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**Nickel alloys — Determination of iron content —
Titrimetric method with potassium dichromate**

Alliages de nickel — Dosage du fer — Méthode titrimétrique avec le dichromate de potassium

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Foreword

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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 7528 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 iron content — Titrmetric method with potassium dichromate

1 Scope

This International Standard specifies a titrmetric method for the determination of the iron content of nickel alloys in the range 1 % (*m/m*) to 50 % (*m/m*). This method is applicable only to alloys containing less than 0,2 % (*m/m*) of vanadium. 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 inter-laboratory tests*.

3 Principle

Dissolution of a test portion in a nitric/hydrochloric acid mixture and oxidation of chromium to chromium(VI) with perchloric acid.

Precipitation of iron with ammonium hydroxide and dissolution of the precipitate in hydrochloric acid.

Reprecipitation and dissolution of the iron.

Reduction of the iron(III) with a slight excess of tin(II) chloride and oxidation of the excess with mercury(II) chloride.

Addition of a sulfuric/phosphoric acid mixture and titration of the iron(II) with potassium dichromate using diphenylamine sulfonate as the indicator.

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

4.2 Ammonium hydroxide, $\rho_{20} = 0,89$ g/ml, diluted 1+2.

4.3 Hydrochloric acid, $\rho_{20} = 1,18$ g/ml.

4.4 Hydrochloric acid, $\rho_{20} = 1,18$ g/ml, diluted 1+1.

4.5 Hydrochloric acid, $\rho_{20} = 1,18$ g/ml, diluted 1+50.

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

4.7 Ammonia, wash solution.

Cautiously add 20 ml of ammonium hydroxide ($\rho_{20} = 0,89$ g/ml) to 1 litre of warm water. Prepare this solution as required.

4.8 Tin(II) chloride, solution.

Dissolve 5 g of tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 10 ml of hydrochloric acid ($\rho_{20} = 1,18$ g/ml). Heat to boiling and dilute to 100 ml. Prepare this solution just before use.

NOTE — It is possible to store this solution in a brown glass bottle with the addition of granular or spongy tin metal.

4.9 Mercury(II) chloride, saturated solution.

WARNING — Mercury(II) chloride is very poisonous. Appropriate precautions shall therefore be taken in handling this chemical.

Add 60 g to 100 g of mercury(II) chloride (HgCl_2) to 400 ml of hot water, shake, and cool to ambient temperature. More water may be added from time to time as long as crystals remain undissolved.

4.10 Nitric/hydrochloric acid, mixture.

WARNING — This acid mixture is highly corrosive and unstable. Noxious gas (chlorine) 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 ($\rho_{20} = 1,41$ g/ml) and 75 ml of hydrochloric acid ($\rho_{20} = 1,18$ g/ml). This mixture is not stable and shall be prepared just before use.

4.11 Sulfuric/phosphoric acid, mixture.

Slowly, and with constant stirring, add 150 ml of sulfuric acid (H_2SO_4 , $\rho_{20} = 1,84$ g/ml) to 500 ml of water. Cool the solution and add 150 ml of phosphoric acid (H_3PO_4 , $\rho_{20} = 1,83$ g/ml). Mix, cool and dilute to 1 litre.

4.12 Potassium dichromate, standard volumetric solution, $c(1/6 \text{K}_2\text{Cr}_2\text{O}_7) = 0,035$ mol/l.

Dissolve exactly 1,716 1 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 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.

4.13 Sodium diphenylamine sulfonate, indicator solution.

Dissolve 0,20 g of sodium diphenylamine sulfonate ($\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{SO}_3\text{Na}$) in 100 ml of water. Store in a dark-coloured bottle.

5 Apparatus

Ordinary laboratory apparatus and

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

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

5.3 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 evaporation 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 60 mg of iron 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 iron content % (m/m)	Mass of sample g	Weighing accuracy g
1 to 5	1,0 to 1,2	0,002
5 to 10	0,5 to 0,6	0,001
10 to 25	0,20 to 0,21	0,000 5
25 to 50	0,10 to 0,11	0,000 2

7.1.2 Add 25 ml of the nitric/hydrochloric acid mixture (4.10) and heat until the sample is dissolved and nitrous fumes are removed. If the alloy resists dissolution, add the hydrochloric acid (4.3) 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 iron levels higher than 10 % (m/m). The solution should be transferred to a 250 ml one-mark volumetric flask and a test portion of 50 ml for 10 % (m/m) to 25 % (m/m) iron or 25 ml for 25 % (m/m) to 50 % (m/m) iron taken, using a pipette, and processed as in 7.1.3.

7.1.3 Add 15 ml of the perchloric acid (4.6) and evaporate to dense white fumes. Continue heating until the solution boils rapidly for 1 min to ensure that the chromium is fully oxidized. Cool the solution, dilute to 200 ml with hot water, and add 10 ml of the hydrochloric acid (4.3) and stir.

7.1.4 Add the ammonium hydroxide (4.1) slowly until the precipitate formed slowly dissolves and the nickel ammine complex is completely formed. Add quickly a 25 ml excess. Simmer the solution for 2 min to 3 min to allow the iron(III) hydroxide precipitate to coagulate. Add a further 5 ml of the ammonium hydroxide to maintain the alkalinity and then filter through a 15 cm paper of medium porosity. Rinse the beaker and wash the precipitate thoroughly with hot ammonia wash solution (4.7).

7.1.5 Wash the precipitate from the filter paper into the original beaker with cold water. Dissolve any remaining par-

icles from the filter paper with about 25 ml of hot hydrochloric acid diluted 1+1 (4.4), collecting the solution in the original beaker. Wash the filter paper thoroughly with the hydrochloric acid diluted 1+50 (4.5). Dissolve any particles of iron(III) hydroxide adhering to the sides of the beaker by drop by drop addition of the hydrochloric acid diluted 1+1. Heat to complete dissolution of the precipitate.

7.1.6 Dilute the solution to 200 ml with hot water and reprecipitate the iron(III) hydroxide by slowly adding the ammonium hydroxide diluted 1+2 until precipitation is complete. Add a 25 ml excess and simmer the solution for 2 min to 3 min to allow the iron precipitate to coagulate.

7.1.7 Add a further 5 ml of the ammonium hydroxide diluted 1+2 to maintain the alkalinity and filter through a 15 cm medium porosity paper. Wash the beaker and the precipitate thoroughly with hot ammonia wash solution (4.7).

7.1.8 Wash the precipitate from the filter paper into the original beaker with water, redissolve any remaining particles from the filter paper with about 25 ml of hot hydrochloric acid diluted 1+1 (4.4), collecting the solution in the original beaker. Wash the filter paper thoroughly with hydrochloric acid diluted 1+50 (4.5). Dissolve any particles of iron(III) hydroxide adhering to the sides of the beaker by drop by drop addition of hydrochloric acid diluted 1+1. Heat to complete dissolution of the precipitate.

7.1.9 Evaporate the iron solution to approximately 30 ml and sparingly wash the inside of the beaker with water. Heat the solution to boiling and cautiously add the tin(II) chloride solution (4.8) dropwise until the yellow colour of the iron(III) is just discharged, then add 1 or 2 drops more. Add 200 ml of cold water and cool quickly to room temperature.

NOTE — The volume of the hydrochloric acid, diluted 1+1, should not exceed 30 ml for effective reduction of the iron(III) with tin(II) chloride.

7.2 Determination

7.2.1 Add 10 ml of the mercury(II) chloride solution (4.9) to the diluted solution from 7.1.9, stir well and allow to stand for approximately 5 min. If the iron has been properly reduced, a light silvery precipitate of mercury(II) chloride should be evident within 2 min. If a black precipitate is obtained, too much tin(II) chloride has been added and the determination should be abandoned.

7.2.2 Add 10 ml of the sulfuric/phosphoric acid mixture (4.11) and 2 or 3 drops of the sodium diphenylamine sulfonate indicator (4.13).

7.2.3 Titrate the iron with the potassium dichromate standard volumetric solution (4.12). As the end-point is approached, the colour deepens to a blue green which changes to a permanent purple or violet-blue on the addition of 1 more drop of the potassium dichromate solution. Note the volume of titrant.

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.

NOTE — Iron(III) must be present in the solution to obtain the purple end-point. If the colour fails to form, the blank is less than the equivalent of 1 drop of 0,02 mol/l iron(II) sulfate, as this contains sufficient iron to yield an end-point.

7.4 Number of determinations

Carry out the determination at least in duplicate.

8 Expression of results

8.1 Method of calculation

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

$$\frac{(V_1 - V_0) \times c \times 0,055\,85}{m} \times 100$$

where

V_0 is the volume, in millilitres, of the potassium dichromate solution (4.12), used in the blank test;

V_1 is the volume, in millilitres, of the potassium dichromate solution, used in the determination;

c is the actual concentration, expressed in moles of 1/6 $K_2Cr_2O_7$ per litre, of the potassium dichromate solution (4.12);

0,055 85 is the mass, in grams, of iron corresponding to 1,00 ml of potassium dichromate solution, $c(1/6 K_2Cr_2O_7) = 1,000 \text{ mol/l}$;

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 inter-laboratory testing of methods for the analysis of nickel alloys. Of these, nine reported a complete set of results for this International Standard. Five 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
7 049	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 No results were rejected as outliers.

9 Test report

The test report shall include the following particulars :

- the reference of the method used;
- the results of the analysis;
- the number of independent replications;
- any unusual features noted during the analysis;
- 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	29,99	0,138	0,282	0,39	0,89
902	47,77	0,087	0,226	0,24	0,68
3 920	3,00	0,015	0,011	0,043	0,052
3 927	44,03	0,102	0,330	0,29	0,98
7 049	7,01	0,027	0,086	0,075	0,25