INTERNATIONAL STANDARD

ISO 2174

Third edition
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Surface active agents — Preparation of water with known calcium hardness

Agents de surface — Préparation d'une eau de dureté calcique déterminée

Reference number
ISO 2174 : 1990 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 2174 was prepared by Technical Committee ISO/TC 91, *Surface active agents.*

This third edition cancels and replaces the second edition (ISO 2174 : 1979), of which it constitutes a minor revision.

Annex A of this International Standard is for information only.

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Surface active agents — Preparation of water with known calcium hardness

1 Scope

1.1 This International Standard specifies a method of preparing water of known calcium hardness for use in testing surface active agents and products containing them.

1.2 Systematic investigations have shown that, in many tests on surface active agents with hard water, there is no essential difference between calcium hardness and magnesium hardness, so that these tests can usually be carried out with an aqueous solution of calcium chloride of known hardness.

If, in certain cases, it is necessary to use other ions that give rise to the hardness of water, this fact shall be mentioned in the test report.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1773 : 1976, *Laboratory glassware — Boiling flasks (narrow-necked).*

ISO 3696 : 1987, *Water for analytical laboratory use — Specification and test methods.*

3 Definition

For the purposes of this International Standard, the following definition applies.

water hardness: The property resulting from the presence of calcium and magnesium salts and, in special cases, salts of strontium and/or barium.

The unit of measurement of water hardness is the millimole per litre (mmol/l). 1 mmol/l of calcium hardness corresponds to 40,08 mg of calcium ions per litre.

The equivalents for other degrees of hardness of water, as well as other units used for measuring water hardness and the relationships between them, are given for information in annex A.

NOTE — Originally, the hardness of a sample of water was determined by measuring its power to destroy the foam formed by soap. This property is primarily due to the presence of calcium and magnesium, but salts of other metals, such as iron, aluminium and manganese, behave in a similar manner, although these seldom occur in natural waters.

4 Principle

Preparation of a stock solution by dissolving an appropriate quantity of calcium chloride in water. Determination of the calcium in this stock solution by complexometric titration with the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA) using a mixture of Mordant Black 11 (C.I. 14645) and methyl red as indicator.

Preparation of dilute solutions, of the hardness required, by dilution of appropriate volumes of the stock solution.

5 Reagents

All reagents shall be of recognized analytical grade and the water used shall be grade 3 as defined in ISO 3696.

5.1 Calcium chloride dihydrate ($CaCl_2.2H_2O$).

If the dihydrate is not available, use an equivalent quantity of another hydrate or the anhydrous salt.

5.2 Ammonia solution.

WARNING — Comply with safety instructions for the handling of poisonous substances.

Dilute 57 ml of ammonia solution (ϱ_{20} 0,90 g/ml) and 1 g of potassium cyanide[1] with water to 100 ml.

5.3 Disodium salt of EDTA (Na_2EDTA), standard volumetric solution, $c(Na_2EDTA.2H_2O)$ = 0,05 mol/l.

Dissolve 18,612 g of the disodium salt of (ethylenedinitrilo) tetraacetate dihydrate in water in a 1 000 ml one-mark volumetric flask (see 6.1), and make up to the mark with water.

1 ml of this solution, which is stable, is equivalent to 0,05 mmol, i.e. 2,004 mg, of calcium ions.

5.4 Mixed indicator.

5.4.1 Preparation of magnesium-disodium salt of EDTA ($MgNa_2EDTA$), hexahydrate

Dissolve 18,6 g of disodium (ethylenedinitrilo)tetraacetate dihydrate in 75 ml of very hot water.

To this solution add 12,3 g of magnesium sulfate heptahydrate dissolved in 25 ml of very hot water. Mix the two solutions thoroughly, cover the mixture and let it cool overnight. Pour off the supernatant solution and wash the residue three times with cold water, pouring off the washings each time.

Wash the crystals with water in a Buchner funnel and dry them under reduced pressure in a desiccator, or in an oven at a temperature of 85 °C.

5.4.2 Preparation of mixed indicator

Grind 200 mg of Mordant Black 11[2] (C.I. 14645) and 37 mg of methyl red with 50 g of ammonium chloride. Add 150 g of ammonium chloride and 10 g of $MgNa_2EDTA$ (5.4.1), and continue grinding until a homogeneous mixture is obtained. Store the mixed indicator in a glass bottle with a ground-glass stopper.

5.4.3 Notes

Because solutions of Mordant Black 11 are unstable, the mixed indicator is prepared and stored as a dry powder; it is used in the ground state with ammonium chloride and it reacts with magnesium ions.

The inclusion of $MgNa_2EDTA$ allows the indicator to react with calcium ions, whilst the addition of methyl red enhances the colour change at the end-point of the titration.

It is also possible to use buffered indicator tablets instead of the mixed indicator; the colour change is from red to green, via grey.

6 Apparatus

Ordinary laboratory apparatus and

6.1 One-mark volumetric flasks, capacity 250 ml and 1 000 ml, complying with ISO 1042.

6.2 One-mark pipettes, capacity 25 ml and 50 ml, complying with ISO 648.

6.3 Bottle, capacity 5 litres, made of dark-brown glass, with a ground-glass stopper.

6.4 Conical flask, capacity 250 ml, complying with ISO 1773.

6.5 Burette, capacity 50 ml, class A, complying with ISO 385-1.

6.6 Analytical balance.

7 Procedure

7.1 Preparation of stock solution

Dissolve 220,5 g of calcium chloride dihydrate (5.1) in water, dilute to 5 litres and store in the bottle (6.3).

From this solution, which contains about 300 mmol of calcium ions per litre, water of the required calcium hardness can be prepared by dilution.

7.2 Determination of calcium content of stock solution

Using a 50 ml pipette (see 6.2), take 50 ml of the stock solution prepared as described in 7.1, transfer it to a 250 ml one-mark volumetric flask (see 6.1) and make up to the mark with water.

Using a 25 ml pipette (see 6.2), take 25 ml of this solution and transfer it to the conical flask (6.4). Dilute with about 100 ml of water, and add 4 ml of ammonia solution (5.2) from a measuring cylinder and 0,3 g of the mixed indicator (5.4). Heat the mixture to about 40 °C and titrate it with Na_2EDTA solution (5.3) to the end-point colour change to green.

Calculate the calcium content c_0 of the stock solution, expressed in millimoles of calcium ions per litre, using the equation

$$c_0 = 0{,}05 \times V \times \frac{250}{25} \times \frac{1\,000}{50} = 10 \times V$$

where

V is the volume, in millilitres, of Na_2EDTA solution (5.3) used for the titration;

1) Potassium cyanide solution may be destroyed by treatment with sodium hypochlorite and hydrogen peroxide.

2) For example Eriochrome Black T.

0,05 is the actual concentration, expressed in moles of $Na_2EDTA.2H_2O$ per litre, of this solution.

7.3 Preparation of water of known calcium hardness

Calculate the volume V_0, expressed in millilitres, of stock solution required to prepare a given volume of solution of known calcium hardness from the equation

$$V_0 = \frac{V_1 c_1}{c_0}$$

where

V_1 is the required volume, in millilitres, of water of known hardness;

c_0 is the hardness, in millimoles of calcium ions per litre, of the stock solution calculated in 7.2;

c_1 is the required hardness, in millimoles of calcium ions per litre, of the solution of volume V_1.

Choose the volume V_1 so that it corresponds to the capacity of a one-mark volumetric flask, and in such a way that V_0 is more than 10 ml and less than 50 ml.

Fill the burette (6.5) with the stock solution (7.1).

Transfer the calculated volume V_0, measured to the nearest 0,1 ml, of the stock solution to a one-mark volumetric flask of capacity V_1 and make up to the mark with water.

Annex A
(informative)

Units used to express water hardness

Name of unit	Definition	Symbol	Conversion factors						
			Ca^{2+}		CaO		$CaCO_3$		
			mmol/l	meq/l	°d	mg/kg[1)]	°e	°a	°f
millimole per litre	1 mmol of calcium ions (Ca^{2+}) in 1 litre of water	mmol/l	1	2,000	5,600	100	7,020	5,850 0	10,00
milliequivalent per litre	20,04 mg of calcium ions (Ca^{2+}) in 1 litre of water	meq/l	0,500	1	2,800	50	3,510	2,925 0	5,00
German degree of hardness	10 mg of calcium oxide (CaO) in 1 litre of water	°d	0,178	0,357	1	17,8	1,250	1,044 0	1,78
milligram per kilogram	1 mg of calcium carbonate ($CaCO_3$) in 1 litre of water	mg/kg[1)]	0,010	0,020	0,056	1	0,070	0,058 5	0,10
English degree of hardness	1 grain of calcium carbonate ($CaCO_3$) in 1 gal (UK) of water	°e	0,142	0,285	0,798	14,3	1	0,829 0	1,43
American degree of hardness	1 grain of calcium carbonate ($CaCO_3$) in 1 gal (US) of water	°a	0,171	0,342	0,958	17,1	1,200	1	1,71
French degree of hardness	1 mol (= 100 g) of calcium carbonate ($CaCO_3$) in 10 m^3 of water	°f	0,100	0,200	0,560	10,0	0,702	0,585 0	1

1) The unit "part per million" (ppm) is often used for mg/kg.