International Standard 7980

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Water quality — Determination of calcium and magnesium — Atomic absorption spectrometric method

Qualité de l'eau — Dosage du calcium et du magnésium — Méthode par spectrométrie d'absorption atomique

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Foreword

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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.

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Water quality — Determination of calcium and magnesium — Atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a method for the determination of dissolved calcium and magnesium by flame atomic absorption spectrometry. It is intended for the analysis of raw and drinking waters and can be used for waters having a calcium content of up to 50 mg/l and a magnesium content of up to 5 mg/l. For samples containing higher concentrations of calcium or magnesium a smaller volume of the sample must be taken for the analysis.

When using the air/acetylene flame and the dilution factor 1 in 10, as described in 6.1, the optimum range is 3 to 50 mg/l for calcium and 0,9 to 5 mg/l for magnesium.

2 Principle

Measurement by flame atomic absorption spectrometry after adding lanthanum chloride (if an air/acetylene flame is used) or caesium chloride (if a nitrous oxide/acetylene flame is used) to reduce interferences. For calcium the absorbance is measured at 422,7 nm and for magnesium at 285,2 nm.

3 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. (Commercially available, ready-made solutions may by used.)

3.1 Hydrochloric acid (HCl), ϱ = 1,18 g/ml.

3.2 Hydrochloric acid (HCl), 0,1 mol/l.

Dilute 8 ml of hydrochloric acid (3.1) to 1 litre.

3.3 Lanthanum chloride ($LaCl_3$) solution, containing 20 g of La per litre.

To a 1 litre one-mark volumetric flask add 24 g of lanthanum oxide (La_2O_3) (atomic absorption spectrometry grade). Slowly and cautiously add 50 ml of hydrochloric acid (3.1) while stirring to dissolve the lanthanum oxide. Make up to the mark with water.

3.4 Caesium chloride (CsCl) solution, containing 20 g of Cs per litre.

Dissolve 25 g of caesium chloride in 1 litre of hydrochloric acid (3.2).

3.5 Calcium, stock solution, 1 000 mg/l.

Dry a portion of calcium carbonate ($CaCO_3$) at 180 °C for 1 h and allow it to cool in a desiccator. Weigh 2,50 ± 0,01 g of the dried material and suspend this in 100 ml of water. Add slowly the minimum amount of hydrochloric acid (3.2) necessary to dissolve the calcium carbonate (approximately 250 ml). Boil briefly to expel dissolved carbon dioxide, then cool. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask and make up to the mark with hydrochloric acid (3.2).

Store the solution in a polyethylene or polypropylene bottle.

3.6 Magnesium, stock solution, 1 000 mg/l.

Dry a portion of magnesium oxide (MgO) at 180 °C for 1 h. Weigh 1,66 ± 0,01 g and dissolve in hydrochloric acid (3.2). Dilute with the same acid to 1 000 ml in a one-mark volumetric flask.

Store the solution in a polyethylene bottle.

3.7 Calcium-magnesium, standard solution corresponding to 20 mg of Ca and 2 mg of Mg per litre.

With pipettes, transfer 20,0 ml of the calcium stock solution (3.5) and 2,0 ml of the magnesium stock solution (3.6) to a 1 000 ml one-mark volumetric flask. Make up to the mark with hydrochloric acid (3.2).

4 Apparatus

Usual laboratory equipment, and

Atomic absorption spectrometer, set up and operated according to the manufacturer's instructions, equipped with an appropriate burner for air/acetylene flame or nitrous oxide/acetylene flame and a hollow cathode lamp for calcium and magnesium determination.

NOTES

1 Clean all glassware with warm, dilute (1 + 1) hydrochloric acid and rinse with water.

2 The choice of flame to be used is left to the user of this International Standard. It has been claimed that the nitrous oxide/acetylene flame is to be preferred for samples with a high content of dissolved matter, or which contain phosphate, sulfate, aluminium or silica. In general the nitrous oxide/acetylene flame should be used if the composition of the sample is complex or unknown.

5 Sampling

Samples shall be collected in clean polyethylene or polypropylene bottles. As soon as possible after collection, acidify them with 8 ml of hydrochloric acid (3.1) per litre of sample, in order to reduce their pH value and prevent precipitation of calcium carbonate. Samples shall be analysed as soon as possible after collection.

6 Procedure

6.1 Preparation of test solution for presentation to instrument

Samples containing particulate material after acidification shall be filtered to prevent clogging of the nebulizer and burner systems.

Prepare a relevant number of 100 ml one-mark volumetric flasks. To each of these add 10 ml of the lanthanum chloride solution (3.3) if an air/acetylene flame is to be used, or 10 ml of the caesium chloride solution (3.4) if a nitrous oxide/acetylene flame is to be used.

With a pipette, add 10,0 ml of the sample, and make up to the mark with hydrochloric acid (3.2).

If the concentrations of calcium or magnesium in the original sample are above the ranges listed in table 2 then an appropriately smaller volume of the sample shall be used.

6.2 Blank test

Carry out a blank test simultaneously with the determination, using the same reagents in the same quantities and following the same procedure, but replacing the volume of the test sample used in 6.1 by an identical volume of water.

6.3 Preparation of the set of calibration solutions

To a series of seven 100 ml one-mark volumetric flasks, add to each either 10 ml of the lanthanum chloride solution (3.3) if an air/acetylene flame is to be used, or 10 ml of the caesium chloride solution (3.4) if a nitrous oxide/acetylene flame is to be used.

With the aid of pipettes add 0; 2,5; 5; 10; 15; 20; and 25 ml of the calcium-magnesium standard solution (3.7) and make up to the mark with hydrochloric acid (3.2).

The calibration solutions will have the concentrations shown in table 1.

Table 1 — Concentration of calibration solutions

Volume of Ca-Mg standard solution (ml)	0	2,5	5	10	15	20	25
Calcium content (mg/l)	0	0,5	1	2	3	4	5
Magnesium content (mg/l)	0	0,05	0,1	0,2	0,3	0,4	0,5

NOTE — These concentrations apply when using the air/acetylene flame. When the nitrous oxide/acetylene flame is used, it may be appropriate to use other concentrations.

Table 2 — Wavelength and optimum concentration ranges

		Calcium	**Magnesium**
Wavelength (nm)		422,7	285,2
Analyte content (mg/l)	Air/acetylene flame	3 to 50	0,9 to 5
	Nitrous oxide/acetylene flame	2 to 20	0,2 to 2

6.4 Calibration and determination

Carry out the measurements at the wavelengths shown in table 2.

Aspirate the calibration and blank solutions in random order and aspirate hydrochloric acid (3.2) between each. Prepare calibration graphs for calcium and magnesium by plotting the appropriate absorbance readings against the calcium and magnesium contents. It is essential that the calibration graph be linear for the concentration ranges given above. If it is not linear, check for and eliminate sources of error and repeat the calibration.

Aspirate the test solutions, with an aspiration of hydrochloric acid (3.2) between each, and determine the absorbances.

NOTES

1 It is good practice to check the slope of the calibration graphs at regular intervals (for example every 10 samples).

2 When using an air/acetylene flame, interference from refractory compounds containing phosphate, sulfate, aluminium or silica is minimized by the addition of lanthanum chloride. When using a nitrous oxide/acetylene flame ionization effects are minimized by the addition of caesium chloride.

7 Expression of results

7.1 Calculation

Read from the calibration graph the actual concentrations of calcium and magnesium in the test solutions and in the blank. From these values, calculate the calcium and magnesium contents of the test sample, taking into account the volume of hydrochloric acid used for acidification, the volume of test sample taken (normally 10 ml), the total volume of the volumetric flask (100 ml), and the blank value as follows.

The mass concentrations of calcium, $\varrho_{\mathrm{Ca},1}$, and of magnesium, $\varrho_{\mathrm{Mg},1}$, expressed in milligrams per litre, are given by the equations

$$\varrho_{\mathrm{Ca},1} = \varrho_{\mathrm{Ca},2} \frac{fV_1}{V_0}$$

$$\varrho_{\mathrm{Mg},1} = \varrho_{\mathrm{Mg},2} \frac{fV_1}{V_0}$$

where

$\varrho_{\mathrm{Ca},2}$ is the concentration, expressed in milligrams per litre, of calcium calculated from the calibration graph, having taken into account the blank value;

$\varrho_{\mathrm{Mg},2}$ is the concentration, expressed in milligrams per litre, of magnesium calculated from the calibration graph, having taken into account the blank value;

f is the dilution factor resulting from the addition of hydrochloric acid (3.1) to the test sample (normally 1,008; see clause 5);

V_0 is the volume, in millilitres, of the original sample (normally 10 ml) taken for analysis;

V_1 is the volume, in millilitres, of the volumetric flask referred to in 6.1 (100 ml).

If required, the amount of substance concentrations of calcium, c_{Ca}, and magnesium, c_{Mg}, expressed in millimoles per litre, may be obtained from the equations

$$c_{\mathrm{Ca}} = \frac{\varrho_{\mathrm{Ca},1}}{40,1}$$

$$c_{\mathrm{Mg}} = \frac{\varrho_{\mathrm{Mg},1}}{24,3}$$

Express the results to the nearest milligram per litre or to the nearest 0,02 millimole per litre.

7.2 Precision

In a single laboratory, using distilled water with added calcium concentrations of 9,0 and 36 mg/l the standard deviations were 0,3 and 0,6 mg/l respectively. Recoveries at both these levels were 99 %.

In an interlaboratory study with over 30 participating laboratories, four waters with calcium contents in the range 100 to 300 mg/l and magnesium contents from 7 to 85 mg/l were analysed. The coefficients of variation varied from 3,5 to 4,6 % for calcium and from 2,9 to 6,9 % for magnesium.

8 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) date and place of testing;

c) precise identification of the sample;

d) the results and the method of expression used;

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

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