



**International
Standard**

ISO 6331

**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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 132, *Ferroalloys*.

This second edition cancels and replaces the first edition (ISO 6331:1983), which has been technically revised.

The main changes are as follows:

- in [6.1](#) (previously in 5.1), the description for the potentiometric titration apparatus has been changed to be in line with the current status of the development of the instrument, including the description of electrodes pairs in [6.1.1](#), titration assembly in [6.1.2](#) and millivoltmeter in [6.1.3](#);
- in [6.2](#), the specifications of crucibles have been added;
- in [8.1](#), the pre-treatment of test portion and the recommended test portion masses have been adjusted;
- in [8.4](#) (previously in 6.2), the decomposition conditions of the test portion have been changed including the specification of beaker, the detailed use of crucibles, the diluted concentration of sulfuric acid, and the option of whether to filter residues or not;
- in [8.5.2](#) (previously in 6.3.2), the 60 ml of the sulfuric acid solution has been omitted;
- in [9.4](#) (previously in 7.4), the paragraph of the "permissible tolerances on results" has been replaced with the "general treatment of results";
- [Clause 10](#), the test report has been added;
- [Annex A](#) (informative), "Additional information on the international interlaboratory test" has been added;
- [Annex B](#) (normative), "Flow sheet of the procedure for the acceptance of test results" has been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document specifies a titrimetric method for the determination of the chromium content of chromium ores and concentrates having a chromium content greater than a mass fraction of 7,00 %.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6129, *Chromium ores — Determination of hygroscopic moisture content in analytical samples — Gravimetric method*

ISO 6153, *Chromium ores — Increment sampling*

ISO 6154, *Chromium ores — Preparation of samples*

ISO 80000-1:2022, *Quantities and units — Part 1: General*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Principle

Decompose a test portion by fusing with sodium peroxide. Leach the melt with water, acidify it with sulfuric acid, and remove the excess of hydrogen peroxide by boiling.

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

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

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 3 water as specified in ISO 3696.

5.1 Sodium peroxide, in powdered and granulated forms.

5.2 Sulfuric acid, ρ 1,84 g/ml.

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

5.4 Urea.

5.5 Sulfuric acid, diluted 1 + 1.

5.6 Sulfuric acid, diluted 1 + 4.

5.7 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.

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

Dilute 10 ml of the manganese (II) sulfate solution (see 5.7) to 1 l with water.

5.9 Silver nitrate, 1 g/l solution.

Dissolve 1 g of silver nitrate in 1 l of water. 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.

5.10 Ammonium peroxodisulfate, 250 g/l solution.

Dissolve 250 g of ammonium peroxodisulfate in 1 l of water. Prepare the solution immediately before use.

5.11 Sodium chloride, 50 g/l solution.

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

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

5.12.1 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 days 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.

5.12.2 Standardization of the solution

Place 0,2 g of anhydrous sodium oxalate, previously dried at 105 °C 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 (see 5.5) and heat to 70 °C to 80 °C. Titrate the solution thus obtained with the potassium permanganate solution (see 5.12) until the pink coloration persists for 1 min to 2 min.

Carry out a blank test, omitting anhydrous sodium oxalate.

The titre of the potassium permanganate solution (see 5.12), T_1 , is given by Formula (1):

$$T_1 = \frac{m_1 \times 0,2587}{V_1 - V_2} \quad (1)$$

where

T_1 is the titre of the potassium permanganate solution (see 5.12), in grams of chromium per millilitre of the solution;

m_1 is the mass, in grams, of the test portion of sodium oxalate;

V_1 is the volume, in millilitres, of potassium permanganate solution (see 5.12) used for titrating sodium oxalate;

V_2 is the volume, in millilitres, of potassium permanganate solution (see 5.12) used for titrating the blank test solution;

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

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

5.13.1 Preparation of the solution

Dissolve 39,5 g of ammonium iron (II) sulfate hexahydrate in 200 ml of the sulfuric acid solution (see 5.6), filter off the solution into a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

5.13.2 Standardization of the solution

Place 0,2 g of potassium dichromate, recrystallized and dried at 180 °C 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 (see 5.6), mix and allow to cool. Place the electrodes (see 6.1.1) into the beaker, switch on the magnetic stirrer (see 6.1.2) and titrate with the ammonium iron (II) sulfate solution (see 5.13), until the maximum peak deflection on the voltmeter (see 6.1) is observed.

Carry out a blank test, omitting potassium dichromate.

The titre of the ammonium iron (II) sulfate solution (see 5.13), T_2 , is given by Formula (2):

$$T_2 = \frac{m_2 \times 0,3535}{V_3 - V_4} \quad (2)$$

where

T_2 is the titre of the ammonium iron (II) sulfate solution (see 5.13), in grams of chromium per millilitre of the solution;

m_2 is the mass, in grams, of the test portion of potassium dichromate;

V_3 is the volume, in millilitres, of ammonium iron (II) sulfate solution (see 5.13) used for titrating potassium dichromate;

V_4 is the volume, in millilitres, of ammonium iron (II) sulfate solution (see 5.13) used for titrating the blank test solution;

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.

5.13.3 Calculation of the factor of ammonium iron (II) sulfate solution (to be carried out just before use).

Measure with a pipette 20 ml of ammonium iron (II) sulfate solution (see 5.13) into a 250 ml conical flask and dissolve with 50 ml to 60 ml of water. Titrate with the potassium permanganate solution (see 5.12) till the slight pink coloration persists for 1 min to 2 min.

The factor of ammonium iron (II) sulfate solution (see 5.13), f , is given by Formula (3):

$$f = \frac{V_5}{V_6} \quad (3)$$

where

V_5 is the volume, in millilitres, of potassium permanganate solution (see 5.12) used for the titration;

V_6 is the volume, in millilitres, of ammonium iron (II) sulfate solution (see 5.13) taken for the titration.

5.14 Potassium nitrite, 10 g/l solution.

Dissolve 10 g of potassium nitrite in 1 l of water.

6 Apparatus

Ordinary laboratory apparatus and the following shall be used.

6.1 Potentiometric titration apparatus

6.1.1 Pair of electrodes, indicator electrode (of platinum) with reference electrode (of tungsten, platinum, calomel or silver/silver chloride) or combined electrode of equivalent performance.

The manufacturer's instructions on the care and maintenance of these electrodes shall be followed.

6.1.2 Titration assembly, consisting of a 500 ml beaker, a burette and a magnetic stirrer.

6.1.3 Millivoltmeter, normally, a pH-meter can be used as a voltmeter. Commercial automatic titrators or potentiographs have an advantage over manual systems in that the titration curve is plotted and the end-point can be evaluated by interpolation of the curve rather than by calculation from the first or second derivative.

6.2 Crucible, Porcelain crucible, capacity 50 ml and having a lid. Corundum crucible, capacity 20 ml.

6.3 Glass boiling beads.

6.4 Volumetric glassware.

All volumetric glassware shall be class A in accordance with either ISO 385, ISO 648 or ISO 1042.

7 Sample

The sampling of chromium ores shall be in accordance with ISO 6153. The preparation of chromium ores shall be in accordance with ISO 6154.

8 Procedure

8.1 Test portion

Take a test portion from the sample dried at 105 °C to 110 °C, or an air-equilibrated sample as specified in [Table 1](#), and weigh to the nearest 0,000 2 g.

When using the sample dried at 105 °C to 110 °C, the test portion should be taken and weighed quickly in order to avoid reabsorption of moisture. Alternatively, when using an air-dried sample, determine the hygroscopic moisture content in accordance with ISO 6129, simultaneously with the taking of the test portion for the determination of chromium content.

Table 1 — Recommended test portion masses

Chromium content (presumed) % in mass fraction		Mass of test portion
≥	<	g
7,00	30,00	0,25
30,00	/	0,20

8.2 Blank test

Carry out a blank test in parallel with the analysis using the same quantities of all reagents but omitting the test portion. The purpose of the blank test in this method is to check the quality of reagents. If a significant blank titration value is obtained as a result of the blank test, check all reagents and rectify the problem.

8.3 Number of determinations

Carry out the determinations at least in duplicate, as far as possible under repeatability conditions, on each test sample.

NOTE Repeatability conditions exist where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment, within short intervals of time.

8.4 Decomposition of the test portion

Transfer the test portion (see [8.1](#)) to a corundum crucible (see [6.2](#)) and add 3 g to 4 g of the sodium peroxide (see [5.1](#)). Rotate gently to mix the contents of the crucible, then cover the contents with a layer of the sodium peroxide (see [5.1](#)) (1 g to 2 g). Place the corundum crucible (see [6.2](#)) into a porcelain crucible with a lid (see [6.2](#)). Heat gently at 400 °C to 500 °C, then at 800 °C to 850 °C and maintaining the temperature constant until a homogenous mass is obtained (5 min to 7 min).

Allow the crucible (see [6.2](#)) to cool, place the corundum crucible (see [6.2](#)) in a 500 ml beaker. If particles of the melt stick to the lid of the crucible (see [6.2](#)), add 7 drops to 8 drops of the sulfuric acid solution (see [5.5](#)) and 2 ml to 3 ml of warm water. After dissolution of the particles of the melt, combine the solution into the beaker. Add few glass boiling beads (see [6.3](#)) into the beaker. Leach the melt with 100 ml to 150 ml of hot water. Add the sulfuric acid solution (see [5.5](#)) until the precipitate of hydroxides dissolves, dilute the solution with water to 200 ml to 250 ml, add 20 ml of the sulfuric acid (see [5.5](#)) and 5 ml of the orthophosphoric acid (see [5.3](#)). Cover the beaker with a watch-glass and boil for 20 min to 25 min to decompose the main mass of hydrogen peroxide. Remove the crucible (see [6.2](#)), wash the crucible (see [6.2](#)) with warm water and add the washings to the solution.

If insoluble residue is formed, filter through a rapid filter paper or lavalan wool and collect the filtrate in a 600 ml beaker. Wash the filter with residue 6 times to 8 times with hot water and discard.

Add 10 ml of the silver nitrate solution (see [5.9](#)) and 1 ml of the manganese (II) sulfate solution (see [5.8](#)) in cases where the ore contains less than 0,1 (in mass fraction) of manganese. Add 25 ml of the ammonium

peroxodisulfate solution (see 5.10) and heat until the crimson colour appears as a result of the complete oxidation of chromium. Boil the solution for 12 min to 15 min to decompose the ammonium peroxodisulfate, add 10 ml of the sodium chloride solution (see 5.11) and boil again for 8 min to 10 min until decomposition of permanganic acid and coagulation of the silver chloride precipitate. Add 5 ml of the manganese (II) sulfate solution (see 5.8) and boil for about 3 min.

If the pink coloration persists, proceed with the determination as follows.

Boil the solution for 12 min to 15 min to decompose the ammonium peroxodisulfate, add 10 ml of the sodium chloride solution (see 5.11) and boil again for 8 min to 10 min until decomposition of permanganic acid and coagulation of the silver chloride precipitate. Add 5 ml of the manganese (II) sulfate solution (see 5.8) and boil for about 3 min.

Cool the solution in cold water to room temperature.

8.5 Determination

8.5.1 Visual titration

Add the ammonium iron (II) sulfate solution (see 5.13) from a burette to the beaker containing the test solution (see 8.4) until the colour of the test solution changes from yellow to bluish-green [chromium (VI) and vanadium (V) are reduced to chromium (III) and vanadium (IV)]. Add a further 5 ml to 10 ml of the ammonium iron (II) sulfate solution (see 5.13) in excess, using a burette. Titrate the solution with the potassium permanganate solution (see 5.12). Take as the end point of titration, the beginning of the slight permanent darkening of the pale green colour. Add a further two drops of the potassium permanganate solution (see 5.12). The violet shade due to excess potassium permanganate shall persist for at least 5 min.

NOTE Simultaneously, the excess ammonium iron (II) sulfate solution (see 5.13) and vanadium (IV) are titrated with potassium permanganate solution (see 5.12). Therefore, the chromium content can be calculated.

8.5.2 Potentiometric titration

Place the electrodes (see 6.1.1) into the beaker containing the test solution (see 8.4), switch on the magnetic stirrer (see 6.1.2) and titrate with the ammonium iron (II) sulfate solution (see 5.13) until the maximum peak deflection on the millivoltmeter 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 (see 5.12), drop by drop, until the slight violet colour appears. Allow to stand for 2 min, maintaining a slight violet colour, to oxidize vanadium. Reduce the excess of potassium permanganate solution by adding the potassium nitrite solution (see 5.14), drop by drop until the slight violet colour is discharged. Add 1 g to 1,5 g of the urea (see 5.4) immediately to decompose the excess of potassium nitrite. Titrate the vanadium with the ammonium iron (II) sulfate solution (see 5.13) 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.

9 Expression of results

9.1 Calculation of chromium content in case of visual titration

The chromium content of the test portion ω_{Cr} , expressed as a percentage by mass, is given by Formula (4):

$$\omega_{Cr} (\%) = \frac{[(V_7 \times f - V_8) - (V_9 \times f - V_{10})] \times T_1 \times 100}{m_3} \times K \quad (4)$$