International Standard ISO 5975

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

Chromium ores — Determination of calcium and magnesium contents — EDTA titrimetric method

Minerais de chrome — Dosage du calcium et du magnésium — Méthode titrimétrique à l'EDTA

First edition — 1983-07-01

UDC 553.461 : 543.24 : 546.41 : 546.46

Ref. No. ISO 5975-1983 (E)

Descriptors : chromate minerals, 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 5975 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in April 1982.

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

Austria
Brazil
China
Czechoslovakia
Egypt, Arab Rep. of
France
India
Italy
Japan
Poland
Romania
South Africa, Rep. of
Spain
Thailand
United Kingdom
USSR

The member body of the following country expressed disapproval of the document on technical grounds:

Australia

Printed in Switzerland

Chromium ores — Determination of calcium and magnesium contents — EDTA titrimetric method

1 Scope and field of application

This International Standard specifies an EDTA titrimetric method for the determination of the calcium and magnesium contents of chromium ores.

The method is applicable to products having a calcium content greater than 0,1 % (*m*/*m*) and magnesium content greater than 3,0 % (*m*/*m*).

This International Standard should be read in conjunction with ISO 6629.

2 Reference

ISO 6629, *Chromium ores and concentrations — Methods of chemical analysis — General instructions.*

3 Principle

Decomposition of the test portion with nitric and perchloric acids.

In the case of ores difficult to decompose — filtration of insoluble residue, incineration, treatment with hydrofluoric acid, fusion with sodium carbonate and combination of the melt solution with the main solution. Separation of the bulk of chromium as chromyl chloride.

Separation of iron, titanium, aluminium and manganese with ammonia solution in the presence of ammonium persulfate.

Determination of calcium in the aliquot portion of the main solution by titration with a standard volumetric EDTA solution (pH ≈ 12,5) using fluorexon as an indicator.

Determination of calcium and magnesium in the second aliquot portion of the main solution by titration with a standard volumetric EDTA solution (pH ≈ 10) using Eriochrome black T as an indicator.

Calculation of the magnesium content by the difference.

4 Reagents

4.1 Sodium carbonate, anhydrous.

4.2 Potassium chloride.

4.3 Nitric acid, ϱ 1,40 g/ml.

4.4 Perchloric acid, ϱ 1,50 g/ml.

4.5 Hydrochloric acid, ϱ 1,19 g/ml.

4.6 Hydrofluoric acid, ϱ 1,13 g/ml, 40 % (*m*/*m*) solution.

4.7 Ammonia solution, ϱ 0,91 g/ml.

4.8 Ammonia solution, diluted 1 + 100.

4.9 Ethanol, rectified.

4.10 Hydrochloric acid, diluted 1 + 3.

4.11 Hydrochloric acid, diluted 1 + 100.

4.12 Sulfuric acid, diluted 1 + 1.

4.13 Ammonium persulfate, 20 % (*m*/*m*) solution.

4.14 Sodium hydroxide, 40 % (*m*/*m*) solution.

Prepare the solution fresh using distilled water, previously boiled for 30 min and cooled.

4.15 Magnesium sulfate, 0,025 mol/l solution.

Dissolve 3,009 3 g of magnesium sulfate previously dried at 220 ± 10 °C till constant mass in water, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.16 Magnesium chloride, 0,025 mol/l solution.

Place 0,607 7 g of spectrally pure magnesium in a 400 ml beaker and add carefully 60 to 70 ml of the hydrochloric acid solution (4.10) in small portions. When dissolution of the magnesium chloride is complete, allow the solution to cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.17 Potassium dichromate, 0,5 % (*m*/*m*) solution.

4.18 ***Di*****sodium dihydrogen(ethylenedinitrilo)tetraacetate (EDTA),** standard volumetric solution, $c(\text{EDTA}) = 0{,}025$ mol/l.

4.18.1 Preparation of the solution

Place 9,3 g of EDTA in a 400 ml beaker, add 250 to 300 ml of water and heat at 50 to 60 °C to dissolve the EDTA. Filter the solution into a 1 000 ml one-mark volumetric flask, cool, dilute to the mark with water and mix.

Store the solution in a polyethylene bottle.

4.18.2 Standardization of the solution

Place 20 ml of the magnesium sulfate solution (4.15) or the magnesium chloride solution (4.16) in a 500 ml conical flask, dilute with water to 100 ml, add 30 ml of the buffer solution (4.21), 2 ml of the potassium dichromate solution (4.17) and 0,1 to 0,15 g of the mixture of Eriochrome black T indicator with potassium chloride (4.24). Mix the solution carefully after addition of each reagent.

Titrate the solution with the EDTA solution (4.18.1) slowly until the wine-red colour changes to blue. While titrating, it is recommended that a titrated solution be used for reference.

Carry out a blank test simultaneously.

4.18.3 Calculation

The concentration, c_{Mg}, of the EDTA solution, expressed in grams of magnesium per millilitre, is given by the formula

$$c_{\text{Mg}} = \frac{m_1 \times 20}{V_1 - V_2}$$

where

m_1 is the mass, in grams, of magnesium in 1 ml of the magnesium sulfate solution (4.15) or magnesium chloride solution (4.16);

V_1 is the volume, in millilitres, of EDTA solution, used for the titration;

V_2 is the volume, in millilitres, of EDTA solution, used for the titration of the blank test solution.

The concentration, c_{Ca}, of the EDTA solution, expressed in grams of calcium per millilitre, is given by the formula

$$c_{\text{Ca}} = c_{\text{Mg}} \times 1{,}648\,5$$

where 1,648 5 is the conversion factor from magnesium to calcium.

4.19 EDTA, standard volumetric solution, $c(\text{EDTA}) = 0{,}012\,5$ mol/l.

Transfer 250 ml of the EDTA solution (4.18) to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.20 EDTA, standard volumetric solution, $c(\text{EDTA}) = 0{,}005$ mol/l.

Transfer 100 ml of the EDTA solution (4.18) to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.21 Buffer solution.

Dissolve 68 g of ammonium chloride in 400 ml of water, add 570 ml of the ammonia solution (4.7), dilute to 1 000 ml with water and mix.

4.22 Malachite green, {4-[4-(dimethylamino)-α-phenylbenzylidene]-2,5-cyclohexadienylidene} dimethylammonium chloride ($C_{23}H_{25}ClN_2$), C.I. 42000, 0,2 % (m/m) alcoholic solution.

4.23 Fluorexon, {[fluorescein-2′, 7′-diyl-bis(methylenenitrilo)]tetraacetic acid} ($C_{30}H_{26}N_2O_{13}$).

Mix 0,1 g of the indicator with 10 g of the potassium chloride (4.2) and grind in a mortar.

4.24 Eriochrome black T, {sodium 3-hydroxy-4-[(1-hydroxy-2-naphthyl)azo]-7-nitro-1-naphthalenesulfonate} ($C_{20}H_{12}N_3NaO_7S$), C.I. 14645.

Mix 0,1 g of the indicator with 10 g of the potassium chloride (4.2) and grind in a mortar.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Photoelectric titrimeter.

6 Procedure

6.1 Test portion

Weigh 0,25 g of the sample for chemical analysis into a 250 ml beaker.

6.2 Decomposition of test portion

6.2.1 Moisten the test portion (6.1) with water, add 5 ml of the nitric acid (4.3) and 50 ml of the perchloric acid (4.4), cover with a watch glass and heat until fumes of perchloric acid appear.

Maintain the solution for 10 to 15 min at a temperature of perchloric acid fuming. Allow the contents of the beaker to cool, wash the walls of the beaker and the watch glass with water and heat again to perchloric fuming, continue heating for a further 10 to 15 min. Repeat the operation to dissolve the test portion completely.

6.2.2 In the case of ores difficult to decompose, add to the contents of the beaker 5 to 10 ml of the hydrochloric acid (4.5), 30 to 40 ml of water and heat to dissolve the salts. Filter off the precipitate on the rapid paper filter containing a small amount of ashless paper pulp. Wash the precipitate on the filter 10 to 12 times with the hot hydrochloric acid (4.11) and combine the washings with the main filtrate, the filtrate being reserved as the main solution.

Place the filter paper with the precipitate in a platinum crucible, dry, ash and ignite at 800 to 900 °C.

Allow the crucible with the residue to cool.

Moisten the residue with a few drops of water, add 3 or 4 drops of the sulfuric acid (4.12), 2 to 3 ml of the hydrofluoric acid solution (4.6), heat till the complete removal of sulfuric acid and ignite at 700 to 800 °C.

Allow the contents of the crucible to cool.

Fuse the residue with 1 to 2 g of the sodium carbonate (4.1) at 1 000 to 1 100 °C. Leach the melt while heating with 20 to 30 ml of the hot hydrochloric acid solution (4.11); combine the solution with the main solution.

6.3 Preparation of test solution

In both cases (6.2.1 and 6.2.2), evaporate the solution to fumes of perchloric acid.

Remove the watch glass and carefully add, drop by drop, the hydrochloric acid (4.5) along the walls of the beaker until brown fumes of chromyl chloride cease to evolve, chromium being reduced to the trivalent form. Cover the beaker with a watch glass and continue to heat the solution to oxidize chromium completely. Repeat the distillation of chromyl chloride to remove the bulk of chromium (until the solution is nearly colourless).

Add 5 to 7 ml of the hydrochloric acid (4.5), 30 to 40 ml of water and heat to dissolve the salts. Allow the contents of the beaker to cool. Wash the walls of the beaker and the watch glass with water.

Dilute the solution with hot water to 80 to 100 ml, add 5 ml of the ammonium persulfate solution (4.13) and the ammonia solution (4.7) until an ammoniacal odour persists. Add a further 2 to 3 ml. Heat the solution with the precipitate to decompose ammonium persulfate. In case an ammoniacal odour disappears, add ammonia solution (4.7) until the ammoniacal odour persists. Allow the precipitate to settle and filter it on a medium texture filter paper then wash with hot ammonia solution (4.8) 5 or 6 times. Reserve the filtrate with the washings as the main solution. Dissolve the precipitate on the filter with 40 to 50 ml of hot hydrochloric acid (4.10) collecting filtrate in the beaker in which the precipitation took place. Wash the filter 10 to 12 times with hot hydrochloric acid (4.11). Add 5 ml of the ammonium persulfate solution (4.13) and the ammonia solution (4.7) until an ammoniacal odour persists. Add a further 2 or 3 ml. Heat the solution with the precipitate to boiling and allow to boil to decompose ammonium persulfate. In case an ammoniacal odour disappears add ammonia solution (4.7) until ammoniacal odour persists.

Allow the precipitate to settle and filter it on a medium texture filter paper. Wash the beaker and the precipitate with hot ammonia solution (4.8) 5 or 6 times. Add the solution thus obtained to the main solution.

Evaporate the combined solution to 100 to 150 ml, transfer to a 250 ml one-mark volumetric flask, allow to cool, dilute to the mark with water and mix.

6.4 Determination of calcium content

Transfer a 100 ml aliquot of the test solution (6.3) to a 500 ml conical flask, add 3 or 4 drops of the malachite green alcoholic solution (4.22) and, while vigorously stirring, add in small portions the sodium hydroxide solution (4.14) to decolorize the solution and a further 8 to 10 ml in excess. Dilute the solution with water to 200 to 250 ml, add 0,1 to 0,15 g of the mixture of the indicator fluorexon with potassium chloride (4.23) and titrate the solution with the EDTA solution (4.20) visually [or using the photoelectric titrimeter (5.1)] for calcium contents from 0,1 to 1,0 % (*m*/*m*) or with the EDTA solution (4.19) for calcium contents over 1,0 % (*m*/*m*) until the fluorescent green colour of the solution changes to orange-red.

6.5 Determination of calcium plus magnesium content

Transfer 100 ml aliquot of the test solution (6.3) to a 500 ml conical flask, add 30 ml of the buffer solution (4.21), 2 ml of the potassium dichromate solution (4.17), 100 to 150 ml of water and 0,1 to 0,15 g of the mixture of Eriochrome black T indicator with potassium chloride (4.24). Mix the solution and titrate the solution with the EDTA solution (4.18) until the wine-red colour changes to blue. It is recommended that during titration comparison of the colour change be made with reference to the colour change in a previously titrated sample in order to obtain the exact end-point.

7 Expression of results

7.1 Calculation of calcium content

The calcium content, expressed as a percentage by mass, is given by the formula

$$\frac{(V_3 - V_4) \times f \times c_{\mathrm{Ca}} \times 100}{m_2} \times K$$

where

V_3 is the volume, in millilitres, of the standard volumetric EDTA solution (4.19 or 4.20), used for the determination of calcium content (6.4);

V_4 is the volume, in millilitres, of the standard volumetric EDTA solution (4.19 or 4.20), used for the titration of the corresponding blank test solution;

f is the factor for conversion of 0,005 mol/l or 0,012 5 mol/l EDTA solution to 0,025 mol/l solution:

f is equal to 0,2 in the case of 0,005 mol/l EDTA solution,

f is equal to 0,5 in the case of 0,012 5 mol/l EDTA solution;

c_{Ca} is the concentration of the standard volumetric EDTA solution (4.19 or 4.20), expressed as grams of calcium per millilitre, calculated in accordance with 4.18.3;

m_2 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution (6.3) taken for the determination of calcium content (6.4);

K is the conversion factor for the expression of the calcium content on the dry basis.

7.2 Calculation of magnesium content

The magnesium content, expressed as a percentage by mass, is given by the formula

$$\frac{[(V_5 - V_6) - (V_3 - V_4) \times f] \times c_{Mg} \times 100}{m_3} \times K$$

where

V_3 is the volume, in millilitres, of the standard volumetric EDTA solution (4.19 or 4.20), used for the determination of calcium content (6.4);

V_4 is the volume, in millilitres, of the standard volumetric EDTA solution (4.19 or 4.20), used for the titration of the corresponding blank test solution;

V_5 is the volume, in millilitres, of the standard volumetric EDTA solution (4.18), used for the determination of calcium plus magnesium content (6.5);

V_6 is the volume, in millilitres, of the standard volumetric EDTA solution (4.18), used for the titration of the corresponding blank test solution;

f is the factor for conversion of 0,005 mol/l or 0,012 5 mol/l EDTA solution to 0,025 mol/l solution:

f is equal to 0,2 in the case of 0,005 mol/l EDTA solution,

f is equal to 0,5 in the case of 0,012 5 mol/l EDTA solution;

c_{Mg} is the concentration of the standard volumetric EDTA solution (4.18), expressed in grams of magnesium per millilitre, calculated in accordance with 4.18.3;

m_3 is the mass, in grams, of the test portion corresponding to the aliquot of the test solution (6.3) taken for the determination of calcium plus magnesium content (6.5);

K is the conversion factor for the expression of the magnesium content on the dry basis.

7.3 Permissible tolerance between the results of duplicate determinations

7.3.1 Determinations of calcium content

Calcium content	**Permissible tolerance**
% (*m/m*)	% (*m/m*)
From 0,1 to 0,2	0,03
From 0,2 to 0,4	0,04
From 0,4 to 0,8	0,06
From 0,8 to 1,6	0,10
From 1,6 to 3,2	0,16

7.3.2 Determinations of magnesium content

Magnesium content	**Permissible tolerance**
% (*m/m*)	% (*m/m*)
From 3 to 6	0,25
From 6 to 12	0,30
Over 12	0,35

This page intentionally left blank

This page intentionally left blank