International Standard 6920

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Crude sodium borates for industrial use — Determination of total and alkali-soluble calcium and magnesium contents — Titrimetric method

Borates de sodium bruts à usage industriel — Dosage du calcium et du magnésium total et du calcium et du magnésium solubles en milieu alcalin — Méthode titrimétrique

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Foreword

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Crude sodium borates for industrial use — Determination of total and alkali-soluble calcium and magnesium contents — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the total and alkali-soluble calcium and magnesium contents of crude sodium borates for industrial use. Modified procedures are described for special cases for the determination of total calcium content to eliminate interference by silica, iron or aluminium.

The method is applicable to products in which the calcium content, expressed as calcium, is not lower than 0,01 % (m/m) and not greater than 1,0 % (m/m), and in which the magnesium content, expressed as magnesium, is not lower than 0,01 % (m/m) and not greater than 0,2 % (m/m).

2 References

ISO 2217, *Crude sodium borates for industrial use — Determination of matter insoluble in alkaline medium and preparation of test solutions.*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Principle

Preparation of test solutions

a) by fusion of a test portion with sodium carbonate in the case of total calcium and magnesium contents, and

b) from an aliquot portion of solution A (see ISO 2217) for alkali-soluble calcium and magnesium contents.

Determination of the calcium content by titration of an aliquot portion of the test solution with ethyleneglycol-bis-(2-aminoethyl)-*N*, *N*, *N'*, *N'* tetra-acetic acid, *di*sodium salt (EGTA) solution using 2-carboxy-2'-hydroxy-5' sulphoformazyl-benzene (Zincon) as indicator.

Determination of the combined magnesium and calcium contents by titration of a further aliquot portion of the test solution with ethylenediaminetetra-acetic acid, *di*sodium salt (EDTA) solution, using Mordant black 11/potassium chloride as indicator, after addition of triethanolamine solution and buffer solution.

Calculation of the magnesium content by difference.

4 Reagents

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

4.1 Sodium carbonate, anhydrous.

4.2 Hydrochloric acid, approximately ϱ 1,19 g/ml, about 37 % (m/m) solution, diluted 1 → 2 with water.

4.3 Triethanolamine, 300 g/l solution.

4.4 Sodium hydroxide, approximately 400 g/l solution.

4.5 Sodium hydroxide, approximately 80 g/l solution.

4.6 Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), approximately 20 g/l solution.

4.7 Buffer solution, pH 10.

Dissolve 67,5 g of ammonium chloride in 250 ml of water, add 570 ml of ammonia solution (ϱ approximately 0,88 g/ml) and dilute with water to 1 litre.

4.8 Zinc chloride, standard reference solution corresponding to 1 g of zinc oxide per litre.

Calcine zinc oxide in a porcelain crucible for 2 h in a muffle furnace maintained at 550 ± 25 °C and then cool in a desiccator. Weigh, to the nearest 0,001 g, 1,0 g of the dried zinc oxide and dissolve in a mixture of 30 ml of water and 40 ml of the hydrochloric acid (4.2). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.9 EDTA, standard volumetric solution, c(EDTA) = 0,01 mol/l.

4.9.1 Preparation of the solution

Dissolve 3,725 g of ethylenediamine tetra-acetic acid, *di*sodium salt (EDTA), in a little water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1,00 ml of solution, c(EDTA) = 0,010 mol/l, corresponds to 0,403 mg of MgO or 0,243 mg of Mg.

4.9.2 Standardization of the solution

Transfer 25 ml of the zinc chloride standard reference solution (4.8) to a 250 ml conical flask and proceed according to 6.3.2.1.2 beginning with "Add 10 ml of the triethanolamine solution...".

4.9.3 Standardization factor

The standardization factor T_1 of the EDTA solution is given by the equation

$$T_1 = \frac{30{,}72\ m_1}{V_A}$$

where

m_1 is the mass, in grams, of dried zinc oxide used in the preparation of the zinc chloride standard reference solution (4.8);

V_A is the volume, in millilitres, of the EDTA solution used in the standardization (4.9.2).

4.10 Calcium chloride, standard reference solution corresponding to 1 g of calcium carbonate per litre.

Dry precipitated calcium carbonate ($CaCO_3$) for 1 h in an oven maintained at 105 ± 2 °C and then cool in a desiccator. Weigh, to the nearest 0,001 g, 1,0 g of the dried calcium carbonate and place in a 600 ml beaker. Add a mixture of 95 ml of water and 5 ml of the hydrochloric acid (4.2) and then boil the contents of the beaker for about 5 min to eliminate carbon dioxide. Cool to about 20 °C, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.11 EGTA, standard volumetric solution, c(EGTA) = 0,01 mol/l.

4.11.1 Preparation of the solution

Dissolve 3,90 g of ethyleneglycol-bis-(2-aminoethyl)-*N*, *N*, *N'*, *N'*-tetra-acetic acid (EGTA) in 20 ml of 40 g/l sodium hydroxide solution. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1,00 ml of solution, c(EGTA) = 0,010 mol/l, corresponds to 0,560 8 mg of CaO or 0,400 8 mg of Ca.

4.11.2 Standardization of the solution

Transfer 25 ml of the calcium chloride standard reference solution (4.10) to a 250 ml beaker and proceed according to the first paragraph of 6.3.2.1.1 beginning with "insert the electrodes of the pH meter (5.2)...".

4.11.3 Standardization factor

The standardization factor T_2 of the EGTA solution is given by the equation

$$T_2 = \frac{24{,}98\ m_2}{V_B}$$

where

m_2 is the mass, in grams, of dried calcium carbonate used in the preparation of the calcium chloride standard reference solution (4.10);

V_B is the volume, in millilitres, of the EGTA solution used in the standardization (4.11.2).

4.12 EGTA-zinc complex solution.

Dissolve 0,288 g of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in 50 ml of water. Transfer the solution quantitatively to a 200 ml one-mark volumetric flask, add 100 ml of the EGTA solution (4.11) by means of a pipette, dilute to the mark and mix.

4.13 Mordant black 11 indicator, 0,4 % (m/m) mixture with potassium chloride.

Triturate 0,1 g of Mordant black 11 with 25 g of potassium chloride until a homogeneous fine powder is obtained.

NOTE — The use of Mordant black 11, mixed with coloured complexones is permitted. For example, triturate 0,08 g of naphthol green B, 0,05 g of cresolphthalein complexone and 0,008 g of Mordant black 11 with 20 g of ammonium chloride.

4.14 Zincon, 0,5 g/l solution.

Dissolve 10 mg of 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in 20 ml of water and add 1 drop of approximately 40 g/l sodium hydroxide solution.

Prepare this solution just before use.

4.15 Ethanol, 95 % (V/V) solution.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Platinum crucible, with lid.

5.2 pH meter, fitted with glass and saturated calomel electrodes.

6 Procedure

6.1 Test portion

6.1.1 Total calcium and magnesium contents

Weigh, to the nearest 0,001 g, in the platinum crucible (5.1), 4 ± 0,1 g of the finely ground and mixed test sample.

6.1.2 Alkali-soluble calcium and magnesium contents

Weigh, to the nearest 0,01 g, in a 500 ml beaker, 10 ± 0,1 g of the finely ground and mixed test sample (see ISO 2217).

6.2 Blank test

6.2.1 Total calcium and magnesium contents

6.2.1.1 Total calcium content

Dissolve 2 ± 0,02 g of the sodium carbonate (4.1) in 50 ml of water and add 0,25 ml of the magnesium chloride solution (4.6) (equivalent to 1 mg of MgO). Add sufficient of the hydrochloric acid solution (4.2) to make the solution just acid and then 2 ml in excess. Boil gently to remove carbon dioxide, cool to room temperature and proceed as specified in 6.3.2.1.1, beginning with "insert the electrodes of the pH meter (5.2)...".

6.2.1.2 Combined total magnesium and calcium content

Dissolve 2 ± 0,02 g of the sodium carbonate (4.1) in 50 ml of water. Add sufficient of the hydrochloric acid solution (4.2) to make the solution just acid and then add 2 ml in excess. Boil gently to remove carbon dioxide. Cool to room temperature and proceed as specified in 6.3.2.1.2, beginning with "Add 10 ml of the triethanolamine solution (4.3)...".

6.2.2 Alkali-soluble calcium and magnesium contents

Transfer a 50,0 ml aliquot portion of solution B (see ISO 2217) to each of two 250 ml conical flasks. Treat one of the aliquot portions as specified in 6.3.2.2.1 (alkali-soluble calcium content) and the other as specified in 6.3.2.2.2 (combined alkali-soluble calcium and magnesium content).

6.3 Determination

6.3.1 Preparation of test solution

6.3.1.1 Total calcium and magnesium contents

Add 8 ± 0,1 g of the sodium carbonate (4.1) to the test portion (6.1.1) in the platinum crucible (5.1), mix thoroughly and cover the crucible with its lid.

If the test portion is anhydrous, heat the crucible with a Bunsen burner until a clear melt is obtained. If, however, the test portion is hydrated, adjust the flame of the Bunsen burner so that it is about 50 mm long and then clamp the Bunsen burner in a nearly horizontal position with the flame angled slightly downwards. Place the crucible (5.1) so that the flame plays on to the lid and heat in this manner for about 30 min. Then, using the bunsen burner in the normal manner, heat the crucible carefully from below until a clear melt is obtained.

Continue heating for 1 h, maintaining the temperature at just above the fusion point of the melt. Allow to cool, place the crucible on its side in a 250 ml beaker and add 100 ml of hot water. When the melt has dissolved, add sufficient of the hydrochloric acid solution (4.2) to make the solution just acid and then add a further 2 ml of the same acid. Boil gently to remove carbon dioxide, allow to cool to ambient temperature and transfer the solution quantitatively to a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix.

6.3.1.2 Alkali-soluble calcium and magnesium contents

Using the test portion (6.1.2), prepare the test solution as specified in ISO 2217 (solution A).

6.3.2 Titration

6.3.2.1 Total calcium and magnesium contents

6.3.2.1.1 Total calcium content

Transfer 50,0 ml of the test solution (6.3.1.1) to a 250 ml beaker, insert the electrodes of the pH meter (5.2) and carefully add the sodium hydroxide solution (4.4) until the pH is approximately 9. Then add the sodium hydroxide solution (4.5) until the pH is 9,5. Add 2 ml of the Zincon solution (4.14) and 1 ml of the EGTA-zinc complex solution (4.12). Stir for 1 min and with further swirling, titrate with the EGTA standard volumetric solution (4.11) until the colour of the solution just changes from blue to orange-red. The end-point may be observed visually or by means of a spectrometer set at a wavelength of approximately 480 nm.

If the sample is known to contain appreciable quantities of silica, iron or aluminium, carry out, as appropriate, the modified procedures specified in clause 8.

6.3.2.1.2 Combined total calcium and magnesium content

Transfer 50,0 ml of the test solution (6.3.1.1) to a 250 ml conical flask. Add 10 ml of the triethanolamine solution (4.3), 10 ml of the buffer solution (4.7) and 0,1 g of the indicator mixture (4.13). Titrate with the EDTA standard volumetric solution (4.9) until the colour just changes to blue.

6.3.2.2 Alkali-soluble calcium and magnesium contents

6.3.2.2.1 Alkali-soluble calcium content

Transfer 50,0 ml of the test solution (6.3.1.2) to a 250 ml conical flask. Add 2 ml of the triethanolamine solution (4.3), 3 ml of the sodium hydroxide solution (4.4), 15 ml of the ethanol (4.15), 2 ml of Zincon solution (4.14) and 1 ml of the EGTA-zinc complex solution (4.12). Stir for 1 min and, with further swirling, titrate with the EGTA standard volumetric solution (4.11) until the colour just changes from blue to orange-red. The end-point may be observed visually or by means of a spectrometer set at a wavelength of approximately 480 nm.

6.3.2.2.2 Combined alkali-soluble calcium and magnesium content

Transfer 50,0 ml of the test solution (6.3.1.2) to a 250 ml conical flask. Add 10 ml of the triethanolamine solution (4.3), 10 ml of the buffer solution (4.7) and 0,1 g of the indicator mixture (4.13). Titrate with the EDTA standard volumetric solution (4.9) until the colour just changes to blue.

7 Expression of results

The total and alkali-soluble calcium and magnesium contents, expressed as percentages by mass, are given by the following formulae:

7.1 Total calcium and magnesium content

7.1.1 Total calcium content

a) Expressed as CaO

$$0{,}560\ 8 \times \frac{T_2(V_1 - V_2) \times 200 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}224\ 3 \times T_2(V_1 - V_2)}{m}$$

b) Expressed as Ca

$$0{,}400\ 8 \times \frac{T_2(V_1 - V_2) \times 200 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}160\ 3 \times T_2(V_1 - V_2)}{m}$$

where

T_2 is the standardization factor of the EGTA solution, calculated in accordance with 4.11.3;

V_1 is the volume, in millilitres, of the EGTA standard volumetric solution (4.11) used in the determination of the total calcium content (6.3.2.1.1);

V_2 is the volume, in millilitres, of the EGTA standard volumetric solution (4.11) used in the blank titration for the determination of the total calcium content (6.2.1.1);

m is the mass, in grams, of the test portion (6.1.1).

7.1.2 Total magnesium content

a) Expressed as MgO

$$0{,}403\ 2 \times \frac{T_1(V_3 - V_4 - V_5) \times 200 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}161\ 3 \times T_1(V_3 - V_4 - V_5)}{m}$$

b) Expressed as Mg

$$0{,}243\ 2 \times \frac{T_1(V_3 - V_4 - V_5) \times 200 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}097\ 3 \times T_1(V_3 - V_4 - V_5)}{m}$$

where

V_3 is the volume, in millilitres, of the EDTA standard volumetric solution (4.9) used in the determination of the combined total calcium and magnesium (6.3.2.1.2);

V_4 is the volume, in millilitres, of the EDTA standard volumetric solution (4.9) used in the blank test titration for the determination of the combined, total calcium and magnesium content (6.2.1.2);

V_5 is the calculated volume, in millilitres, of the EDTA standard volumetric solution (4.9) which would be required to react with the calcium present in the test portion (6.1.1) used for the determination of the combined, total calcium and magnesium content (if the concentrations of the EDTA and EGTA standard volumetric solutions are numerically equal, $V_5 = V_1 - V_2$);

T_1 is the standardization factor of the EDTA solution, calculated in accordance with 4.9.3;

m is as defined in 7.1.1.

7.2 Alkali-soluble calcium and magnesium contents

7.2.1 Alkali-soluble calcium content

a) Expressed as CaO

$$0{,}560\ 8 \times \frac{T_2(V_1 - V_2) \times 500 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}560\ 8 \times T_2(V_1 - V_2)}{m}$$

b) Expressed as Ca

$$0{,}400\ 8 \times \frac{T_2(V_1 - V_2) \times 500 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}400\ 8 \times T_2(V_1 - V_2)}{m}$$

where

T_2 is the standardization factor of the EGTA solution, calculated in accordance with 4.11.3;

V_1 is the volume, in millilitres, of the EGTA standard volumetric solution (4.11) used in the determination of the alkali-soluble calcium content (6.3.2.2.1);

V_2 is the volume, in millilitres, of the EGTA standard volumetric solution (4.11) used in the blank titration for the determination of the alkali-soluble calcium content (6.2.2);

m is the mass, in grams, of the test portion (6.1.2).

7.2.2 Alkali-soluble magnesium content

a) Expressed as MgO

$$0{,}403\ 2 \times \frac{T_1(V_3 - V_4 - V_5) \times 500 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}403\ 2 \times T_1(V_3 - V_4 - V_5)}{m}$$

b) Expressed in Mg

$$0{,}243\,2 \times \frac{T_1(V_3 - V_4 - V_5) \times 500 \times 100}{m \times 1\,000 \times 50}$$

$$= \frac{0{,}243\,2 \times T_1(V_3 - V_4 - V_5)}{m}$$

where

V_3 is the volume, in millilitres, of the EDTA standard volumetric solution (4.9) used in the determination of the combined, alkali-soluble calcium and magnesium content (6.3.2.2.2);

V_4 is the volume, in millilitres, of the EDTA standard volumetric solution (4.9) used in the blank titration for the determination of the combined, alkali-soluble calcium and magnesium content (6.2.2);

V_5 is the calculated volume, in millilitres, of the EDTA standard volumetric solution (4.9) which would be required to react with the calcium present in the test portion (6.1.2) used for the determination of the combined, alkali-soluble calcium and magnesium content (if the concentrations of the EDTA and EGTA standard volumetric solutions are numerically equal, $V_5 = V_1 - V_2$);

T_1 is the standardization factor of the EDTA solution, calculated in accordance with 4.9.3;

m is as defined in 7.2.1.

8 Special cases

8.1 General

This clause describes modified procedures for the determination of total calcium content if interference by silica, iron, or aluminium is known or suspected.

8.2 Reagents

Use the reagents specified in clause 4 and

8.2.1 Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), approximately 10 g/l solution.

1 ml of this solution contains approximately 2 mg of Fe.

8.2.2 Congo red test paper.

8.3 Apparatus

8.3.1 Sintered glass crucibles, grade P 16, pore size index 10 to 16 µm (see ISO 4793).

8.4 Modified procedure

8.4.1 Silica present

Transfer 50,0 ml of the test solution (6.3.1.1) to a suitable evaporating basin, add 2 ml of the hydrochloric acid solution (4.2) and evaporate carefully until white fumes of hydrogen chloride are evolved. Cool and dilute to approximately 40 ml with water. Filter off any insoluble residue, collecting the filtrate in a 250 ml beaker. Wash the filter paper and residue with a small quantity of the hydrochloric acid solution (4.2), which has been further diluted 1 → 2 with water, collecting the washings, with the filtrate, in the 250 ml beaker. Using the combined filtrate and washings, carry out the procedure specified in 6.3.2.1.1.

8.4.2 Iron present

Follow the procedure specified in 6.3.2.1.1 until the pH has been adjusted to 9,5. Remove any residue by filtering the test solution through one of the sintered glass crucibles (8.3.1), wash the residue with a little water and quantitatively transfer the combined filtrate and washings back to the 250 ml beaker. Carry out the remainder of the procedure specified in 6.3.2.1.1.

8.4.3 Aluminium present

Transfer 50,0 ml of the test solution (6.3.1.1) to a 250 ml beaker and carefully add the sodium hydroxide solution (4.4) until the test solution is just neutral to the Congo red test paper (8.2.2). Add 1 more drop of the sodium hydroxide solution (4.4) and 2 ml of the iron(III) chloride solution (8.2.1). Heat the solution, allowing it to boil gently for about 2 min, and remove any residue by filtering the solution through one of the sintered glass crucibles (8.3.1). Do not wash the residue on the sintered glass crucible. Transfer the filtrate quantitatively to the 250 ml beaker and carry out the procedure specified in 6.3.2.1.1.

9 Test report

The test report shall include the following particulars:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in ISO 2217 to which reference is made, or regarded as optional.

Annex

ISO publications relating to crude sodium borates for industrial use

ISO 1918 — Determination of sulphur compounds — Volumetric method.

ISO 2216 — Determination of sodium oxide and boric oxide contents — Volumetric method.

ISO 2217 — Determination of matter insoluble in alkaline medium and preparation of test solutions.

ISO 2218 — Determination of loss in mass after heating at 900 °C.

ISO 2760 — Determination of total aluminium content — Titrimetric method.

ISO 2761 — Determination of total titanium content — Photometric method.

ISO 3120 — Determination of water content — Gravimetric method.

ISO 3122 — Determination of iron content — 2,2′-Bipyridyl photometric method.

ISO 3124 — Determination of iron soluble in alkaline medium — 2,2′-Bipyridyl photometric method.

ISO 3125 — Determination of aluminium soluble in alkaline medium — EDTA titrimetric method.

ISO 5933 — Determination of total nickel content of boric acid, boric oxide and *di*sodium tetraborates and the alkali-soluble nickel content of crude sodium borates — Furil α-dioxime photometric method.

ISO 5934 — Determination of alkali soluble copper and manganese contents — Zinc bis(dibenzyldithiocarbamate) and formaldehyde oxime photometric methods.

ISO 5935 — Determination of total and alkali-soluble silica contents — Molybdosilicate spectrometric method.

ISO 5936 — Determination of carbonate content — Gravimetric method.

ISO 6918 — Determination of total and alkali-soluble calcium and magnesium contents — Flame atomic absorption spectrometric method.

ISO 6920 — Determination of total and alkali-soluble calcium and magnesium contents — Titrimetric method.