International Standard 6058

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

Water quality — Determination of calcium content — EDTA titrimetric method

Qualité de l'eau — Dosage du calcium — Méthode titrimétrique à l'EDTA

First edition — 1984-06-01

UDC 543.3 : 543.24 : 546.41 **Ref. No. ISO 6058-1984 (E)**

Descriptors : water, quality, chemical analysis, determination of content, calcium, volumetric analysis.

Price based on 3 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (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 authorized 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 6058 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in January 1983.

It has been approved by the member bodies of the following countries:

- Australia
- Austria
- Belgium
- Brazil
- Canada
- China
- Czechoslovakia
- Denmark
- Finland
- France
- Germany, F. R.
- Hungary
- India
- Iran
- Iraq
- Italy
- Japan
- Korea, Dem. P. Rep. of
- Korea, Rep. of
- Netherlands
- New Zealand
- Norway
- Poland
- Romania
- South Africa, Rep. of
- Spain
- Sweden
- Switzerland
- Thailand
- United Kingdom
- USSR

No member body expressed disapproval of the document.

Printed in Switzerland

Water quality — Determination of calcium content — EDTA titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method using ethylenediaminetetraacetic acid (EDTA) for the determination of the calcium content of ground waters, surface waters and drinking waters. It can also be used for municipal and industrial raw waters, provided they do not contain interfering amounts of heavy metals.

The method is not applicable to sea waters and other similar waters with a high concentration of salts. It is applicable to waters with calcium contents ranging from 2 to 100 mg/l (0,05 to 2,5 mmol/l).

For waters containing more calcium than 100 mg/l, a diluted sample shall be used.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*[1]

ISO 5667, *Water quality — Sampling —*

Part 1: Guidance on the design of sampling programmes.

Part 2: Guidance on sampling techniques.

Part 3: Guidance on the preservation and handling of samples.[2]

3 Principle

Complexometric titration of calcium ions with an aqueous solution of the disodium salt of EDTA at a pH value of between 12 and 13. HSN, which forms a red complex with calcium, is used as the indicator. Magnesium is precipitated as the hydroxide and does not interfere with the determination.

In the titration, the EDTA first reacts with the free calcium ions and then with the calcium ions combined with the indicator. The indicator then changes its colour from red to bright blue.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sodium hydroxide, 2 mol/l, solution.

Dissolve 8 g of sodium hydroxide in 100 ml of freshly distilled water. Store in a polyethylene bottle.

NOTE — Take precautions to avoid contamination by atmospheric carbon dioxide.

4.2 EDTA, standard volumetric solution, $c(\text{Na}_2\text{EDTA}) \approx 10$ mmol/l.

4.2.1 Preparation

Dry a portion of the disodium salt of EDTA dihydrate ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$) at 80 °C for 2 h, dissolve 3,725 g of the dry salt in water and dilute to 1 000 ml in a volumetric flask.

Store the EDTA solution in a polyethylene bottle and check the concentration at regular intervals.

4.2.2 Standardization

Standardize the solution (4.2.1) against the calcium standard reference solution (4.3) by the procedure described in clause 7.

Use 20,0 ml of the calcium standard reference solution (4.3) and dilute to 50 ml.

4.2.3 Calculation of the concentration

The concentration of the EDTA solution, c_1, expressed in millimoles per litre, is given by the equation

$$c_1 = \frac{c_2 V_1}{V_2}$$

---

[1] At present at the stage of draft. (Partial revision of ISO/R 385-1964.)

[2] At present at the stage of draft.

where

c_2 is the concentration, expressed in millimoles per litre, of the calcium standard reference solution (4.3);

V_1 is the volume, in millilitres, of the calcium standard reference solution;

V_2 is the volume, in millilitres, of the EDTA solution used for the standardization.

4.3 **Calcium**, standard reference solution, $c(CaCO_3) = 10$ mmol/l.

Dry a sample of pure calcium carbonate for 2 h at 150 °C, and allow to cool to room temperature in a desiccator.

Place 1,001 g in a 500 ml conical flask, and moisten it with water. Add dropwise 4 mol/l hydrochloric acid until all the carbonate has dissolved. Avoid adding excess acid. Add 200 ml of water and boil for a few minutes to expel carbon dioxide. Cool to room temperature and add a few drops of methyl red indicator solution. Add 3 mol/l ammonia solution until the solution turns orange. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask and make up to the mark with water.

1 ml of the solution contains 0,400 8 mg (0,01 mmol) of calcium.

NOTE — Commercially available solutions may be used.

4.4 **HSN**, indicator.

Mix thoroughly 0,2 g HSN [2-hydroxy-1(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid] ($C_{21}H_{14}N_2O_7S{\cdot}3H_2O$) and 100 g of sodium chloride (NaCl).

NOTE — This indicator is also known under the name "calcon carboxylic acid".

Another indicator that may be used for calcium is calcein {2,7-bis [*N*, *N*-di-(carboxymethyl)-aminomethyl]-fluorescein} ($C_{30}H_{26}N_2O_{13}$).

5 Apparatus

Ordinary laboratory apparatus, and:

Burette, 25 ml capacity, graduated in divisions of 0,05 ml, conforming to the requirements of ISO 385/1, class A, or equivalent equipment.

6 Sampling and samples

The samples should be taken in accordance with the relevant parts of ISO 5667.

7 Procedure

7.1 Preparation of the test portion

The test portion should contain between 2 and 100 mg/l (0,05 and 2,5 mmol/l) of calcium. If a concentration in excess of 100 mg/l (2,5 mmol/l) is expected, dilute a known volume of test solution so as to bring the concentration within the required range and record the dilution factor F.

If the test portions have been acidified for preservation, neutralize them with the calculated amounts of the sodium hydroxide solution (4.1). In the calculation of the results, take into account any dilution of the sample or test portion by acid or alkali.

7.2 Determination

By means of a pipette, transfer 50,0 ml of the test solution to a 250 ml conical flask. Add 2 ml of the sodium hydroxide solution (4.1) and approximately 0,2 g of the HSN indicator (4.4).

Mix and titrate immediately. Add the EDTA solution (4.2) from a burette (clause 5) under continuous stirring. Titrate rather rapidly at the beginning and slowly towards the end of the titration. The end-point is reached when the colour has changed to a distinct blue. The colour should not change any more on addition of another drop of EDTA solution.

8 Expression of results

The calcium content, c_{Ca}, expressed in millimoles per litre, is given by the equation

$$c_{Ca} = \frac{c_1 V_3}{V_0}$$

where

c_1 is the concentration, expressed in millimoles per litre, of the EDTA solution;

V_0 is the volume, in millilitres, of the test portion;

V_3 is the volume, in millilitres, of EDTA used in the titration.

If required, the calcium content, ϱ_{Ca}, expressed in milligrams per litre, is given by the equation

$$\varrho_{Ca} = \frac{c_1 V_3}{V_0} \times A$$

where A is the relative atomic mass of calcium (40,08).

If a diluted test portion has been used, modify the calculation accordingly, using the dilution factor F.

9 Precision

Results obtained on the same test solution in different laboratories should agree within ± 5 mg/l in the range 30 to 100 mg/l.

10 Interferences

WARNING — Sodium cyanide is a poison. Take the necessary precautions when handling and disposing of the chemical. Solutions containing sodium cyanide must not be acidified.

The metal ions of aluminium, barium, lead, iron, cobalt, copper, manganese, tin and zinc interfere with the determination, either because they are titrated as calcium, or because they obscure the colour change at the end-point. Orthophosphate in concentrations greater than 1 mg/l precipitates calcium at the pH of the titration. Calcium carbonate may precipitate if the determination is performed too slowly or if the calcium content is high (above 100 mg/l or 2,5 mmol/l).

Interfering metal ions can be masked. The interference from iron at concentrations of 30 mg/l or less can be masked by the addition of either 250 mg of sodium cyanide or a few millilitres of triethanolamine to the sample just before the titration. Cyanide also minimizes interference from zinc, copper and cobalt, and triethanolamine reduces interference from aluminium. Ensure that the solution is alkaline before adding sodium cyanide.

If the interferences cannot be eliminated, use an atomic absorption method. A suitable method will form the subject of a future International Standard.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) complete identification of the sample;

c) the result, expressed in milligrams per litre, to the nearest 1 mg/l, or in millimoles per litre, to the nearest 0,02 mmol/l;

d) the preparation of the test portion (if any);

e) any deviation from the procedure specified in this International Standard or any other circumstances that may have affected the results.

Bibliography

[1] American Public Health Association, American Waterworks Association, Water Pollution Control Federation, Joint Editorial Board. *Standard Methods for the Examination of Water and Wastewater*, 15th ed., Denver, Colorado, USA, 1980, p. 185.

[2] Schwarzenbach, G. and Flaschka, H. *Complexometric Titrations*, 2nd ed., New York, Barnes & Noble, 1969.

[3] Who. *International Standards for Drinking-Water*, Geneva, World Health Organization, 1971.

This page intentionally left blank