

Indian Standard

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

PART 21 TOTAL HARDNESS

(First Revision)

(Incorporating Amendment No. 1)

1. Scope — Prescribes two methods for determination of total hardness, namely:

- Ethylenediamine tetraacetic acetate acid (EDTA) method, and
- Method based on analytical data.

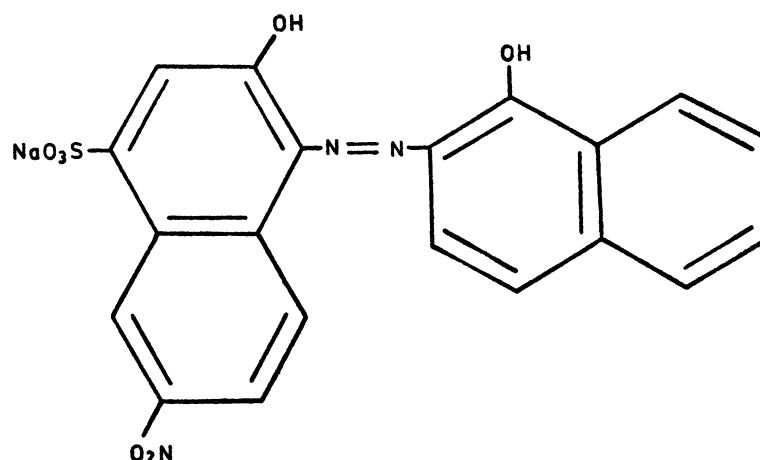
1.1 The first method is based on the reaction of calcium and magnesium salts with ethylenediamine tetra acetic acid or its disodium salt and is applicable to all types of water but not applicable to waste water. The analytical data method is based on computation from analytical results of the sample and is applicable to water and waste water. In case of dispute, the method based on analytical data shall be used.

2. EDTA Method

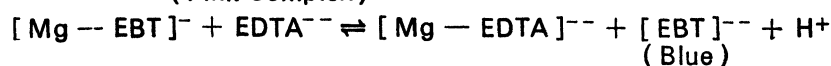
2.1 Principle — This method depends on ability of ethylenediamine tetraacetic acid ($C_{10}H_{16}O_8N_2$)



or its disodium salt to form stable complexes with calcium and magnesium ions. When the dye eriochrome black T (EBT) ($C_{20}H_{13}N_3O_7S$)



is added to a solution containing calcium and magnesium ions at pH 10.0 a wine red complex is formed. This solution is titrated with standard solution of disodium salt of EDTA, which extracts calcium and magnesium from the dye complex and the dye is changed back to its original blue colour. Eriochrome black T is used to indicate the end-point for the titration of calcium and magnesium together.

**2.2 Interferences**

2.2.1 The EDTA forms stable complexes with iron, manganese, copper, lead, cobalt, zinc and nickel. Heavy metal interferences can be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure may be used even when iron, copper, zinc or lead concentrations are as high as 10 mg/l.

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Price Group 2

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2.2.2 The higher oxidation states of manganese above Mn^{++} react rapidly with the indicator to form discoloured oxidation products. Hydroxylamine hydrochloride reagent may be used to reduce manganese to divalent state. The divalent manganese interference can be removed by addition of one or two small crystals of potassium ferrocyanide.

2.2.3 In presence of high aluminium concentrations, the blue colour near end point starts disappearing and reverts to red.

2.2.4 Phosphate and carbonate ions may precipitate calcium at the $p\text{H}$ of titration.

2.3 Reagents

2.3.1 Buffer solution — Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 ml concentrated ammonium hydroxide (NH_4OH), add 1.25 g of magnesium salt of EDTA and dilute to 250 ml with distilled water.

Store the solution in a polyethylene bottle tightly stoppered to prevent loss of ammonia or pick-up of carbon dioxide for no longer than 1 month. Dilute 10 ml of the solution to 100 ml with distilled water and check that the $p\text{H}$ value is 10.0 ± 0.1 .

2.3.2 In the absence of magnesium salt of EDTA, dissolve 1.179 g disodium salt of EDTA (AR quality) and 780 mg magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or 644 mg magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in 50 ml of distilled water. Add this solution to 16.9 g ammonium chloride and 143 ml concentrated ammonium hydroxide with mixing and dilute to 250 ml with distilled water. To attain the highest accuracy, adjust to exact equivalence through appropriate addition of a small amount of EDTA or magnesium sulphate or chloride. The exact amount can be determined by taking an appropriate aliquot of buffer and titrate it with disodium salt of EDTA as in **2.4.1**. Keep the solutions tightly stoppered to prevent loss of ammonia or absorbance of carbon dioxide and do not store for more than a month. Dilute 10 ml of the solution to 100 ml with distilled water and check that the $p\text{H}$ value is 10.0 ± 0.1 .

2.3.3 Standard calcium solution — 1.00 ml = 1.00 mg calcium carbonate (CaCO_3). Dry analytical grade calcium carbonate (CaCO_3) in an oven at 180°C for 1 hour. Weigh 1.000 g, suspend it in distilled water and add 1 : 1 hydrochloric acid AR quality, dropwise slowly to dissolve the solid. Use minimum amount of acid. Boil for a few minutes, cool, add a few drops of methyl red indicator and adjust to orange colour with 3N ammonium hydroxide or 1 : 1 hydrochloric acid. Dilute to 1 000 ml with distilled water.

2.3.4 Eriochrome black T indicator solution — Dissolve 0.40 g eriochrome black T and 4.5 g hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 100 ml 95 percent ethanol. This indicator is stable for more than 2 months. Alternatively, dissolve 0.5 g eriochrome black T in 100 ml triethanolamine or 2-methoxyethanol or mixed 0.5 g EBT dye and 100 g sodium chloride in a pestle and mortar. Store in a tightly stoppered bottle. All indicator formulations tend to deteriorate especially when exposed to moisture. If the end point colour change is not sharp enough it is either due to the presence of some interfering ions or due to deterioration of the indicator. In the latter case, addition of inhibitor sodium cyanide or sodium sulphide (NaCN or Na_2S) does not sharpen the end point colour change.

2.3.5 Inhibitors — For most waters inhibitors are not necessary. If interfering ions are present, inhibitors given in **2.3.5.1** to **2.3.5.4** may be used.

2.3.5.1 Hydroxylamine hydrochloride solution — Dissolve 45 g hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in demineralised water and dilute to 1 litre, or dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95 percent ethanol or isopropanol.

2.3.5.2 Potassium ferrocyanide crystals

2.3.5.3 Sodium sulphide inhibitor — Dissolve 5.0 g sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) or 3.7 g $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ in 100 ml distilled water. Tightly stopper so as to avoid excessive contact with air.

2.3.5.4 Sodium cyanide solution — Dissolve 2.5 g sodium cyanide (NaCN) in demineralised water and dilute to 100 ml. As sodium cyanide is extremely poisonous, it should be handled with care. The solution should not be made acidic and should be flushed down the drain with large amounts of water when it is to be disposed off.

2.3.6 Standard EDTA solution — Dissolve 3.723 g EDTA ($\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O} \cdot \text{N}_2 \cdot 2 \text{H}_2\text{O}$) which has been dried overnight in a sulphuric acid desiccator, in demineralised water and dilute to 1 000 ml. The reagent is stable for several weeks and large volume is usually prepared. Check the reagent by titrating 25 ml of standard calcium solution as described in 2.4.1. Store in polyethylene bottles.

2.4 Procedure

2.4.1 Standardization — Pipette 25.0 ml of standard calcium solution in a porcelain basin and adjust the volume to 50 ml with distilled water. Add 1 ml buffer solution (2.3.1). Add 1 to 2 drops of indicator (2.3.4), titrate slowly with continuous stirring until the redish tinge disappears, adding last few drops at 3 to 5 second interval. At the end point the colour is sky blue.

2.4.2 Procedure for drinking, surface and saline waters — Pipette an aliquot of water sample, maximum 50 ml, in a porcelain dish or 150-ml beaker and adjust the volume to approximately 50 ml. Add 1 ml hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$), solution. Add 1 to 2 ml buffer solution so as to achieve pH of 10.0 to 10.1. If the end point is not sharp (as determined by practice) add 2 ml sodium cyanide or sodium sulphide inhibitor solution. The addition of sodium cyanide or sodium sulphide may be omitted if copper, zinc, lead, cobalt and nickel are absent and if the sample contains less than 0.25 mg of iron and 0.025 mg of manganese. If manganese is present, add 1 or 2 small crystals of potassium ferri cyanide [$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$]. Stir and wait for at least 5 minutes until sodium ferri cyanide precipitates. Add 2 ml eriochrome black T indicator solution, titrate with standard EDTA solution stirring rapidly in the beginning and slowly towards the end till end point is reached when all the traces of red and purple colour disappear and solution is clear sky blue in colour. Blank titration, carried out in a similar way as that for sample, may be used for comparison.

2.4.3 Procedure for waste waters and highly polluted waters — Digest an aliquot of the sample with 3 ml of distilled concentrated nitric acid in a beaker on a hot plate and evaporate to near dryness cautiously making sure that the sample does not boil. Repeat digestion with nitric acid till the digestate is light in colour. Evaporate to near dryness and cool the beaker. Add a small quantity of 1 : 1 hydrochloric acid (5 ml) and warm on a hot-plate or steam-bath to dissolve the residue. Cool, adjust to a suitable volume and take an aliquot of this digested sample. Proceed as given in 2.4.2.

Note 1 — For water with very low hardness (less than 5 mg/l) micro burette may be used.

Note 2 — Selection of sample size may be made such that the result lies between 200 to 300 mg/l of hardness (as CaCO_3).

2.5 Calculation — Calculate the hardness as follows:

$$\text{Total hardness as } (\text{CaCO}_3), \text{ mg/l} = [100 (V_1 - V_2) / V_3] \times CF$$

where

V_1 = volume in ml of the EDTA standard solution used in the titration for the sample,

V_2 = volume in ml of the EDTA solution used in the titration for blank,

V_3 = volume in ml of the sample taken for the test,

$CF = X_1/X_2$ = correction factor for standardization of EDTA,

X_1 = volume in ml of standard calcium solution taken for standardization, and

X_2 = volume of ml of EDTA solution used in the titration.

2.6 Report — Report hardness in mg/l as CaCO_3 rounded to the first decimal place when the value is less than 10 mg/l and to the nearest unit if the value is more than 10 mg/l.

2.7 Precision and Accuracy — The precision is within 1 mg/l. The accuracy depends on the interfering substances present. In the absence of any interference, it is within 1 mg/l.

Note — Standard deviation of 1.2 mg/l has been reported.

3. Method Based on Analytical Data

3.1 Principle — Total hardness computed from the concentration of the different metallic cation (other than alkali metals) in the sample but most often the cations taken into account are calcium, magnesium, iron, aluminium, zinc, strontium, barium and manganese.

3.2 Calculation

$$\begin{aligned} \text{Total hardness (as } \text{CaCO}_3), \text{ mg/l} = & (2.497 \times \text{mg/l Ca}) + (4.116 \times \text{mg/l Mg}) + (2.69 \times \text{mg/l Fe}) + \\ & (5.567 \times \text{mg/l Al}) + (1.531 \times \text{mg/l Zn}) + (1.822 \times \text{mg/l Mn}) + \\ & (0.894 \times \text{mg/l Ba}) + (1.319 \times \text{mg/l Sr}). \end{aligned}$$

E X P L A N A T O R Y N O T E

Total hardness of water is the sum of the concentrations of all the metallic cations other than cations of alkali metals, expressed as equivalent calcium carbonate concentration. In most natural waters, hardness is mainly due to calcium and magnesium ions. In some waters, measurable concentrations of iron, aluminium, manganese, barium, zinc and other metals may be present. When the hardness is numerically greater than the sum of carbonate alkalinity and bicarbonate alkalinity; the amount of hardness which is equivalent to total alkalinity is called 'carbonate hardness' and the amount of hardness in excess of this is called 'non-carbonate hardness'. Some waters containing high concentrations of borates, phosphates, silicates, may contribute to total alkalinity.

This edition 2.1 incorporates Amendment No. 1 (January 2000). Side bar indicates modification of the text as the result of incorporation of the amendment.