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Steel and iron — Determination of chromium content — Indirect titration method

Acier et fonte — Dosage de la teneur en chrome — Méthode par titrage indirect

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15355 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annexes A and B of this International Standard are for information only.

Steel and iron — Determination of chromium content — Indirect titration method

1 Scope

This International Standard specifies a potentiometric titration method for the determination of chromium content in steel and iron.

The method is applicable to chromium contents between 1 % (*m*/*m*) and 35 % (*m*/*m*).

Vanadium contents in steel and iron should be less than 1 % (*m*/*m*) for chromium contents higher than 10 % (*m*/*m*) and less than 0,2 % (*m*/*m*) for chromium contents less than 10 % (*m*/*m*).

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 4942:1988, *Steel and iron — Determination of vanadium content — N-BPHA spectrophotometric method*.

ISO 4947:1986, *Steel and cast iron — Determination of vanadium content — Potentiometric titration method*.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*.

ISO 9647:1989, *Steel and iron — Determination of vanadium content — Flame atomic absorption spectrometric method*.

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*.

3 Principle

Fusion of the sample with sodium peroxide followed by acidification with sulfuric acid.

Oxidization of chromium (III) to dichromate with peroxodisulfate using silver as a catalyst.

Reduction of the dichromate with an excess of a solid iron (II) salt and potentiometric back titration of the excess with a dichromate solution.

Any interference from vanadium is corrected mathematically.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade and only grade 2 water as specified in ISO 3696.

4.1 Sulfuric acid, ρ approximately 1,84 g/ml

4.2 Sulfuric acid, diluted 1 + 6

4.3 Sulfuric acid, diluted 1 + 1

4.4 Hydrochloric acid, diluted 1 + 1

4.5 Sodium peroxide, Na_2O_2

NOTE It is recommended to use as fine a powder as possible.

4.6 Silver nitrate solution, approximately 1 %

Dissolve 5 g of $AgNO_3$ in 300 ml of water. Dilute to 500 ml and mix.

4.7 Ammonium peroxodisulfate solution, approximately 20 %

Dissolve 100 g of $(NH_4)_2S_2O_8$ in 300 ml of water. Dilute to 500 ml and mix.

4.8 Potassium dichromate, $K_2Cr_2O_7$, with known purity minimum 99,5 %.

Immediately prior to use dry the salt at 105 °C for at least 2 h. Allow to cool to room temperature in a desiccator.

4.9 Potassium dichromate solution, 0,1 N

Weigh, to the nearest 0,1 mg, 4,9 g of the salt (4.8) and dissolve it in 500 ml of water in a 1 000 ml volumetric flask. Let the flask stand for 6 h to dissolve the salt completely. Temper the solution to 20 °C, dilute to the mark with water and mix carefully.

Calculate the normality of the solution, N:

$$N = \frac{m \times 6 \times p}{M \times 100}$$

where

m is the mass, expressed in grammes, of potassium dichromate;

p is purity, expressed as a percentage by mass, of potassium dichromate;

M is the molar mass for potassium dichromate (294,191 8 g/mol).

4.10 Ferroammonium disulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$

The reduction grade of the salt shall be determined for each batch that is to be used.

Thoroughly grind a portion of 300 g to 400 g of the salt so that no large crystals are left. Store the salt in a jar that can be tightly closed. Transfer, to five 400 ml glass beakers, about 300 mg (to the nearest 0,01 mg) of the potassium dichromate (4.8) and dissolve in 200 ml of water and 35 ml of sulfuric acid (4.2). Add to each beaker about 2 700 mg (to the nearest 0,01 mg) of the ground iron salt. Stir with a glass rod to dissolve all crystals. Titrate the solutions with the dichromate solution (4.9).

Calculate the reduction grade, R:

$$R = \frac{(A \times \mathrm{B}) + (C \times D)}{E}$$

where

A is the factor given by the formula: $A = \frac{\mathrm{F} \times G \times H}{M \times 100}$;

B is the factor for conversion of chromium to ferroammonium disulfate (22,625 2 g/mol);

C is the factor given by the formula: $C = \mathrm{L} \times N$;

D is the volume, expressed in millilitres, of added potassium dichromate solution (4.9);

E is the mass, expressed in miligrammes, of ferroammonium disulfate;

F is twice the molar mass for chromium (103,993 g/mol);

G is the purity of the potassium dichromate salt used (4.8);

H is the mass, expressed in miligrammes, of potassium dichromate;

M is the molar mass for potassium dichromate (294,191 8 g/mol);

L is the factor for conversion of potassium dichromate to ferroammonium sulfate (392,138 3 mg/ml);

N is the concentration, expressed as a normality, of the potassium dichromate solution (4.9).

Calculate the average and the relative standard deviation for the five values. The relative standard deviation shall not exceed 0,03 %.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 or ISO 1042 as appropriate. Ordinary laboratory apparatus, and

5.1 Potentiometric titration device, consisting of

5.1.1 Redox electrode, combination Pt-Ag/AgCl

5.1.2 Titration assembly, consisting of a 400 ml beaker, a 10 ml burette complying with the requirements of ISO 385-1, class A and a magnetic stirrer

5.1.3 High impedance electronic voltmeter.

Normally a pH-meter can be used as a voltmeter but 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. See clause 9.

5.2 Muffle furnace, able to provide a constant temperature of 650 °C and an argon atmosphere

5.3 Zirconium crucible

The crucible shall be clean and not worn in order to avoid zirconium interference.

5.4 Zirconium lid

The lid shall be clean and not worn in order to avoid zirconium interference.

5.5 Glass granules, for anti-bumping

6 Sampling and samples

Carry out sampling in accordance with ISO 14284.

7 Determination procedure

7.1 Preparation of the test solution

7.1.1 Weigh, to the nearest 0,01 mg, 0,25 g of the laboratory sample and transfer to a 50 ml zirconium crucible (5.3). Add 5 g of sodium peroxide (4.5), mix well and cover with a zirconium lid (5.4).

The sample shall be in chip or powder form with size less than 2 000 μm.

7.1.2 Put the crucible in the muffle furnace (5.2) heated to 650 °C for 2 h to 3,5 h and with an argon atmosphere. Swirl the crucible gently once or twice to make sure that the melt is properly mixed.

NOTE It is important that the temperature be accurate. Too high a temperature will cause positive interference.

7.1.3 Take the crucible from the furnace and allow to cool.

7.1.4 Put the lid and the crucible (on its side) in a 400 ml beaker.

7.1.5 Carefully add a few millilitres of water and allow this water to slowly find its way into the crucible. The reaction is violent and all splashing shall be avoided. Continue to add water until the reaction has ceased and then up to about 100 ml. Then add 24 ml of sulfuric acid (4.3). Heat the solution to dissolve all hydroxides. Carefully observe the solution in order to ensure that there is no undissolved matter.

7.1.6 Remove the crucible and lid and carefully rinse them with water.

7.1.7 Dry the crucible on the outside and pour 5 ml of sulfuric acid (4.1) into it. Heat until sulfuric acid fumes are given off. Swirl the crucible in order to dissolve all salts. Allow the acid to cool and carefully add it to the beaker. Rinse and fill up with water to about 200 ml.

7.1.8 Boil the solution with some glass granules (5.5) for at least 5 min.

7.2 Titration

7.2.1 Add to the solution (see 7.1.8) 5 ml of silver nitrate solution (4.6) and 60 ml of ammonium peroxydisulfate solution (4.7). Heat to boiling and boil for 20 min.

7.2.2 Add 7 ml of hydrochloric acid (4.4) and boil for another 2 min. Allow to cool.

7.2.3 Calculate the amount of iron (II) salt, E (in miligrammes), that is to be added to the test solution:

$$E = (M \times \mathrm{B} \times i \times 10) + 300$$

where

i is the mass, in grammes, of the test portion;

B is the factor for conversion of chromium to ferroammonium disulfate (22,625 2 g/mol);

M is the expected mass, expressed as a percentage by mass, of chromium in the sample.

7.2.4 Weigh, to the nearest 0,01 mg, the calculated amount of iron (II) salt and transfer it quantitatively to the test solution. Stir the solution carefully with a glass rod to dissolve all salt.

7.2.5 Place the beaker on the magnetic stirrer and start it. Titrate slowly with the potassium dichromate solution (4.9) until the end-point is approached. Continue the titration in 0,1 ml or drop increments and record the burette and potential readings when equilibrium is reached after each incremental addition. Continue the titration through the end-point. Determine the end-point by interpolation or from the titration curve. See clause 9.

8 Expression of results

8.1 Method of calculation

The content of chromium in the sample, Cr_{T}, expressed in percent in mass, is calculated using the formula:

$$Cr_{\mathrm{T}} = \frac{m_1 \times R - (v \times \mathrm{L} \times N)}{\mathrm{B} \times m_2} \times 100$$

where

m_1 is the mass, expressed in miligrammes, of ferroammonium disulfate (4.10) added;

R is the reduction grade of the iron salt (4.10).

v is the volume, in millilitres, of added potassium dichromate;

L is the factor for conversion of potassium dichromate to ferroammonium sulfate (392,138 3 mg/ml);

N is the concentration, expressed as a normality, of the potasium dichromate solution (4.9);

B is the factor for conversion of chromium to ferroammonium disulfate (22,625 2 g/mol);

m_2 is the mass, expressed in miligrammes, of the test portion;

8.2 Correction for the interference of vanadium

The vanadium content of the sample shall be known in order to be able to calculate the interference. It can be determined by the procedures specified in ISO 4942, ISO 4947 or ISO 9647.

If the vanadium content of the sample is less than 0,03 %, the interference is negligible and the chromium content is the same as has been calculated from the titration.

If the vanadium content of the sample is between 0,03 % and 1 % the chromium content has to be corrected thus:

$$Cr = Cr_T - (V \times 0{,}34)$$

where

Cr_T is the chromium content that has been calculated from the titration;

V is the vanadium content of the sample.

8.3 Precision

A planned trial of this method was carried out by 6 laboratories, using 7 levels of chromium content, each laboratory making three determinations of chromium content at each level (see notes 1 and 2).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1, using the same apparatus with a new calibration.

The details of the test samples used and the mean results obtained are given in Tables A.1 and A.2.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between the chromium content and the repeatability limit (r) and reproducibility limits (R_W and R) of the test results (see note 3), as summarized in Table 1. The graphical representation of the data is shown in Figure B.1.

NOTE 3 From the two values obtained on day 1, the repeatability limit (r) and reproducibility limit (R) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility limit (R_W) was calculated using the procedure specified in ISO 5725-3.

Table 1 — Results for repeatability limit and reproducibility limits

Chromium content	Repeatability limit	Reproducibility limits	
% (m/m)	r	R_W	R
1	0,019	0,018	0,040
2	0,026	0,027	0,057
5	0,038	0,048	0,092
10	0,051	0,074	0,132
20	0,068	0,114	0,190
35	0,086	0,161	0,254

9 Interpretation of the results

9.1 The accurate and reproducible evaluation of the potentiometric end-point differs from the normal visual end-point detection in that the titration is normally carried out well past the equivalence point. The classical S-shaped titration curve shows a steep rise of the potential in the vicinity of the equivalence point. The mid-point of the steep portion of the curve is usually the inflection point and as such coincides with the equivalence point for a

symmetrical titration curve. For an asymmetrical titration curve where the true equivalence point does not coincide with the mid-point, the change in potential is usually large enough to make the titration error negligible.

9.2 Manual potentiometric titrations are slow as the equilibrium potential shall be established and recorded after each addition of titrant. In the vicinity of the equivalence point, the titrant shall be added in small increments and at least three measurements shall be taken after a large change in potential has been observed. From the data recorded, the end-point can be determined by plotting the titration curve and interpolating the end-point from the steep part of the curve. However, it is more desirable to calculate the first derivative (dE/dV), which has a maximum at the equivalent point. The exact value of the end-point volume can be determined by calculation of the second derivative of the potential, with respect to volume, which shall be numerically equal to zero. If equal increments of titrant are added just before and after the large potential change it is easy to see that the second derivative function changes sign between two additions. Thus, it must have passed through zero at some point which is determined by interpolation.

9.3 There is a great advantage in using automatic titrators which record the titration curve directly or process the data in a digital form. Such instrumentation is recommended for application of this International Standard.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the data of analysis;

b) reference to this International Standard, i.e. ISO 15355;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annexe A
(informative)

Additional information on international cooperative tests

Table A.1 was derived from the results of international analytical trials carried out in 1996 on 7 test samples in 5 countries involving 6 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1141, August 1996, and were shown in Table A.2. The graphical representation of the precision data is given in annex B.

The test samples used are listed in Table A.1.

Table A.1 — Test samples used in the interlaboratory tests

Sample	Chemical composition, % (*m/m*)										
	Cr	C	Si	Mn	Ni	Mo	W	Co	V	Ti	Nb
NBS 362 (Unalloyed steel)	0,3	0,16	0,39	1,04	0,59	0,07	0,20	0,30	0,041	0,08	0,29
JK 7A (Low alloy steel)	1,15	0,35	0,21	0,56	3,28	0,25			0,010		
JSS 607-8 (High speed steel)	3,97	0,78	0,3	0,35	0,05	0,54	17,48	4,59	0,84		
NBS 892 (Cast iron)	10,18	3,33	0,76	0,05	5,53	0,20	0,05	0,31	0,041	0,02	
JK 8F (High alloy steel)	16,91	0,039	0,42	1,55	11	2,78		0,13	0,022		0,001
JK 37 (High alloy steel)	26,72	0,013	0,14	1,73	30,8	3,55	0,02	0,06	0,075		0,002
NBS 890 (Cast iron)	32,4	2,91	0,67	0,62	0,4	0,02		0,03	0,45		