·04
40	1·69	3·55	4·04	6·84	9·07	11·99
50	1·71	3·55	4·06	6·83	9·01	11·70
60	1·72	3·56	4·09	6·85	8·96	11·45

2.6 *Procedure* — Follow the manufacturer's instructions for operation of *p*H meter. After required warm-up period, standardize the instrument with a buffer solution of *p*H near that of the sample and check electrode against at least one additional buffer of different *p*H value. Measure the temperature of the water and if temperature compensation is available in the instruments adjust it accordingly. Rinse and gently wipe the electrodes with solution. If field measurements are being made, the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode sensing element as indicated by drift free readings. ($< 0·1$ *p*H unit). If necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogenity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air-water interface of the sample. Note and record sample *p*H and temperature However, if there is a continuous drift, take a second reading with the fresh aliquot of sample without stirring and report it as the *p*H value.

2.7 *Calculation* — Report *p*H to the nearest coefficient or 0·01 unit (if instrument reads up to 2 decimal places) and temperature to the nearest °C.

3. Colorimetric Method

3.1 *Principle* — A series of indicators and buffer solutions are used for determination of *p*H value by visual comparision.

3.2 *Reagents*

3.2.1 *Indicators* — Prepare universal indicator by disolving 0·05 g of methyl orange 0·15 g of methyl red, 0·3 g of bromethymol blue and 0·35 g of phenolphthalein in one litre of alcohol (66 percent). The colour changes are:

p*H*	*Colour*
up to 3	Red
4	Orange red
5	Orange
6	Yellow
7	Yellowish green
8	Greenish blue
9	Blue
10	Violet
11	Reddish voilet

3.2.1.1 Prepare other indicators as given in Table 2.

TABLE 2 INDICATORS

Sl No.	Name of Indicator	pH Range	Colour Change	Method of Preparation
(1)	(2)	(3)	(4)	(5)
(i)	Thymol blue (acid range)	1·2 to 2·8	Red to yellow	Triturate 0·10 g in 10·75 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(ii)	Bromophenol blue	3·0 to 4·6	Yellow to blue violet	Triturate 0·10 g in 7·45 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(iii)	Bromocresol green	3·8 to 5·4	Yellow to blue	Triturate 0·10 g in 7·15 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(iv)	Methyl red	4·2 to 6·3	Red to yellow	Triturate 0·10 g in 18·60 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(v)	Bromocresol purple	5·2 to 6·8	Yellow to blue violet	Triturate 0·10 g in 9·25 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(vi)	Bromothymol blue	6·0 to 7·6	Yellow to blue	Triturate 0·10 g in 8·00 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(vii)	Phenol red	6·8 to 8·4	Yellow to red	Triturate 0·10 g in 14·20 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml

(Continued)

TABLE 2 INDICATORS — *Contd*

Sl No.	Name of Indicator	*p*H Range	Colour Change	Method of Preparation
(viii)	Cresol red	7·2 to 8·8	Yellow to red	Triturate 0·10 g in 13·10 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(ix)	Thymol blue (alkali range)	8·0 to 9·6	Yellow to blue	Triturate 0·10 g in 10·75 ml of N/50 sodium hydroxide solution and dilute with water to 250 ml
(x)	Thymolphthalein	9·3 to 10·5	Colourless to blue	Dissolve 0·10 g in 100 ml of rectified spirit [*see* IS : 323-1959 Specification for rectified spirit (*revised*)].
(xi)	Thymol violet	9·0 to 13·0	Yellow to green to violet	Dissolve 0·10 g of tropaeolin 0 in 100 ml of water. Dissolve 0.04 g of thymolphthalein in a mixture of 50 ml of rectified spirit and 50 ml of water. Mix one part of tropaeolin O solution with 4 parts of thymolphthalein solution

3.2.2 *Buffer solutions* — Prepare buffer solutions as given in IS : 3225-1965 'Metheds for preparation of buffer solutions '.

3.3 *Procedure* — Take 100 ml of the sample in a hard glass tube and determine the approximate *p*H by using the universal indicators. Repeat using a solution of the indicator (about 1/20 of the volume of the liquid being tested) which corresponds to the approximate *p*H found above. Compare the colour produced with a series of buffer solutions of known *p*H each containing the same proportion of the indicators.

3.4 *Report* — Report the *p*H of that buffer solution which matches with that of the sample to the nearest 0·1 unit.

EXPLANATORY NOTE

*p*H value is the logrithm of reciprocal of hydrogen ion activity in moles per litre. In water solution, variations in *p*H value from 7 are mainly due to hydrolysis of salts of strong bases and weak acids or *vice versa.* Dissolved gases such as carbon dioxide, hydrogen sulphide and ammonia also affect *p*H value of water. The overall *p*H value range of natural water is generally between 6 and 8. In case of alkaline thermal spring waters *p*H value may be more than 9 while for acidic thermal spring waters the *p*H may be 4 or even less than 4. Industrial wastes may be strongly acidic or basic and their effect on *p*H value of receiving water depends on the buffering capacity of water. The *p*H value obtained in the laboratory may not be the same as that of water at the time of collection of samples due to loss or absorption of gases, reactions with sediments, hydrolysis and oxidation or reduction taking place within the sample bottle. *p*H value should preferably be determined at the time of collection of sample.

The *p*H value may be determined either electrometrically or colorimetrically. The electrometric method is more accurate but requires special apparatus. The colorimetric method is simple and requires less expensive apparatus, and is sufficiently accurate for general work. It is, however, subject to interference by colour, turbidity, high saline content, free chlorine and various oxidants and reductants.

This method supersedes clause 9 of IS : 2488 (Part I)-1966 'Methods of sampling and test for industrial effluents, Part I' and clause 8 of IS : 3025-1964 'Methods of sampling and test (physical and chemical) for water used in industry'.

Printed at New India Printing Press, Khurja, India