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Nickel alloys — Determination of cobalt content — Potentiometric titration method with potassium hexacyanoferrate(III)

Alliages de nickel — Dosage du cobalt — Méthode par titrage potentiométrique avec l'hexacyanoferrate(III) de potassium

Reference number
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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.

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9389 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

Annex A of this International Standard is for information only.

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Nickel alloys — Determination of cobalt content — Potentiometric titration method with potassium hexacyanoferrate(III)

1 Scope

This International Standard specifies a potentiometric titration method for the determination of the cobalt content in nickel alloys in the range 2 % (*m/m*) to 25 % (*m/m*). Typical compositions of some nickel alloys are given in annex A.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO 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 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725 : 1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by interlaboratory tests.*

ISO 7530-2 : —1), *Nickel alloys — Chemical analysis by flame atomic absorption — Part 2 : Determination of cobalt content.*

3 Principle

Dissolution of a test portion in a nitric/hydrochloric acid mixture and oxidation of chromium by fuming with perchloric acid.

Addition of sodium pyrophosphate to complex the manganese and removal of dissolved chlorine and oxygen with a stream of nitrogen.

Addition of the test solution to a solution containing ammonium citrate, ammonium sulfate, ammonium hydroxide and an excess of standard potassium hexacyanoferrate(III) solution and titration of the excess with a standard cobalt solution using potentiometric end-point detection.

4 Reagents

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

4.1 Hydrochloric acid, $\varrho_{20} = 1{,}18$ g/ml.

4.2 Nitric acid, $\varrho_{20} = 1{,}41$ g/ml.

4.3 Nitric acid, $\varrho_{20} = 1{,}41$ g/ml, diluted 1 + 1.

4.4 Perchloric acid ($HClO_4$), $\varrho_{20} = 1{,}66$ g/ml.

4.5 Phosphoric acid, $\varrho_{20} = 1{,}75$ g/ml.

4.6 Ammonium hydroxide, $\varrho_{20} = 0{,}89$ g/ml.

4.7 Nitric/hydrochloric acid, 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 cupboard and shall not be kept in a closed container.

Carefully mix 25 ml of nitric acid ($\varrho_{20} = 1{,}41$ g/ml) and 75 ml of hydrochloric acid ($\varrho_{20} = 1{,}18$ g/ml). This mixture is not stable and shall be prepared just before use.

4.8 Sodium pyrophosphate, solution.

Dissolve 200 g of sodium pyrophosphate decahydrate ($Na_4P_2O_7.10H_2O$) in about 800 ml of boiling water and dilute to 1 000 ml while still hot. Prepare the solution as required immediately before use.

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1) To be published.

4.9 Ammonium citrate, solution.

Dissolve 125 g of citric acid ($C_6H_8O_7.H_2O$) in approximately 250 ml of water. Cautiously, and with constant stirring, add 170 ml of ammonium hydroxide. Cool, dilute to 500 ml and mix.

4.10 Ammonium sulfate, solution.

Dissolve 125 g of ammonium sulfate [$(NH_4)_2SO_4$] in 250 ml of water, dilute to 500 ml and mix.

4.11 Cobalt, standard solution, corresponding to 2,00 g of Co per litre.

Weigh, to the nearest 0,001 g, 2,000 g of cobalt metal of 99,9 %(*m*/*m*) minimum purity, transfer to a 600 ml beaker and dissolve in 40 ml of nitric acid diluted 1+1. Heat to complete dissolution, boil gently to expel oxides of nitrogen, cool and transfer to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water, mix, and store in a polyethylene bottle.

1 ml of this solution contains 2,00 mg of Co.

4.12 Potassium hexacyanoferrate(III), standard volumetric solution.

4.12.1 Preparation

4.12.1.1 Dissolve 5,6 g of potassium hexacyanoferrate(III) [$K_3Fe(CN)_6$] in 250 ml of water. Filter the solution through a pulp pad and wash thoroughly with water. Transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix. Refilter and standardize this solution as specified in 4.12.2 immediately prior to use.

4.12.2 Standardization

4.12.2.1 Dissolve three portions of a nickel alloy, having a similar iron and chromium content as the test sample and having a known cobalt content not exceeding 0,1 % (*m*/*m*), as specified in 7.1. Use the same mass of this alloy as is used for the test sample. See table 1. Add, using a pipette, 20,0 ml of the cobalt standard solution (4.11).

NOTE — If a similar nickel alloy is not available, prepare a synthetic solution of similar composition to the test solution, having a known cobalt content not exceeding 0,1 % (*m*/*m*).

4.12.2.2 Prepare an ammoniacal solution of potassium hexacyanoferrate(III) as specified in 7.2.1 and 7.2.2.

4.12.2.3 Transfer the alloy solution quantitatively to this ammoniacal solution while stirring continuously and titrate the excess potassium hexacyanoferrate(III) as specified in 7.2.3. Record the volume of cobalt solution used in the titration of each of the three portions and take the average.

4.12.2.4 The factor T, in milligrams of cobalt per millilitre of potassium hexacyanoferrate(III) solution, is given by the formula

$$\frac{\varrho_{Co}(V_1 + V_2) + m_1}{V_3}$$

where

ϱ_{Co} is the concentration, in milligrams per millilitre, of the cobalt standard solution (4.11);

V_1 is the volume, in millilitres, of the cobalt standard solution taken in 4.12.2.1 (= 20,0 ml);

V_2 is the volume, in millilitres, of the cobalt standard solution used in the titration (4.12.2.3);

V_3 is the total volume, in millilitres, of potassium hexacyanoferrate(III) solution used in the titration (4.12.2.3);

m_1 is the mass, in milligrams, of cobalt in the portion of the low-cobalt alloy taken in 4.12.2.1.

NOTE — The cobalt content of the low-cobalt nickel alloy can be determined by the flame atomic absorption spectrometric method (ISO 7530-2).

5 Apparatus

Ordinary laboratory apparatus and

5.1 Potentiometric titration apparatus

5.1.1 Indicator electrode, of bright platinum, which shall be kept in a clean, highly polished condition. It shall be cleaned by dipping in the nitric acid (4.2) and rinsed with water prior to use.

5.1.2 Reference electrode, of silver/silver chloride, calomel or mercury(I) sulfate. The manufacturer's instructions on the care and maintenance of these electrodes shall be followed.

5.1.3 Titration assembly, consisting of a 400 ml beaker, two 50 ml burettes complying with the requirements of ISO 385-1, class A, and a magnetic stirrer.

5.1.4 High-impedance electronic 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 9.1.

5.2 Volumetric glassware

5.2.1 Burette, of capacity 50 ml, graduated in 0,1 ml divisions, complying with the requirements of ISO 385-1, class A.

5.2.2 One-mark pipettes, complying with the requirements of ISO 648, class A.

5.2.3 One-mark volumetric flasks, complying with the requirements of ISO 1042, class A.

6 Sampling and sample preparation

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by the relevant International Standard.

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

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

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

7 Procedure

WARNING — Fuming perchloric acid is a powerful oxidant and can cause an explosive mixture when in contact with organic materials. All evaporations must be carried out in fume cupboards suitable for use with perchloric acid.

7.1 Preparation of the test solution

7.1.1 Weigh a test portion containing between 10 mg and 40 mg of cobalt 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 cobalt content % (m/m)	Mass of sample g	Weighing accuracy g
2 to 10	0,39 to 0,41	0,000 5
10 to 25	0,19 to 0,21	0,000 5

7.1.2 Add 25 ml of the nitric/hydrochloric acid mixture (4.7) and heat until the sample is dissolved. If the alloy resists dissolution, add the hydrochloric acid (4.1) in 1 ml increments and continue heating to dissolve the sample. For some alloys, an acid mixture containing 30 ml of hydrochloric acid and 2 ml of nitric acid is more effective.

NOTE — If the laboratory sample consists of large pieces, a 1 g test portion may be taken for analysis. The solution should be transferred to a 250 ml one-mark volumetric flask and a test portion of 100 ml for 2 % (m/m) to 10 % (m/m) cobalt or 50 ml for 10 % (m/m) to 25 % (m/m) cobalt taken, using a pipette, and processed as specified in 7.1.3.

7.1.3 Add 8 ml of the perchloric acid (4.4) and heat the solution to heavy white fumes until the chromium is fully oxidized. Cautiously add 2 ml of the phosphoric acid (4.5) to the fuming solution and continue heating for a further 2 min. Cool, and rinse the cover and the inside of the beaker with about 10 ml of water.

7.1.4 Add 50 ml of hot sodium pyrophosphate solution (4.8) to complex the manganese, heat to boiling and boil for a few minutes.

7.1.5 Cool the solution slightly and pass a rapid stream of nitrogen through it for 10 min to 15 min to remove dissolved chlorine and oxygen. Cool to room temperature.

7.2 Determination

7.2.1 To a 600 ml low-form beaker, add 30 ml of the ammonium citrate solution (4.9) and 20 ml of the ammonium sulfate solution (4.10). Add, using a burette (5.2.1), sufficient potassium hexacyanoferrate(III) solution (4.12) to titrate the cobalt present in the test solution *plus* an excess of 3 ml to 5 ml. Record the total volume of potassium hexacyanoferrate(III) solution added (V_4).

7.2.2 Dilute the solution to about 300 ml and add 60 ml of the ammonium hydroxide (4.6). Place the beaker on the magnetic stirrer of the titration assembly (5.1.3) and start the stirrer.

7.2.3 Transfer the alloy solution quantitatively to the 600 ml beaker while stirring continuously. Immerse the indicator and reference electrodes (5.1.1 and 5.1.2) in the solution. Titrate slowly with the cobalt standard solution (4.11) until the end-point is approached. Continue the titration in 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 9.1.

7.3 Number of determinations

Carry out the determination at least in duplicate

8 Expression of results

8.1 Method of calculation

The cobalt content, expressed as a percentage by mass, is given by the formula

$$\frac{V_4 T - V_5 \varrho_{Co}}{m_0} \times 0,1$$

where

V_4 is the volume, in millilitres, of the potassium hexacyanoferrate(III) solution (4.12) used in the determination;

V_5 is the volume, in millilitres, of the cobalt standard solution (4.11) used in the determination;

T is the concentration factor of the potassium hexacyanoferrate(III) solution as calculated in 4.12.2.4;

ϱ_{Co} is the concentration, in milligrams per millilitre, of the cobalt standard solution (4.11);

m_0 is the mass, in grams, of the test portion.

8.2 Precision

8.2.1 Laboratory tests

Fourteen laboratories in six countries participated in the interlaboratory testing of methods for the analysis of nickel alloys. Of these, nine reported a complete set of results for this International Standard. Two samples of nominal composition given in table 2 were analysed in duplicate on different days.

8.2.2 Statistical analysis

8.2.2.1 Results from the inter-laboratory test programme were evaluated according to ISO 5725, using the means of the duplicate analysis. The data were tested for statistical outliers by the Cochran and Dixon tests given in ISO 5725.

8.2.2.2 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. 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.

8.2.2.3 Repeatability and reproducibility were calculated according to ISO 5725 at the 95 % confidence level. Results of the statistical analysis are given in table 3.

8.2.2.4 No outliers were identified by statistical tests.

9 Notes on procedure

9.1 Determination of the end-point

9.1.1 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.

9.1.2 Manual potentiometric titrations are slow as the equilibrium potential must be established and recorded after each addition of titrant. In the vicinity of the equivalence point, the titrant must be added in small increments and at least three measurements must 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 $(\mathrm{d}E/\mathrm{d}V)$, which has a maximum at the equivalence 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 must 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.

9.1.3 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 this International Standard.

10 Test report

The test report shall include the following particulars :

a) the reference of the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

e) any operation not included in this International Standard or regarded as optional.

Table 2 — Nominal composition of test samples [% (m/m)]

Sample reference	Al	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti
3 920	0,15	2	19	0,1	3	0,3	Remainder	0,6	2,3
7 013	1,5	17	20	0,2	0,2	0,05	Remainder	0,7	2,4

Table 3 — Results of statistical analysis [% (m/m)]

Sample reference	Mean	Within-laboratory standard deviation	Between-laboratory standard deviation	Repeatability	Reproducibility
3 920	2,05	0,023	0,048	0,06	0,15
7 013	17,04	0,064	0,18	0,18	0,53