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Nickel alloys — Determination of chromium content — Potentiometric titration method with ammonium iron(II) sulfate

Alliages de nickel — Détermination du chrome — Méthode par titrage potentiométrique avec du sulfate de fer(II) et d'ammonium

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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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

This second edition cancels and replaces the first edition (ISO 7529:1989), which has been technically revised with the following changes:

- the scope has been modified;
- Table 1 has been modified.

Nickel alloys — Determination of chromium content — Potentiometric titration method with ammonium iron(II) sulfate

1 Scope

This document specifies a potentiometric titration method for the determination of chromium content in nickel alloys which do not contain insoluble carbides and which have a vanadium content less than a mass fraction of 0,2 %. The method is applicable to chromium contents between a mass fraction of 5 % to a mass fraction of 22 %.

Vanadium, which can be present as an impurity in the alloy, will give a positive bias interference. However, at a level of a mass fraction of 0,2 %, this bias is equivalent to a mass fraction of 0,068 % chromium, which is about half the reproducibility of the method.

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*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

4 Principle

Dissolution of a test portion in a nitric/hydrochloric acids mixture, and evaporation to fumes of sulfuric acid.

Dissolution of the salts in water and oxidation of chromium to chromium(VI), with ammonium peroxydisulfate using silver nitrate as a catalyst.

Removal of excess peroxydisulfate by boiling, and reduction of manganese(VII) with hydrochloric acid.

Titration of chromium(VI) with ammonium iron(II) sulfate using potentiometric end-point detection.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Hydrochloric acid, ρ_{20} = 1,19 g/ml.

5.2 Hydrochloric acid, ρ_{20} = 1,19 g/ml, diluted 1 + 3.

5.3 Nitric acid, ρ_{20} = 1,41 g/ml.

5.4 Sulfuric acid, ρ_{20} = 1,84 g/ml, diluted 1 + 1.

5.5 Silver nitrate ($AgNO_3$), 15 g/l solution.

5.6 Ammonium peroxydisulfate [$(NH_4)_2S_2O_8$].

5.7 Nitric/hydrochloric acids, mixture.

WARNING — This acid mixture is highly corrosive and unstable. Noxious chlorine gas is liberated on standing. It shall be prepared and used in a fume hood and shall not be kept in a closed container.

Carefully mix 25 ml of nitric acid (5.3) and 75 ml of hydrochloric acid (5.1).

This mixture is not stable and shall be prepared just before use.

5.8 Potassium dichromate, standard solution, $c(1/6\ K_2Cr_2O_7) = 0{,}100$ mol/l.

Dissolve exactly 4,903 g of potassium dichromate ($K_2Cr_2O_7$, 99,95 % minimum purity), previously dried at 105 °C for 1 h, in 500 ml of water.

Transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.9 Ammonium iron(II) sulfate, standard solution, $c[(NH_4)_2Fe(SO_4)_2] = 0{,}1$ mol/l.

5.9.1 Preparation

Dissolve 40 g of ammonium iron(II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] in 400 ml of water. Add slowly, with constant stirring, 100 ml of sulfuric acid (5.4).

Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.9.2 Standardization

Add, using a burette, 40,0 ml of the potassium dichromate solution (5.8) to 200 ml of water in a 400 ml tall-form beaker. Add 10 ml of sulfuric acid (5.4), 5 ml of the silver nitrate solution (5.5) and 5 ml of hydrochloric acid (5.2). Titrate this solution potentiometrically with the ammonium iron(II) sulfate solution (5.9), as specified in 8.2.

The real concentration, *c*, of the ammonium iron(II) sulfate solution (5.9), expressed in moles of iron per litre, is given by Formula (1):

$$\frac{V_1}{V_2}\times 0{,}1 \tag{1}$$

where

V_1 is the volume, in millimetres, of the potassium dichromate solution (5.8) taken for the standardization (= 40,0 ml);

V_2 is the volume, in millimetres, of ammonium iron(II) sulfate solution (5.9), used for the titration.

6 Apparatus

Ordinary laboratory apparatus and the following.

6.1 Potentiometric titration apparatus.

6.1.1 Indicator electrode, of bright platinum, which shall be kept in a clean, highly polished condition. It shall be cleaned by dipping in nitric acid (5.3) or aqua regia and rinsed with water prior to use.

6.1.2 Reference electrode, of silver/silver chloride or calomel.

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

6.1.3 Titration assembly, consisting of a 400 ml beaker, two 50 ml burettes complying with the requirements of ISO 385, class A, and a magnetic stirrer.

6.1.4 High impedance electric voltmeter.

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 (see 10.2).

6.2 Volumetric glassware.

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

7 Sampling and sample preparation

Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by appropriate national standards.

The laboratory sample normally is in the form of millings or drillings and no further preparation of the sample is necessary.

If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned with high purity acetone and then dried in air.

If the laboratory sample contains particles or pieces of widely varying sizes, the test sample should be obtained by riffling.

8 Procedure

8.1 Preparation of the test solution

8.1.1 Weigh a test portion containing between 20 mg and 80 mg of chromium according to Table 1 and transfer to a 400 ml or 600 ml tall-form beaker.

Table 1 — Mass of sample to be taken

Expected chromium content % in mass fraction	**Mass of sample** g	**Weighing accuracy** g
5 to 8	0,5 to 1,0	0,001
8 to 15	0,3 to 0,5	0,000 5
15 to 22	0,2 to 0,3	0,000 2

8.1.2 Add 20 ml of the nitric/hydrochloric acids mixture (5.7) and heat until the sample is dissolved. If the alloy resists dissolution, add hydrochloric acid (5.1) in 1 ml increments and continue heating to dissolve the sample. For some alloys, an acid mixture containing 30 ml of hydrochloric acid (5.1) and 2 ml of nitric acid (5.3) is more effective.

If the laboratory sample consists of large pieces, a 1 g test portion is taken for chromium contents higher than a mass fraction of 10 %. The solution is transferred to a 100 ml one-mark volumetric flask and aliquots of 50 ml for a mass fraction of 10 % to a mass fraction of 15 % chromium or 25 ml for a mass fraction of 15 % to a mass fraction of 22 % chromium should be taken, using a pipette, and processed as in 8.1.3.

8.1.3 Add 20 ml of sulfuric acid (5.4) and evaporate to fumes. Cool slightly, add 100 ml of hot water and boil until residues are dissolved.

8.1.4 Dilute the solution to 200 ml, add a piece of porous porcelain and heat to boiling. Add 5 ml of the silver nitrate solution (5.5) and 5 g of ammonium peroxydisulfate (5.6). Boil gently for 15 min to oxidize the chromium completely to chromium(VI). This is indicated by a pink colour which persists for about 10 min if the manganese content of the sample is significant. For samples with a very high chromium content associated with a low manganese content, add a few drops of a potassium permanganate solution (10 g/l) to supply this indication of complete oxidation.

8.1.5 Add 5 ml of hydrochloric acid (5.2) and continue boiling for a further 5 min, when all the pink permanganate colour should disappear. If the permanganate colour persists after boiling for the further 5 min, add 5 ml more of hydrochloric acid (5.2) and boil again for 5 min. Repeat, if necessary, until the permanganate colour is completely removed.

8.1.6 Cool the solution to room temperature and titrate potentiometrically with the ammonium iron(II) sulfate solution (5.9) as specified in 8.2.

8.2 Determination

Place the beaker containing the test solution on the stirrer of the titration apparatus (6.1). Insert the indicator electrode (6.1.1) and reference electrode (6.1.2) and connect to the electronic voltmeter (6.1.4). Switch on the stirrer and titrate with the ammonium iron(II) solution (5.9). Add the titrant quite rapidly until the end-point is approached. Continue the titration by adding 0,1 ml or one 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 10.2).

8.3 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination.

8.4 Number of determination

Carry out the determination at least in duplicate.

9 Expression of results

9.1 Method of calculation

The chromium content, expressed as a percentage by mass, is given by Formula (2):

$$\frac{(V_3 - V_0) \times c \times 0{,}017\,33}{m} \times 100 \qquad (2)$$

where

V_0	is the volume, in millimetres, of the ammonium iron(II) sulfate solution (5.9) used for the blank test;
V_3	is the volume, in millimetres, of the ammonium iron(II) sulfate solution (5.9) used for the determination;
c	is the real concentration, expressed in moles of $(NH_4)_2Fe(SO_4)_2$ per litre, of the ammonium iron(II) sulfate solution (5.9);
0,017 33	is the mass, in grams, of chromium corresponding to 1,00 ml of ammonium iron(II) sulfate solution, $c[(NH_4)_2Fe(SO_4)_2] = 1{,}000$ mol/l;
m	is the mass, in grams, of the test portion.

9.2 Precision

9.2.1 Interlaboratory tests

Fourteen laboratories in six countries participated in the interlaboratory testing of methods for the analysis of nickel alloys. Of these, 10 reported a complete set of results for this document. Six samples having the nominal composition given in Table 2 were analysed in duplicate on different days.

Table 2 — Nominal composition of test samples (% in mass fraction)

Sample label	Al	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti
825	0,2	0,07	21	1,6	30	0,7	Remainder	0,4	1,1
902	0,4	0,05	5	0,04	48	0,4	Remainder	0,35	2,5
3920	0,15	2	19	0,1	3	0,3	Remainder	0,6	2,3
3927	0,1	1	20	0,05	44	0,4	Remainder	0,8	0,6
7013	1,5	17	20	0,2	0,2	0,05	Remainder	0,7	2,4
7049	1	0,01	15	0,15	7	0,8	Remainder	0,3	2,3

9.2.2 Statistical evaluation

Results from the interlaboratory test programme were evaluated according to ISO 5725:1986, using the means of the duplicate results. The data were tested for statistical outliers by the Cochran and Dixon tests described in ISO 5725:1986.

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. Dixon's test is to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

Repeatability and reproducibility were also calculated according to ISO 5725:1986 at the 95 % confidence level.

Precision data are given in Table 3.

Table 3 — Precision data (% in mass fraction)

Sample label	Mean values	Repeatability	Reproducibility
825	21,37	0,12	0,12
902	5,17	0,14	0,14
3920	19,19	0,13	0,16
3927	20,31	0,16	0,22
7013	19,52	0,20	0,20
7049	15,04	0,14	0,20

For sample 825, one laboratory was rejected as both a Cochran and a Dixon outlier and two laboratories were rejected as Cochran outliers. For samples 3920 and 7049, one laboratory in each was rejected as a Cochran outlier. However, all of these results could be classified as statistical stragglers and would not have been rejected at the less critical test level given in ISO 5725:1986.

10 Notes on procedure

10.1 Alloys containing vanadium

Vanadium, if present in the alloy, causes a positive bias in the results of chromium. The ratio of the milliequivalent weights of chromium to vanadium is 0,340. Therefore, if the vanadium content is known, a correction may be applied by subtracting the vanadium content multiplied by 0,340 from the chromium content. At a vanadium level of a mass fraction of 0,2 %, this correction is a mass fraction of 0,068 %, which is about half of the reproducibility of the method and is not considered to be significant.

The vanadium content of nickel alloys can be determined by flame atomic absorption spectrometry or by any other appropriate method.

10.2 Determination of the end-point

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.

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 on 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 will have passed through zero at some point which is determined by interpolation.

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 this document.

11 Test report

The test report shall include the following information:

a) the method used by reference to this document, i.e. ISO 7529;

b) all information necessary for the identification of the sample, the laboratory, and the date of analysis or of the test report;

c) results and the units in which they are expressed;

d) the number of independent replications;

e) any unusual characteristics noted during the determination;

f) any operation not specified in this document or any operation which might have influenced the results;

g) signature of the responsible person.