# International Standard ISO 6059

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

# Water quality — Determination of the sum of calcium and magnesium — EDTA titrimetric method

*Qualité de l'eau — Dosage de la somme du calcium et du magnésium — Méthode titrimétrique à l'EDTA*

**First edition — 1984-06-01**

**UDC 543.3 : 543.24 : 546.41 : 546.46** **Ref. No. ISO 6059-1984 (E)**

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

Price based on 4 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 6059 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 the sum of calcium and magnesium — 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 sum of the calcium and magnesium concentrations in ground waters, surface waters and drinking waters.

The method is not intended for effluents and waters having a high concentration of salts, such as sea waters. The lowest concentration that can be determined is 0,05 mmol/l.

## 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 and magnesium with an aqueous solution of the disodium salt of EDTA at a pH value of 10. Mordant black 11, which forms a claret or violet colour in the presence of calcium and magnesium ions, is used as the indicator.

In the titration, the EDTA, reacts first with the free calcium and magnesium ions in solution, and then, at the equivalence point, with those calcium and magnesium ions which are combined with the indicator, liberating the indicator and causing the colour to change from claret or violet to blue.

The results are given in amount of substance concentration units. If the calcium content has been determined separately, the mass concentration of magnesium can be computed.

## 4 Reagents

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

### 4.1 Buffer solution.

Dissolve 67,5 g of ammonium chloride ($NH_4Cl$) in 570 ml of ammonia solution [25 % $(m/m)$; $\varrho_{20}$ = 0,910 g/ml]. Then add 5,0 g of the disodium magnesium salt of EDTA ($C_{10}H_{12}N_2O_8Na_2Mg$) and dilute to 1 000 ml with water.

Store the solution (shelf-life limited) 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 ± 0,1, discard the original solution.

### 4.2 EDTA, standard volumetric solution, $c(Na_2EDTA) \approx 10$ 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 **Mordant black 11**, indicator.

Dissolve 0,5 g of mordant black 11, the sodium salt of [1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid] ($C_{20}H_{12}N_3O_7SNa$), in 100 ml of triethanolamine [$(HOCH_2CH_2)_3N$]. Up to 25 ml ethanol may be added instead of triethanolamine to reduce the viscosity of the solution.

NOTE — To facilitate the detection of the end-point, the indicator may be modified by the addition of 0,17 g methanil salt (4-anilido-azobenzene-sulfonic acid sodium salt). The colour will now change from red to pale grey or green.

## 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 samples do not require pretreatment except that samples containing gross amounts of particulate matter should be filtered through a 0,45 µm pore size filter as soon as possible after collection. If filtration is carried out there is a risk of removing some calcium and magnesium.

Dilute test portions having a total calcium and magnesium content exceeding 3,6 mmol/l until they are below that concentration and record the dilution factor $F$.

If the test portions have been acidified for preservation, neutralize them with the calculated amounts of 2 mol/l sodium hydroxide solution. In the calculation of results, take into account any dilution of the sample, or test portion, by acid or alkali.

### 7.2 Determination

**7.2.1** By means of a pipette, transfer 50,0 ml of the test solution to a 250 ml conical flask. Add 4 ml of the buffer solution (4.1) and 3 drops of mordant black 11 indicator (4.4). The colour of solution should now turn to claret or violet and its pH value should be 10,0 ± 0,1.

Titrate immediately, adding 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. Add the EDTA solution when the colour of the solution starts to change from claret or violet to blue. The end-point is reached when the last red shade has disappeared. The colour should not change any more on addition of another drop of EDTA solution.

**7.2.2** Titrate an additional test portion in the following manner.

Transfer 50,0 ml of the test solution to a flask. Add an amount of EDTA solution that is 0,5 ml less than that consumed in the first titration (7.2.1). Add 4 ml of the buffer solution (4.1) and 3 drops of the mordant black 11 indicator (4.4). Add EDTA dropwise until the end-point is reached.

**7.2.3** If the consumption of EDTA solution is less than 4,5 ml, titrate using a larger test portion, and increase the volume of the buffer solution (4.1) in proportion.

If the consumption of EDTA solution exceeds 20 ml, titrate using a smaller test portion. Add water so that the starting volume is 50 ml.

## 8 Expression of results

The sum of the calcium and magnesium contents, $c_{Ca + Mg}$, expressed in millimoles per litre, is given by the equation

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

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 (normally 50 ml);

$V_3$ is the volume, in millilitres, of EDTA used in the titration (see 7.2.2).

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

For calculation of hardness, see the annex.

## 9 Precision

The repeatability of the procedure is ± 0,04 mmol/l, corresponding to approximately 2 drops of the EDTA solution.

## 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 and magnesium, or because they obscure the colour change at the end-point. Orthophosphate and carbonate ions may precipitate calcium at the pH of the titration. Also some organic matter may interfere with the determination.

The interference from iron ions at concentrations of 10 mg/l or less can be masked by the addition of 250 mg of sodium cyanide to the test portion. Cyanide also minimizes interference from zinc, copper and cobalt. 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 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.

# Annex

# Concepts of hardness of water

(This annex does not form part of the Standard.)

## A.0 Introduction

Hardness of water is an old concept used to describe the content of calcium and magnesium in waters. There are different kinds of hardness (total hardness, carbonate hardness and others) and various countries have adopted different definitions of the concept. Some definitions are given in clause A.1 as examples.

## A.1 Definitions

**A.1.1 total hardness:** The total concentration of calcium and magnesium.

**A.1.2 carbonate hardness:** Part of the total hardness, equivalent to the carbonate and hydrogen carbonate contents of the water.

## A.2 Scales of hardness

### A.2.1 German hardness degrees

1 German hardness degree (1 °DH) is the hardness caused by a calcium oxide content of 10 mg/l, or as an amount of substance concentration, 0,178 mmol/l.

NOTE — German hardness degrees are no longer in use.

### A.2.2 UK hardness degrees

1 UK hardness degree (1 °Clark) is the hardness caused by a calcium carbonate content of 1 grain per imperial gallon, i.e. 14,3 mg/l or as an amount of substance concentration, 0,143 mmol/l.

### A.2.3 French hardness degrees

1 French hardness degree is the hardness caused by a calcium carbonate content of 10 mg/l, or as an amount of substance concentration, 0,1 mmol/l.

### A.2.4 US hardness degrees

In the USA the hardness is reported in parts per million (ppm) of calcium carbonate, or milligrams of calcium carbonate per litre. 1 mg/l of calcium carbonate corresponds to an amount of substance concentration of 0,01 mmol/l.

## A.3 Conversion table

For conversion of hardness values the following table may be useful.

| | | | **Germany** | **UK** | **France** | **USA** |
|---|---|---|---|---|---|---|
| | | mmol/l | °DH | °Clark | degree F | ppm |
| | mmol/l | 1 | 5,61 | 7,02 | 10 | 100 |
| **Germany** | °DH | 0,178 | 1 | 1,25 | 1,78 | 17,8 |
| **UK** | °Clark | 0,143 | 0,80 | 1 | 1,43 | 14,3 |
| **France** | degree F | 0,1 | 0,56 | 0,70 | 1 | 10 |
| **USA** | ppm | 0,01 | 0,056 | 0,070 | 0,1 | 1 |