International Standard 2174

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Surface active agents — Preparation of water with known calcium hardness

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

Second edition — 1979-11-01

UDC 661.185 : 546.212 : 543.32 **Ref. No. ISO 2174-1979 (E)**

Descriptors : surfactants, water, hardness (of water), preparations, complexometric analysis, calcium chlorides, determination of content, calcium, chemical reagents, units of measurement.

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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.

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

This second edition was submitted directly to the ISO Council, in accordance with clause 5.10.1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 2174-1972), which had been approved by the member bodies of the following countries :

Australia	Ireland	Spain
Austria	Israel	Sweden
Chile	Netherlands	Switzerland
Egypt, Arab Rep. of	New Zealand	Thailand
France	Poland	Turkey
Germany, F. R.	Portugal	United Kingdom
Greece	Romania	USSR
Hungary	South Africa, Rep. of	

The Member Bodies of the following countries had expressed disapproval of the document on technical grounds :

Belgium
Japan
USA

Printed in Switzerland

Surface active agents — Preparation of water with known calcium hardness

0 Introduction

Systematic investigations have shown that, in many tests on surface active agents with hard water, there is usually 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 should be mentioned in the test report.

1 Scope and field of application

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

2 References

ISO/R 385, *Burettes*.

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

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

ISO 1773, *Laboratory boiling flasks (narrow-necked)*.

3 Definition

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

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

The equivalents for other amounts of hardness of water, as well as the other units currently used for measuring hardness of water and the relation between them, are given for information in the annex.

NOTE — Originally the hardness of a water was evaluated as its power to destroy the lather 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. Determination of the calcium in this stock solution by complexometric titration with (ethylenedinitrilo)tetraacetic acid, *di*sodium salt, 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

The reagents shall be of recognized analytical quality. Distilled water, or water of at least equivalent purity shall be used.

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

If the dihydrate is not available, use an equivalent quantity of anhydrous calcium chloride or other hydrate.

5.2 Ammonia solution.

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

1) Comply with security instructions for the handling of poisonous substances. Potassium cyanide solution may be destroyed by treatment with sodium hypochlorite and hydrogen peroxide.

5.3 *Di*sodium EDTA, (Na_2EDTA) 0,050 mol/l standard volumetric solution.

Dissolve 18,612 g of *di*sodium ethylenedinitrilotetraacetate dihydrate in water and dilute to 1 litre.

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

5.4 Mixed indicator.

5.4.1 Preparation of magnesium EDTA ($MgNa_2EDTA$) hexahydrate

Dissolve 18,6 g of *di*sodium ethylenedinitrilotetraacetate dihydrate in 75 ml of very hot water.

To this solution add 12,3 g of magnesium sulphate heptahydrate dissolved in 25 ml of very hot water. When the two solutions have been carefully mixed, 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 on a filter 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[1] (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 (II) ions.

The inclusion of $MgNa_2EDTA$ allows the indicator to react with calcium(II) 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, the end-point corresponding to grey.

6 Apparatus

Ordinary laboratory apparatus and

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

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

6.3 Glass stoppered and dark amber-coloured bottle, capacity 5 litres.

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

6.5 Burette, capacity 50 ml, complying with ISO/R 385, class A.

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(II) ions per litre, water of the calcium hardness required can be prepared by dilution.

7.2 Determination of calcium content of stock solution

With a pipette (6.2) take 50 ml of the stock solution prepared as described in 7.1, run it into the 250 ml one-mark volumetric flask (6.1) and fill the flask to the mark with water.

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

The calcium (C_0) content of the stock solution, expressed in millimoles of $\left[\frac{1}{2}\ \mathrm{Ca(II)}\right]$ per litre is given by the formula

$$C_0 = 0{,}1 \times V \times \frac{250}{25} \times \frac{1\,000}{50} = 20 \times V$$

where V is the volume, in millilitres, of solution (5.3) used.

1) For example Eriochrome Black T.

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 formula

$$V_0 = \frac{V_1 \times C_1}{C_0}$$

where

V_0 is the required volume, in millilitres, of water of known hardness;

C_0 is the hardness, in millimoles per litre, of the stock solution;

C_1 is the hardness required, in millimoles per litre, of the solution V_1.

Choose the volume V_1 corresponding 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, to the nearest 0,1 ml, of the stock solution to a one-mark volumetric flask of capacity V_1 and dilute to the mark with water.

Annex

Units currently used for expressing the hardness of water

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(II) 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(II) 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.