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

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

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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 7529 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 chromium content — Potentiometric titration method with ammonium iron(II) sulfate

## 1 Scope

This International Standard specifies a potentiometric titration method for the determination of 1 % (*m/m*) to 25 % (*m/m*) chromium content in nickel alloys which do not contain insoluble chromium carbides, and which have a vanadium content of less than 0,2 % (*m/m*). Typical compositions of some nickel alloys are given in annex A.

Vanadium, which may be present as an impurity in the alloy, will give a positive bias interference. However, at a level of 0,2 % (*m/m*) this bias is equivalent to 0,068 % (*m/m*) chromium, which is about half the reproducibility of the method. See clause 9.

## 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 inter-laboratory tests.*

## 3 Principle

Dissolution of a test portion in a nitric/hydrochloric acid 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) by hydrochloric acid.

Titration of chromium(VI) with ammonium iron(II) sulfate 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 Hydrochloric acid,** $\varrho_{20}$ = 1,18 g/ml, diluted 1+3.

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

**4.4 Sulfuric acid,** $\varrho_{20}$ = 1,83 g/ml, diluted 1+1.

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

**4.6 Ammonium peroxydisulfate** [$(NH_4)_2S_2O_8$].

**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 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.

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

### 4.9.1 Preparation

Dissolve 40 g of ammonium iron(II) sulfate hexahydrate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ in 400 ml of water. Add slowly, with constant stirring, 100 ml of sulfuric acid diluted 1+1. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

### 4.9.2 Standardization

Add, using a burette, 40,0 ml of the potassium dichromate solution (4.8) to 200 ml of water in a 400 ml tall-form beaker. Add 10 ml of sulfuric acid diluted 1+1, 5 ml of the silver nitrate solution (4.5) and 5 ml of hydrochloric acid diluted 1+3. Titrate this solution potentiometrically with the ammonium iron(II) sulfate solution as specified in 7.2.

The actual concentration $c$ of the ammonium iron(II) sulfate solution, expressed in moles of Fe per litre, is given by the formula

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

where

$V_1$ is the volume, in millilitres, of potassium dichromate solution used for the titration (= 40,0 ml);

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

## 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 (4.3) or aqua regia 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 10.1.

### 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

### 7.1 Preparation of the test solution

**7.1.1** 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<br>% $(m/m)$ | Mass of sample<br>g | Weighing accuracy<br>g |
|---|---|---|
| 1 to 4 | 1,5 to 2,0 | 0,002 |
| 4 to 8 | 0,5 to 1,0 | 0,001 |
| 8 to 15 | 0,3 to 0,5 | 0,000 5 |
| 25 to 30 | 0,2 to 0,3 | 0,000 2 |

**7.1.2** Add 20 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 chromium levels higher than 10 % (*m*/*m*). The solution should be transferred to a 100 ml one-mark volumetric flask and a test portion of 50 ml for 10 % (*m*/*m*) to 15 % (*m*/*m*) chromium or 25 ml for 15 % (*m*/*m*) to 30 % (m/m) chromium taken, using a pipette, and processed as in 7.1.3.

**7.1.3** Add 20 ml of the sulfuric acid diluted 1 + 1 (4.4) and evaporate to fumes. Cool slightly, add 100 ml of hot water and boil until the residue is dissolved.

**7.1.4** Dilute the solution to 200 ml, add a piece of porous porcelain or boiling chip and heat to boiling. Add 5 ml of the silver nitrate solution (4.5) and 5 g of ammonium peroxydisulfate (4.6). 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 a sample with a very high chromium content associated with a low manganese content, add a few drops of potassium permanganate solution (10 g/l) to supply this indication of complete oxidation.

**7.1.5** Add 5 ml of the hydrochloric acid diluted 1 + 3 (4.2) 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 the hydrochloric acid and boil again for 5 min. Repeat, if necessary, until the permanganate colour is completely removed.

**7.1.6** Cool the solution to room temperature and titrate potentiometrically with the ammonium iron(II) sulfate solution (4.9) as specified in 7.2.

## 7.2 Determination

Place the beaker containing the test portion on the stirrer of the titration apparatus (5.1). Insert the indicator electrode (5.1.1) and reference electrode (5.1.2) and connect to the electronic voltmeter (5.1.4). Switch on the stirrer and titrate with the ammonium iron(II) solution (4.9). Add the titrant fairly rapidly 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 10.1).

## 7.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same reagents as in the determination.

## 7.4 Number of determinations

Carry out the determination at least in duplicate.

# 8 Expression of results

## 8.1 Method of calculation

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

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

where

$V_0$ is the volume, in millilitres, of the ammonium iron(II) sulfate solution (4.9) used in the blank test;

$V_3$ is the volume, in millilitres, of the ammonium iron(II) sulfate solution used in the determination;

$c$ is the actual concentration, expressed in moles of $(NH_4)_2Fe(SO_4)_2$ per litre, of the ammonium iron(II) sulfate solution (4.9);

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.

## 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, ten reported a complete set of results for this International Standard. Six samples of nominal composition given in table 2 were analysed in duplicate on different days.

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

| Sample reference | 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 |
| **3 920** | 0,15 | 2 | 19 | 0,1 | 3 | 0,3 | Remainder | 0,6 | 2,3 |
| **3 927** | 0,1 | 1 | 20 | 0,05 | 44 | 0,4 | Remainder | 0,8 | 0,6 |
| **7 013** | 1,5 | 17 | 20 | 0,2 | 0,2 | 0,05 | Remainder | 0,7 | 2,4 |
| **7 049** | 1 | 0,01 | 15 | 0,15 | 7 | 0,8 | Remainder | 0,3 | 2,3 |

### 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 results. 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** 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.

## 9 Special cases : Alloys containing vanadium

Vanadium, if present in the alloy, causes a positive bias in the results for 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 0,2 % ($m/m$), this correction is 0,068 % ($m/m$), which is about half 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.

## 10 Notes on procedure

### 10.1 Determination of the end-point

**10.1.1** 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.

**10.1.2** 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.

**10.1.3** 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.

## 11 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 3 — Results of statistical analysis** [% ($m/m$)]

| Sample reference | Mean | Within-laboratory standard deviation | Between-laboratory standard deviation | Repeatability | Reproducibility |
|---|---|---|---|---|---|
| **825** | 21,37 | 0,042 | 0,00 | 0,12 | 0,12 |
| **902** | 5,17 | 0,051 | 0,00 | 0,14 | 0,14 |
| **3 920** | 19,19 | 0,046 | 0,032 | 0,13 | 0,16 |
| **3 927** | 20,31 | 0,057 | 0,055 | 0,16 | 0,22 |
| **7 013** | 19,52 | 0,071 | 0,00 | 0,20 | 0,20 |
| **7 049** | 15,04 | 0,048 | 0,022 | 0,14 | 0,20 |