
International Standard



6331

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Chromium ores and concentrates — Determination of chromium content — Titrimetric method

Minerais et concentrés de chrome — Dosage du chrome — Méthode titrimétrique

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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.

International Standard ISO 6331 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 :

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

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

Italy

Chromium ores and concentrates — Determination of chromium content — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the chromium content of chromium ores and concentrates having a chromium content greater than 7 % (m/m).

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

2 Reference

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

3 Principle

Decomposition of a test portion by fusing with sodium peroxide. Leaching the melt with water, acidifying with sulfuric acid and removing the excess of hydrogen peroxide by boiling.

Oxidation of chromium(III) ions to chromate with ammonium peroxodisulfate in the presence of silver nitrate as catalyst.

Titration of chromium(VI) with ammonium iron(II) sulfate, the end-point being obtained either visually, by adding an excess of ammonium iron(II) sulfate and back-titrating with potassium permanganate, or directly by potentiometric titration.

4 Reagents

4.1 Sodium peroxide.

4.2 Sulfuric acid, ρ 1,84 g/ml.

4.3 Sulfuric acid, diluted 1 + 1.

4.4 Sulfuric acid, diluted 1 + 4.

4.5 Orthophosphoric acid, ρ 1,70 g/ml.

4.6 Manganese(II) sulfate, 100 g/l solution.

Dissolve 100 g of manganese(II) sulfate heptahydrate ($\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$) in 1 l of water.

4.7 Manganese(II) sulfate, 1 g/l solution.

Dilute 10 ml of the manganese(II) sulfate solution (4.6) to 1 l with water.

4.8 Silver nitrate, 1 g/l solution.

To ensure greater stability of the silver nitrate, add 0,5 ml of nitric acid for each 1 l of solution.

Store the solution in a brown glass bottle.

4.9 Ammonium peroxodisulfate, 250 g/l solution.

Prepare the solution immediately before use.

4.10 Sodium chloride, 50 g/l solution.

Dissolve 50 g of sodium chloride in 1 l of water.

4.11 Potassium permanganate, standard volumetric solution, $c(1/5 \text{ KMnO}_4) \approx 0,1 \text{ mol/l}$.¹⁾

4.11.1 Preparation of the solution

Dissolve 32 g of potassium permanganate in 1 000 ml of water, transfer to a 10 l brown glass bottle, add 9 l of water, mix and allow to stand for 7 to 10 days. Transfer the solution, using a siphon to another brown glass bottle (insert the siphon pipe in the bottle so that its end is 15 mm above the bottom). Alternatively, the solution can be filtered through calcined asbestos.

4.11.2 Standardization of the solution

Place 0,2 g of anhydrous sodium oxalate, previously dried at 105 to 110 °C, into a 250 ml conical flask and dissolve with slight heating in 75 ml of water, add 15 ml of the sulfuric acid solution (4.3) and heat to 70 to 80 °C. Titrate the solution thus

1) Hitherto expressed as "approximately 0,1 N standard volumetric solution".

obtained with the potassium permanganate solution (4.11.1) till the pink coloration persists for 1 to 2 min.

The titre T of the potassium permanganate solution is given by the equation

$$T = \frac{m \times 0,2587}{V}$$

where

T is the titre of the potassium permanganate solution, in grams of chromium per millilitre of the solution;

m is the mass, in grams, of the test portion of sodium oxalate;

V is the volume, in millilitres, of potassium permanganate solution used for the titration;

0,2587 is the conversion factor from sodium oxalate to chromium.

4.12 Ammonium iron(II) sulfate, standard volumetric solution, $c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}] \approx 0,1 \text{ mol/l.}^{(1)}$

4.12.1 Preparation of the solution

Dissolve 39,5 g of ammonium iron(II) sulfate hexahydrate in 200 ml of the sulfuric acid solution (4.4), filter off the solution into a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

4.12.2 Standardization of the solution

Place 0,2 g of potassium dichromate, recrystallized and dried at 180 to 200 °C to constant mass, in a 600 ml beaker, dissolve in 200 ml of water, add 50 ml of the sulfuric acid solution (4.4), mix and allow to cool. Place the electrodes (5.1.1) into the beaker, switch on the magnetic stirrer (5.1.2) and titrate with the ammonium iron(II) sulfate solution (4.12.1), until the maximum peak deflection on the voltmeter (5.1.3) is observed.

The titre T_1 of the ammonium iron(II) sulfate solution is given by the equation

$$T_1 = \frac{m \times 0,3535}{V}$$

where

T_1 is the titre of the ammonium iron(II) sulfate solution, in grams of chromium per millilitre of the solution;

m is the mass, in grams, of the test portion of potassium dichromate;

V is the volume, in millilitres, of ammonium iron(II) sulfate solution used for the titration;

0,3535 is the conversion factor from potassium dichromate to chromium.

The titre of the ammonium sulfate solution is variable and shall be checked in each series of determinations.

4.12.3 Calculation of the factor of ammonium iron(II) sulfate solution

Measure with a burette 20 ml of ammonium iron(II) sulfate solution into the blank test solution, previously titrated with the potassium permanganate solution (4.11). Then add 50 to 60 ml of water and titrate again with the potassium permanganate solution (4.11) till the slight pink coloration persists for 1 to 2 min.

$$f = \frac{V}{V_1}$$

where

V is the volume, in millilitres, of potassium permanganate solution (4.11) used for the titration;

V_1 is the volume, in millilitres, of ammonium iron(II) sulfate solution taken for the titration.

4.13 Potassium nitrite, 10 g/l solution.

4.14 Urea.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Apparatus for potentiometric titration

5.1.1 Pair of electrodes : indicator platinum electrode and reference electrode of calomel or tungsten.

5.1.2 Magnetic stirrer.

5.1.3 Millivoltmeter, high impedance electronic type for pH measurements is suitable for recording the potential deflection at the equivalence point whilst titrating with the chosen indicator/reference electrode system (5.1.1).

6 Procedure

6.1 Test portion

Weigh 0,5 g of the test sample.⁽²⁾

1) Hitherto expressed as "approximately 0,1 N standard volumetric solution".

2) International Standards dealing with the sampling of chromium ores are in preparation.

6.2 Decomposition of the test portion

Transfer the test portion (6.1) to a corundum, nickel, or iron crucible and add 3 to 4 g of the sodium peroxide (4.1). Mix the contents of the crucible with a glass rod, cover the contents with a layer of the sodium peroxide (1 to 2 g) and heat gently at 400 to 500 °C, then at 800 to 850 °C regularly mixing the contents of the crucible and maintaining the temperature constant until a homogenous mass is obtained (5 to 7 min).

Allow the crucible to cool, place it in a 600 ml beaker and leach the melt with 100 to 150 ml of hot water. Wash the crucible with water. If particles of the melt stick to the walls of the crucible, add 7 to 8 drops of the sulfuric acid solution (4.3) and 2 to 3 ml of water. After dissolution of the particles of the melt, combine the solution thus obtained with the contents of the beaker and again wash the crucible with water.

Add the sulfuric acid solution (4.3) until the precipitate of hydroxides dissolves, dilute the solution with water to 300 to 350 ml, add 10 ml of the sulfuric acid (4.2) and 5 ml of the orthophosphoric acid (4.5) and boil for 20 to 25 min to decompose the main mass of hydrogen peroxide.

Filter to remove the insoluble residue through a rapid filter paper or lavsan wool, collecting the filtrate in an 800 ml beaker. Wash the filter with residue 6 to 8 times with hot water and discard.

Add 10 ml of the silver nitrate solution (4.8) to the filtrate, and 1 ml of the manganese(II) sulfate solution (4.7) in cases where the ore contains less than 0,1 % (*m/m*) of manganese. Add 25 ml of the ammonium peroxodisulfate solution (4.9) and heat until the crimson colour appears as a result of the complete oxidation of chromium. Boil the solution for 12 to 15 min to decompose the ammonium peroxodisulfate, add 10 ml of the sodium chloride solution (4.10) and boil again for 8 to 10 min until decomposition of permanganic acid and coagulation of the silver chloride precipitate. Add 5 ml of the manganese(II) sulfate solution (4.7) and boil for about 3 min.

If the pink coloration persists, proceed with the determination as indicated above from the words "Boil the solution for 12 to 15 min..."

Cool the solution in running water to room temperature.

6.3 Determination

6.3.1 Titration with visual adjustment of the equivalence point

Add the ammonium iron(II) sulfate solution (4.12) from a burette to the beaker containing the test solution until the colour of the test solution changes to green from yellow [chromium(VI) and vanadium(V) are reduced to chromium(III) and vanadium(IV)]. Add a further 5 to 10 ml of the ammonium iron(II) sulfate solution in excess, using a burette. Titrate the solution with the potassium permanganate solution (4.11) until the pink coloration persists for 1 to 2 min.

NOTE — Simultaneously, vanadium(IV) is titrated with potassium permanganate solution. Therefore, the volume of ammonium iron(II) sulfate solution corresponds only to the chromium content.

6.3.2 Potentiometric titration

Add 60 ml of the sulfuric acid solution (4.4) to the beaker containing the test solution, place the pair of electrodes (5.1.1) into the beaker, switch on the magnetic stirrer (5.1.2) and titrate with the ammonium iron(II) sulfate solution until the maximum peak deflection on the millivoltmeter (5.3.1) is observed. At the end, the titration shall be carried out slowly.

NOTE — The volume of the reagent consumed corresponds to the total content of chromium and vanadium.

Add the potassium permanganate solution (4.11), drop by drop, until the pink colour appears. Allow to stand for 2 min, maintaining a pink colour, to oxidize vanadium. Reduce the excess of potassium permanganate solution by adding the potassium nitrite solution (4.13), drop by drop until the pink colour is discharged. Add 1 to 1,5 g of the urea (4.14) immediately to decompose the excess of potassium nitrite. Titrate the vanadium with the ammonium iron(II) sulfate solution until the maximum peak deflection on the millivoltmeter is observed.

The difference in the volumes of ammonium iron(II) sulfate solution used for the first and second titrations corresponds to the chromium content.

7 Expression of results

7.1 Calculation of chromium content in case of titration with visual adjustment of the equivalence point

The chromium content (Cr), expressed as a percentage by mass, is given by the formula

$$\frac{[(V_0 \times f - V_1) - (V_2 \times f - V_3)] \times T \times 100}{m} \times K$$

where

V_0 is the volume, in millilitres, of the ammonium iron(II) sulfate solution used in the determination;

V_1 is the volume, in millilitres, of the potassium permanganate solution used for titration of the excess of ammonium iron(II) sulfate solution;

V_2 is the volume, in millilitres, of the ammonium iron(II) sulfate solution added to the blank test solution;

V_3 is the volume, in millilitres, of the potassium permanganate solution used for titration of the excess of ammonium iron(II) sulfate solution in the blank test;

f is the factor of the ammonium iron(II) sulfate solution for a concentration of 0,1 mol/l;

T is the titre of the potassium permanganate solution, in grams of chromium per millilitre of the solution;

m is the mass, in grams, of the test portion;

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

7.2 Calculation of chromium content in case of potentiometric titration

The chromium content (Cr), expressed as a percentage by mass, is given by the formula

$$\frac{(V_1 - V_2) \times T_1 \times 100}{m} \times K$$

where

V_1 is the volume, in millilitres, of the ammonium iron(II) sulfate solution used for the titration of chromium and vanadium;

V_2 is the volume, in millilitres, of the ammonium iron(II) sulfate solution used for the titration of vanadium;

T_1 is the titre of the ammonium iron(II) sulfate solution, in grams of chromium per millilitre of the solution;

m is the mass, in grams, of the test portion;

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

7.3 Conversion from chromium content to chromium oxide content (percentage)

$$\text{Cr}_2\text{O}_3 [\% (m/m)] = 1,461\,5 \text{ Cr } [\% (m/m)]$$

7.4 Permissible tolerance between the results of duplicate determinations

Chromium content	Permissible tolerance
% (m/m)	% (m/m)
From 7 to 15	0,2
From 15 to 30	0,3
Over 30	0,4