DETERMINATION OF HARDNESS OF WATER

Method WHO/M/26.R1
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1. Outline of method

The determination of the total hardness of water is based on a complexometric titration of calcium and magnesium with an aqueous solution of the disodium salt of EDTA at pH value of 10.

The determination of calcium in the presence of magnesium is based on the same principle, but at a pH value of 12. In this condition, magnesium ions are precipitated as hydroxide and do not interfere with the determination of calcium.

The magnesium present in the sample may be calculated by substracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination for equal volumes of the sample.

2. Scope

This method is intended to check the hardness of water used in the determination of some physical properties required for WHO specification (e.g. suspensibility of wettable powder, emulsion stability of emulsifiable concentrate).

3. Reagents

Ethylenediaminetetraacetic acid (EDTA), disodium salt, dihydrate (not less than 99% purity). Dry for 2 h at about 80^0C before use.

Calcium carbonate (not less than 99% purity). Dry for 4 h at about 105^0C before use.

Sodium hydroxide, 2 mol/l solution. Dissolve 8 g of NaOH in 100 mL of freshly distilled water. Store in a polyethylene bottle. Take precautions to avoid contamination by atmospheric carbon dioxide.

Buffer solution. Dissolve 67.5 g ammonium chloride (NH_4Cl) in 570 mL of ammonia solution (25% m/m, ds^{20} = 0.910 g/mL). Then, add 5.0 g of the disodium-magnesium salt of EDTA and dilute to 1000 mL with deionized water.

Store in a polyethylene bottle. Dilute 10 mL of the solution to 100 mL with water. If this solution fails to give a pH value of 10 $\pm$ 0.1, discard the original solution.

EDTA solution, 0.01 mol/L. Dissolve 3.725g of EDTA disodium salt in deionized water. Transfer, quantitatively, to a 1000 mL volumetric flask and make up to volume with deionized water. Store in a polyethylene bottle.

Standard calcium solution. Weigh (to the nearest 0.1 mg) 1.0 g of dried calcium carbonate and transfer to a 500 mL conical flask. Add slowly (drop by drop in the beginning), 21 mL of 1 mol/L hydrochloric acid solution. Swirl the contents of the flask until all the carbonate is dissolved. Add 200 mL of water, boil to expel the carbon dioxide and cool.

Add a few drops of methyl red indicator solution and adjust to an intermediate orange colour with 2 mol/L ammonium hydroxide solution or 1 mol/L hydrochloric acid solution, as required. Transfer, quantitatively, to a 1000 mL volumetric flask and make up to volume.

1 mL of this solution = 1 mg calcium carbonate.

Mordant black 11 (Eriochrome black T) (C.I. 14645), 0.5% solution. Dissolve 0.5 g in 100 mL of ethanol-water (80 + 20, v/v).

Or alternatively, dissolve 0.5 g in 100 mL of triethanolamine. Up to 25 mL ethanol may be added instead of triethanolamine to reduce the viscosity of the solution. The indicator solution is used in the determination of the total hardness of water.

Solochrome dark blue (calcon) (C.I. 15 705), 0.5% solution. Dissolve 0.5 g in 100 mL of methanol.

Or alternatively, use the: HSN indicator (calcon carboxylic acid) {2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid}.

Mix 0.2 g HSN indicator and 100 g of sodium chloride. These indicators are used in the determination of calcium.

4. Procedure

4.1 Standardization of EDTA solution

Pipette 20.0 mL of the calcium standard solution into a 250 mL conical flask and dilute to 100 mL, preferably with deionized water. Add 4 mL of the buffer solution and 6 drops of the Mordant black 11 solution. The colour of the solution should now turn to claret or violet and its pH value should be 10.0 $\pm$ 0.1.

Titrate with the EDTA solution, rather rapidly at the beginning and slowly towards the end of the titration. Add the EDTA solution until the colour of the solution starts to change from claret or violet to blue and then to a distinct blue endpoint ($\underline{t}$ mL).

1 mL of the EDTA solution equivalent to calcium carbonate (in mg)

$$E\,(CaC0_3) = \frac{20 \times 1 \text{ mg } (CaCO_3)}{\underline{t}}$$

4.2 Determination of total hardness (calcium + magnesium) of water

In case of WHO standard hard water:

Pipette 50.0 mL of the sample into a 250 mL conical flask and dilute to 100 mL, preferably with deionized water. Add 4 mL of the buffer solution and 6 drops of the Mordant black 11 solution.

Titrate with the EDTA solution as described in 4.1 to a distinct blue endpoint ($\underline{v}$ mL).

$$CaCO_3 \text{ content (in mg / l)} = \frac{\underline{v} \times E\,(CaCO_3) \times 1000}{50}$$

4.3 Determination of calcium in presence of magnesium

Pipette 50.0 mL of the sample into a 250 mL conical flask and dilute to 100 mL, preferably with deionized water. Add 2 mL of 2 mol/l of NaOH solution and approximately 0.2 g of the HSN indicator or 6 drops of the Solochrome dark blue solution. The colour of the solution should now turn to claret or violet and its pH value should be at least 12.0.

Titrate with the EDTA solution as described in 4.1 to a distinct blue endpoint ($\underline{v}_1$ mL).

$$CaCO_3 \text{ content (in mg / l)} = \frac{\underline{v}_1 \times E\,(CaCO_3) \times 1000}{50}$$

4.4 Determination of magnesium

The magnesium present in the sample may be calculated by substracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination, for equal volumes of the sample.

1 mL 0.01M EDTA = 0.2432 mg magnesium.