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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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Contents

Foreword

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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 (ll) sulfate, 100 g/l solution.

Dissolve 100 g of manganese (II) sulfate heptahydrate ($MnSO_4{\cdot}7H_2O$) 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 $KMnO_4$) ≈ 0,1 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):

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

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;
0,258 7	is the conversion factor from sodium oxalate to chromium.

5.13 Ammonium iron (II) sulfate, standard volumetric solution, c[$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] ≈ 0,1 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):

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

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 dichromat;
V_4	is the volume, in millilitres, of ammonium iron (II) sulfate solution (see 5.13) used for titrating the blank test solution;
0,353 5	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):

$$f = \frac{V_5}{V_6} \tag{3}$$

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 lavsan 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):

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

where

V_7 is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) used in the determination;

V_8 is the volume, in millilitres, of the potassium permanganate solution (see 5.12) used for titration of the excess of ammonium iron (II) sulfate solution (see 5.13);

V_9 is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) added to the blank test solution;

V_{10} is the volume, in millilitres, of the potassium permanganate solution (see 5.12) used for titration of the excess of ammonium iron (II) sulfate solution (see 5.13) in the blank test solution;

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

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

m_3 is the mass, in grams, of the test portion;

K is 1,00 for predried test samples, and for air-equilibrated test samples is the conversion factor found from Formula (5):

$$K = \frac{100}{100 - A} \tag{5}$$

where A is the hygroscopic moisture content, as a percentage mass fraction, determined in accordance with ISO 6129.

9.2 Calculation of chromium content in case of potentiometric titration

The chromium content of the test portion ω_{Cr}, expressed as a percentage by mass, is given by Formula (6):

$$\omega_{Cr}\,(\%) = \frac{[(V_{11} - V_{12}) - (V_{13} - V_{14})] \times T_2 \times 100}{m_3} \times K \tag{6}$$

where

V_{11} is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) used for the titration of chromium and vanadium in the determination;

V_{12} is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) used for the titration of vanadium in the determination;

V_{13} is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) used for the titration of chromium and vanadium in the blank test solution;

V_{14} is the volume, in millilitres, of the ammonium iron (II) sulfate solution (see 5.13) used for the titration of vanadium in the blank test solution;

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_3 is the mass, in grams, of the test portion;

K is 1,00 for predried test samples, and for air-equilibrated test samples is the conversion factor found from Formula (5).

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

$$Cr_2O_3 \text{ [\% (mass fraction)]} = 1{,}461\ 5 \text{ Cr [\% (mass fraction)]} \quad (7)$$

9.4 General treatment of results

9.4.1 Expression of precision

The precision of this analytical method is expressed by Formulae (8) to (15):

a) Visual titration method

$$lgR = -\ 1{,}044\ 6 + 0{,}476\ 0\ lgm \quad (8)$$

$$lgr = -\ 1{,}200\ 5 + 0{,}301\ 3\ lgm \quad (9)$$

$$lgS_R = -\ 1{,}491\ 7 + 0{,}476\ 0\ lgm \quad (10)$$

$$lgS_r = -\ 1{,}647\ 7 + 0{,}301\ 3\ lgm \quad (11)$$

b) Potentiometric titration method

$$lgR = -\ 0{,}875\ 8 + 0{,}384\ 3\ lgm \quad (12)$$

$$lgr = -\ 0{,}976\ 9 + 0{,}193\ 2\ lgm \quad (13)$$

$$lgS_R = -\ 1{,}322\ 9 + 0{,}384\ 3\ lgm \quad (14)$$

$$lgS_r = -\ 1{,}424\ 1 + 0{,}193\ 2\ lgm \quad (15)$$

where

m is the mean content of chromium, expressed as a percentage by mass, in the samples;

R is the between-laboratories reproducibility;

r is the within-laboratory repeatability;

S_R is the between-laboratories reproducibility standard deviation;

S_r is the within-laboratory repeatability standard deviation.

NOTE Additional information is given in Annex A.

9.4.2 Determination of analytical result

Having computed the independent duplicate results according to Formula (4) or Formula (6), compare them with the repeatability limit, r, using the procedure given in Annex B, and obtain the final laboratory result.

9.4.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the procedure described in 9.4.2. Compute the following quantity by Formula (16):

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{16}$$

where

$\mu_{1,2}$ is the mean of the final results;

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2.

If $|\mu_1 - \mu_2| \leq R$, the final results are in agreement.

9.4.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM). Calculate the analytical result, μ_C, for the CRM/ RM, and compare it with the reference or certified value A_C. There are two possibilities:

a) $|\mu_c - A_c| \leq C$, in which case the difference between the reported result and the certified/reference value is statistically insignificant;

b) $|\mu_c - A_c| > C$, in which case the difference between the reported result and the certified/reference value is statistically significant;

where

μ_C is the final result for the CRM;

A_C is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

CRMs used for this purpose shall be prepared and certified in accordance with ISO 33405[2]. C shall be calculated using Formula (17):

$$C = \frac{1}{\sqrt{2}} \sqrt{R^2 - \frac{n-1}{n} r^2 + 8u^2} \tag{17}$$

where

R is the between-laboratories reproducibility;

r is the within-laboratory repeatability;

n is the number of replicate determinations carried out on the CRM/RM;

u is the uncertainty of certified values of CRM/RM.

9.4.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operation specified in Annex B, calculated to four decimal places and rounded off to the second decimal place as follows:

a) where the figure in the third decimal place is less than 5, it shall be discarded and the figure in the second decimal place is kept unchanged, in accordance with ISO 80000-1:2022, B.3, Rule A;

b) where the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or where the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) where the figure in the third decimal place is 5 and there is a figure 0 in the fourth decimal place, the 5 is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

10 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) a reference to this document, i.e. ISO 6331:2024;

d) details necessary for the identification of the sample;

e) the results and unit in which they are expressed;

f) any characteristics noticed during the determination and any operations not specified in this document which can have had an influence on the result, for either the test sample or the CRM(s).

Annex A
(informative)

Additional information on the international interlaboratory test

A.1 General

This document was tested in an interlaboratory test programme involving 27 laboratories. Eight samples of chromium ores and concentrates covering the range 3,88 % (mass fraction) to 39,55 % (mass fraction) were analysed to determine the chromium content. The test programme was designed to determine the within-laboratory repeatability and between-laboratories reproducibility in general, using the principles of ISO 5725-2.

A.2 Design of the test programme

The analytical test programme was designed with the aim of providing maximum information. Each laboratory made three determinations for each sample.

A.3 Test samples

This test programme used eight samples of chromium ores and concentrates. The composition of these samples is shown in Table A.1.

Table A.1 — Chemical composition of chromium ores and concentrates samples (% in mass fraction)

Number	ID number of CRM	Cr		Mn	V	Al_2O_3	Fe_2O_3	MgO	SiO_2	Origin of material
		Content	Type of error							
S-1	AIMS 0389	3,88	0,30 [a]	0,174	0,035	4,27	14,80	23,48	49,50	South Africa
S-2	GBW 07818	12,04	0,14 [a]	0,088	0,043	11,86	10,57	28,12	20,30	China
S-3	GBW(E) 070132	18,85	0,06 [a]	0,114	0,077	18,94	13,95	20,48	12,55	China
S-4	GBW 07819	23,56	0,10 [a]	0,090	0,044	11,37	11,84	23,32	12,24	China
S-5	GBW(E) 070137	27,51	0,06 [a]	0,142	0,162	15,97	23,93	13,41	4,73	China
S-6	MIN T61001	28,62	0,29 [b]	0,147	0,232	14,60	30,70	9,15	3,13	South Africa
S-7	ALY T61252	32,16	0,07 [c]	n.d.	0,044	7,20	13,33	21,60	8,79	Russia
S-8	GBW 07821	39,55	0,12 [a]	0,097	0,048	10,53	13,70	16,45	1,10	China

[a] The expanded uncertainty (at a confidence level of 95 %) is acquired from a CRM certificate, which is an estimate of the “true” value based upon the best available date at the time of certification.

[b] The standard deviation for reference value is acquired from a CRM certificate.

[c] The 95 % confidence limits for reference value is acquired from a CRM certificate.

n.d. = not determined.

A.4 Detailed results obtained in the international cooperative test

The original data of the international cooperative test are presented in Table A.2 (visual titration method) and Table A.3 (potentiometric titration method).

Table A.2 — Original data — Visual titration of chromium ores and concentrates

Laboratory	Level, % (mass fraction)							
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Lab 1	3,878	12,022	18,877	23,805	27,312	28,870	32,028	39,716
	3,803	12,060	18,840	23,739	27,289	28,804	32,044	39,887
	3,780	12,000	18,914	23,937	27,131	28,789	32,055	39,697
Lab 2	3,922	11,873	18,976	23,436	27,541	28,659	31,958	39,501
	3,876	11,972	18,877	23,693	27,508	28,694	32,068	39,317
	3,922	11,877	18,891	23,524	27,514	28,687	31,877	39,525
Lab 3	3,882	12,183	18,651	23,276	27,400	28,673	32,182	39,188
	3,776	12,108	18,697	23,194	27,343	28,531	32,117	39,283
	3,865	12,092	18,657	23,222	27,481	28,585	32,044	39,361
Lab 4	3,892	12,077	19,006	23,577	27,538	28,715	32,026	39,645
	3,949	12,077	18,955	23,501	27,555	28,633	31,997	39,625
	3,916	12,076	18,931	23,500	27,564	28,638	31,998	39,630
Lab 5	3,831	11,901	18,735	23,380	27,412	28,630	31,583	39,357
	3,811	11,875	18,670	23,387	27,389	28,559	31,751	39,356
	3,838	11,873	18,693	23,392	27,427	28,566	31,700	39,406
Lab 6	3,934	12,141	18,672	23,609	27,488	28,627	32,132	39,792
	3,982	11,988	18,821	23,652	27,652	28,823	32,067	39,861
	3,896	12,083	18,597	23,711	27,734	28,732	32,242	39,684
Lab 7	3,903	11,905	18,829	23,401	27,400	28,601	32,205	39,315
	3,951	11,932	18,761	23,402	27,375	28,575	32,200	39,308
	3,931	11,897	18,891	23,406	27,364	28,525	32,206	39,318
Lab 8	3,991	12,082	18,809	23,620	27,569	28,689	31,782	39,597
	3,935	12,156	18,746	23,584	27,659	28,773	31,744	39,525
	3,926	11,979	18,873	23,748	27,563	28,589	31,908	39,687
Lab 9	3,820	11,937	18,889	23,424	27,413	28,684	31,970	39,458
	3,835	11,964	18,842	23,429	27,508	28,600	32,035	39,537
	3,918	11,943	18,834	23,494	27,482	28,586	31,933	39,431
Lab 10	3,842	12,009	18,873	23,709	27,391	28,619	32,037	39,431
	3,785	11,951	18,747	23,537	27,488	28,572	31,935	39,519
	3,809	11,887	18,801	23,584	27,302	28,597	31,969	39,483
Lab 11	3,950	12,001	18,991	23,440	27,275	28,531	32,251	39,771
	3,981	11,942	19,092	23,340	27,294	28,564	32,291	39,714
	3,924	11,972	19,094	23,440	27,334	28,502	32,371	39,811
Lab 12	3,902	11,967	18,893	23,403	27,671	28,482	31,856	39,512
	3,940	11,949	18,854	23,482	27,577	28,516	31,961	39,567
	3,993	12,022	18,804	23,457	27,614	28,537	31,883	39,432
Lab 13	4,015	12,116	18,991	23,594	27,627	28,801	32,138	39,727
	3,974	12,063	18,941	23,513	27,561	28,997	32,067	39,547
	3,982	12,135	18,844	23,462	27,609	28,817	32,152	39,676

Table A.2 *(continued)*

Laboratory	Level, % (mass fraction)							
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Lab 14	3,901	11,723	18,682	23,157	27,182	28,390	31,646	39,436
	3,861	11,739	18,677	23,270	27,199	28,431	31,697	39,402
	3,908	11,779	18,723	23,231	27,265	28,544	31,625	39,344
Lab 15	3,872	11,804	18,713	23,253	27,383	28,643	31,704	39,532
	3,920	11,872	18,792	23,182	27,320	28,590	31,683	39,351
	3,936	11,867	18,848	23,300	27,401	28,719	31,822	39,497
Lab 16	3,963	12,134	19,042	23,510	27,711	29,015	32,170	39,557
	3,902	12,254	19,102	23,632	27,727	28,922	32,192	39,604
	3,894	12,202	19,166	23,554	27,837	28,938	32,014	39,662
Lab 17	3,943	11,993	19,068	23,527	27,661	28,853	32,076	39,671
	3,938	12,056	19,020	23,516	27,532	28,806	31,889	39,606
	3,906	12,047	19,020	23,487	27,479	28,751	31,979	39,621
Lab 18	3,915	12,009	18,882	23,866	27,413	28,672	32,358	39,443
	3,908	11,921	18,869	23,853	27,348	28,602	32,318	39,467
	3,941	11,938	18,907	23,935	27,315	28,639	32,356	39,385
Lab 19	3,989	11,932	18,754	23,480	27,495	28,687	31,889	39,607
	3,939	11,992	18,945	23,486	97z109	28,727	31,887	39,504
	3,980	12,011	18,912	23,656	27,511	28,706	31,995	39,568
Lab 20	3,905	11,985	18,823	23,247	27,452	28,613	31,885	39,425
	3,906	11,996	18,870	23,326	27,435	28,684	31,886	39,405
	3,939	11,959	18,845	23,293	27,336	28,661	31,835	39,501

Table A.3 — Original data — Potentiometric titration of chromium ores and concentrates

Laboratory	Level, % (mass fraction)							
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Lab 1	3,868	11,850	18,855	23,322	27,560	28,609	31,844	39,705
	3,760	11,976	19,031	23,541	27,513	28,615	31,991	39,709
	3,791	11,913	18,933	23,503	27,599	28,614	31,945	39,692
Lab 2	3,954	11,991	18,780	23,596	27,542	28,691	31,908	39,516
	3,944	11,967	18,981	23,644	27,593	28,716	31,900	39,561
	3,929	11,935	19,005	23,446	27,509	28,762	31,954	39,544
Lab 3	3,643	12,164	18,614	23,407	27,315	28,643	32,035	39,222
	3,742	12,037	18,773	23,300	27,377	28,506	32,188	39,344
	3,796	12,011	18,719	23,246	27,206	28,465	32,053	39,465
Lab 4	3,975	12,074	18,993	23,409	27,480	28,865	32,046	39,695
	4,045	12,071	18,914	23,409	27,454	28,918	31,989	39,760
	3,858	12,034	18,963	23,420	27,610	28,820	32,052	39,681
Lab 5	3,902	12,038	18,642	23,624	27,397	28,593	32,092	39,731
	3,951	12,072	18,731	23,661	27,562	28,761	32,142	39,842
	3,887	12,163	18,687	23,548	27,481	28,840	32,251	39,780
Lab 6	3,973	11,947	18,831	23,406	27,416	28,560	32,209	39,318
	3,936	11,845	18,945	23,400	27,374	28,566	32,209	39,310
	3,926	11,758	18,925	23,405	27,297	28,541	32,200	39,313

Table A.3 *(continued)*

Laboratory	Level, % (mass fraction)							
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Lab 7	3,838	12,208	18,614	23,767	27,415	28,542	31,831	39,450
	3,975	12,021	18,853	23,635	27,535	28,626	31,864	39,545
	4,010	12,188	18,890	23,665	27,370	28,683	32,040	39,432
Lab 8	3,961	12,065	18,916	23,574	27,523	28,749	32,053	39,601
	3,990	12,043	18,969	23,519	27,591	28,764	32,032	39,678
	3,929	12,191	18,950	23,596	27,534	28,752	32,106	39,626
Lab 9	3,900	11,958	18,789	23,522	27,445	28,546	31,928	39,629
	3,892	11,930	18,820	23,467	27,348	28,538	32,036	39,599
	3,918	11,885	18,803	23,348	27,386	28,566	31,989	39,558
Lab 10	3,901	11,993	18,761	23,411	27,443	28,661	31,911	39,354
	3,911	11,932	18,812	23,483	27,472	28,682	31,924	39,391
	3,891	11,960	18,861	23,363	27,361	28,631	31,964	39,453
Lab 11	3,882	12,172	18,957	23,490	27,613	28,522	31,966	39,383
	3,917	12,110	18,945	23,582	27,708	28,630	31,871	39,472
	3,912	12,087	18,968	23,588	27,782	28,506	32,014	39,537
Lab 12	3,860	11,972	18,823	23,531	—	28,504	31,935	39,472
	3,891	11,991	18,842	23,550	27,286	28,652	31,962	39,378
	3,874	11,921	18,701	23,282	27,253	28,648	31,898	39,483
Lab 13	3,956	11,963	18,876	23,551	27,465	28,977	31,964	39,773
	4,000	12,022	18,996	23,647	27,670	28,915	32,090	39,779
	3,968	12,001	19,034	23,617	27,601	28,897	32,093	39,764
Lab 14	3,890	11,862	18,732	23,252	27,363	28,741	31,683	39,581
	3,941	11,870	18,802	23,324	27,432	28,690	31,664	39,372
	3,918	11,898	18,919	23,386	27,460	28,557	31,772	39,500
Lab 15	3,664	11,956	19,065	23,516	27,563	28,920	32,406	39,772
	3,816	12,033	19,125	23,421	27,669	28,907	32,483	39,786
	3,778	12,102	19,174	23,489	27,702	29,011	32,363	39,609
Lab 16	3,886	12,112	18,885	23,387	27,373	28,773	31,824	39,566
	3,858	12,241	19,012	23,519	27,482	28,816	31,783	39,473
	3,924	12,068	18,963	23,467	27,522	28,756	31,966	39,492
Lab 17	3,896	11,979	18,955	23,885	27,415	28,486	32,395	39,308
	3,930	12,031	18,890	23,877	27,407	28,709	32,285	39,418
	3,891	12,017	18,890	23,836	27,405	28,652	32,321	39,395
Lab 18	3,957	12,058	18,915	23,685	27,618	28,828	32,053	39,616
	3,963	12,075	19,003	23,636	27,658	28,754	32,064	39,473
	3,976	12,091	19,012	23,651	27,645	28,878	32,117	39,746
Lab 19	3,905	11,917	18,999	23,461	27,606	28,663	31,992	39,907
	3,820	11,855	19,095	23,737	27,616	28,671	31,901	39,995
	3,806	11,905	19,053	23,462	27,603	28,736	31,936	40,022
Lab 20	3,828	11,889	18,520	23,789	27,679	28,824	31,834	39,231
	3,751	11,747	18,535	23,567	27,724	28,742	31,478	39,455
	3,808	11,802	18,741	23,585	27,804	28,638	31,674	39,372

Table A.3 *(continued)*

Laboratory	Level, % (mass fraction)							
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Lab 21	3,964	11,958	18,728	23,255	27,266	28,304	31,701	39,360
	3,828	11,951	18,882	23,432	27,225	28,382	31,681	39,419
	3,853	12,071	18,823	23,341	27,225	28,404	31,639	39,247
Lab 22	4,036	12,183	19,024	23,927	27,684	28,946	32,105	39,991
	4,036	12,214	19,148	23,818	27,820	29,051	32,196	39,975
	4,023	12,215	19,197	23,677	27,753	29,051	32,253	40,152
Lab 23	3,984	11,918	18,814	23,011	27,354	28,794	31,873	39,344
	3,994	11,814	18,876	23,209	27,453	28,862	31,842	39,577
	4,011	12,025	18,903	23,112	27,533	28,790	31,784	39,414
Lab 24	4,030	12,060	18,821	23,420	27,473	28,381	32,052	39,461
	3,971	11,902	18,891	23,512	27,540	28,583	31,873	39,380
	3,931	12,001	18,802	23,250	27,551	28,460	31,881	39,570

A.5 Statistical evaluation

Results from the interlaboratory test programme were evaluated according to ISO 5725-2. The data were tested for statistical outliers by the Cochran and Grubbs' tests described in ISO 5725-2.

The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to others. The Grubbs' test is to determine whether the largest and smallest observations are outliers.

The regression formulae of the estimated precisions (r, R, S_r, and S_R) against sample means were computed and presented in Table A.4 (visual titration method) and Table A.5 (potentiometric titration method). The precision data are presented in graphical form in Figure A.1 (visual titration method) and Figure A.2 (potentiometric titration method).

Table A.4 — Summary of precisions — Visual titration of chromium ores and concentrates

Sample number	*m*	*R*	*r*	S_R	S_r
S-1	3,907	0,162	0,095	0,058	0,034
S-2	11,988	0,310	0,125	0,111	0,045
S-3	18,859	0,363	0,161	0,130	0,057
S-4	23,496	0,528	0,182	0,188	0,065
S-5	27,464	0,416	0,170	0,148	0,061
S-6	28,666	0,371	0,161	0,133	0,057
S-7	31,994	0,550	0,179	0,196	0,064
S-8	39,530	0,439	0,188	0,157	0,067
Regression formulae			**Correlation coefficient**		
$lgR = -1{,}044\,6 + 0{,}476\,0\ lgm$			0,917 2		
$lgr = -1{,}200\,5 + 0{,}301\,3\ lgm$			0,967 1		
$lgS_R = -1{,}491\,7 + 0{,}476\,0\ lgm$			0,917 2		
$lgS_r = -1{,}647\,7 + 0{,}301\,3\ lgm$			0,967 1		