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Nickel alloys — Determination of Nickel content — Inductively coupled plasma atomic emission spectrometric method

Alliages de nickel — Détermination du nickel — Méthode par spectrométrie d'émission atomique avec source à plasma induit par haute fréquence

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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).

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The committee responsible for this document is ISO/TC 155, *Nickel and nickel alloys*.

Nickel alloys — Determination of Nickel content — Inductively coupled plasma atomic emission spectrometric method

1 Scope

This Technical Specification describes an inductively coupled plasma atomic emission spectrometric method for the determination of nickel content (mass fraction) between 20,0 % and 80,0 % in nickel alloys.

Besides alloys where nickel is the main component regarding its content level, this method may also apply to alloys in which nickel has a content as high as several other elements (Fe, Cr, Co,...) and in which the “main element” cannot be specified.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

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

3 Principle

Dissolution of a test portion in a mixture of hydrofluoric, hydrochloric, nitric and phosphoric acid, and fuming after addition of perchloric acid.

If necessary, addition of extra hydrofluoric acid and, if desired, addition of an internal reference element (scandium recommended).

Dilution of the test solution to a known volume. Nebulisation of this solution into an inductively coupled plasma atomic emission spectrometer and measurement of the intensity of the emitted light (including, where appropriate, that of the internal reference element).

The method uses a calibration based on a very close matrix matching of the calibration solutions to the sample composition and a bracketing of the mass fractions between ±2 % of the approximate content of nickel in the sample to be analysed.

The content of all elements in the sample has, therefore, to be approximately known. If the composition is not known, the sample shall be analysed by some semi quantitative method.

The advantage with this procedure is that all possible matrix interferences will be minimized which will result in a higher trueness. This is important for spectral interferences which can be severe in very highly alloyed matrixes. All possible interferences shall be kept at a minimum level. Therefore, it is essential that the spectrometer used meets the performance criteria recommended for the selected analytical lines.

The wavelengths reported in Table 1 have been investigated and the strongest possible interferences are given. If other wavelengths are used, they shall be carefully checked. The wavelength for the internal reference element should be selected carefully. The use of scandium at 363,07 nm is recommended. This line is interference-free for the elements and contents generally found in nickel alloys.

Table 1 — Examples of wavelengths for Nickel

Element	**Wavelengths**, nm	**Interferences**
Nickel	231,604	Co, Mo
	230,299	/
	222,486	Co
	222,295	V, Co
	217,514	/
	227,877	/
	239,452	/
	221,647	Co
	227,021	/

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only “grade 2” water as specified in ISO 3696, or water of equivalent purity.

The same reagents should be used for the preparation of calibration solutions and of sample solutions.

4.1 **Hydrofluoric acid**, **HF**, 40 % (m/m), ρ = 1,14 g/ml, or 50 % (m/m), ρ = 1,17 g/ml.

WARNING — Hydrofluoric acid is extremely irritating and corrosive for the skin and the mucous membranes producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water, apply a topical gel containing 2,5 % (mass fraction) calcium gluconate, and seek immediate medical treatment.

4.2 **Hydrochloric acid**, **HCl**, ρ = 1,19 g/ml.

4.3 **Nitric acid**, **HNO_3**, ρ = 1,40 g/ml.

4.4 **Phosphoric acid**, **H_3PO_4**, ρ = 1,70 g/ml.

4.5 **Perchloric acid**, **$HClO_4$**, 60 % (m/m) ρ = 1,54 g/ml or 70 % (m/m), ρ = 1,67 g/ml.

WARNING — Perchloric acid vapour may cause explosion in the presence of ammonia, nitrous fume, or organic matter, in general. All evaporation shall be carried out by using fume hoods specifically designed for perchloric acid evaporations.

4.6 **Internal reference element solution, 100 mg/l**.

Choose a suitable element to be added as internal reference and prepare a 100 mg/l solution.

NOTE 1 Commercially available standard solutions can be used for this purpose.

NOTE 2 Scandium was used during the precision test of this method.

4.7 **Nickel standard solution, 10 g/l**.

Weigh 5 g ± 0,001 g of high purity nickel [min 99,9 % (m/m)], transfer it to a beaker and dissolve in 50 ml of water and 100 ml of nitric acid (4.3). Cover with a watch glass and heat gently until the nickel is completely dissolved. Cool and transfer quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 10 mg of nickel.

NOTE Commercially available standard solutions are not allowed.

4.8 Nickel standard solution, 5 g/l.

Weigh 5 g ± 0,001 g of high purity nickel [min 99,9 % (m/m)], transfer it to a beaker, and dissolve in 50 ml of water and 100 ml of nitric acid (4.3). Cover with a watch glass and heat gently until the nickel is completely dissolved. Cool and transfer quantitatively into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 5 mg of nickel.

NOTE Commercially available standard solutions are not allowed.

4.9 Standard solutions of matrix elements.

Prepare standard solutions for each element whose content (mass fraction) is higher than 1 % in the sample. Use pure metals or chemical substances with nickel content (mass fraction) less than 100 µg/g.

5 Apparatus

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

5.1 Polytetrafluoroethylene (PTFE) beakers or Perfluoroalkyoxy-polymer (PFA) beakers with a graphite base.

5.2 Polypropylene or polyethylene volumetric flasks, of capacity 250 ml, calibrated according to ISO 1042.

5.3 Optical emission spectrometer, equipped with inductively coupled plasma.

This shall be equipped with a nebulisation system resistant to hydrofluoric acid. The instrument used will be satisfactory if, after adjustment according to 7.6, it meets the performance criteria given in 5.3.

The spectrometer can be either a simultaneous or a sequential one. If a sequential spectrometer can be equipped with an extra device or simultaneous measurement of the internal reference element line, it can be used with the internal reference method. If the sequential spectrometer is not equipped with this device, an internal reference cannot be used and an alternative technique without an internal reference element shall be used.

5.3.1 Practical resolution of a sequential spectrometer.

Calculate the bandwidth (full width at half maximum), according to A.1, for the line used, including that for the internal reference element. The bandwidth shall be less than 0,030 nm.

5.3.2 Short-term stability.

Calculate the standard deviation of 10 measurements of the absolute intensity or intensity ratio corresponding to nickel and to the internal reference element, by using the most concentrated calibration solution for nickel, according to A.2. The relative standard deviation should not exceed 0,2 %.

NOTE Short-term stability values from 0,12 % to <0,8 % were obtained during the precision test of this method.

5.3.3 Background equivalent concentration.

Calculate the background equivalent concentration (BEC) according to A.3, for the analytical line, using a solution containing only the analyte (nickel). Maximum BEC values should be less than 0,4 mg/l.

NOTE Background equivalent concentration values between 0,045 mg/l and 0,30 mg/l were obtained during the precision test program.

6 Sampling and sample preparation

Sampling and sample preparation shall be carried out by normal agreed procedures.

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

The laboratory sample shall be cleaned by washing with pure acetone and drying in air.

If brazed alloy tools are used in the preparation of the laboratory sample, then the sample shall be further cleaned by pickling in 15 % (m/m) nitric acid for a few minutes. It shall then be washed several times with distilled water, followed by washing in acetone and drying in air.

7 Procedure

7.1 Sample composition

The approximate chemical composition of each sample (nickel content and all other matrix elements which content is above 1 %) shall be known preliminarily.

7.2 Test portion

Weigh, to the nearest 0,001 g, 0,25 g of the test sample.

7.3 Preparation of test solution, T_{Ni}

A PTFE or PFA beaker (5.1) should be used when using HF (4.1).

7.3.1 Transfer the test portion (7.2) into a 250 ml PTFE or PFA beaker with a graphite base (5.1).

7.3.2 Add 5 ml HF (4.1), 30 ml HCl (4.2), and 3 ml HNO_3 (4.3) and allow the sample to dissolve overnight at room temperature. Add 2,5 ml H_3PO_4 (4.4). If necessary, heat gently to complete dissolution. Add 7,5 ml $HClO_4$ (4.5) and heat until the perchloric acid starts to fume. Continue fuming for two to three minutes.

NOTE 1 Other HF and HCl volumes can be used, depending on the composition of the sample.

NOTE 2 5 ml H_3PO_4 (4.4) and 5 ml $HClO_4$ (4.5) can also be used, instead of 2,5 ml H_3PO_4 (4.4) and 7,5 ml $HClO_4$ (4.5).

7.3.3 Cool the solution and add 10 ml of water to dissolve the salts. Some residues may remain undissolved. In this case, add 2 ml of HF (4.1) and heat gently in a water bath until the residues dissolve completely.

7.3.4 Cool the solution to room temperature and transfer it quantitatively into a 250 ml polypropylene or polyethylene volumetric flask labelled T_{Ni}. If internal reference element (4.6) is used, add 10 ml of this internal standard.

NOTE 3 Depending on the instrument performances, the volume and/or the concentration of the internal reference element solution may be different.

7.3.5 Dilute to the mark with water and mix.

7.4 Preparation of rinsing solution, T_0

In a 250 ml polypropylene or polyethylene volumetric flask (5.2) labelled T_0, add 2,5 ml H_3PO_4 (4.4), 7,5 ml $HClO_4$ (4.5), and 10 ml of the internal reference element (4.6). Dilute to mark with water and mix.

7.5 Preparation of calibration solutions for bracketing: $T_{l,Ni}$ and $T_{h,Ni}$

For each test solution, T_{Ni}, prepare two matrix matched calibration solutions, $T_{l,Ni}$ and $T_{h,Ni}$, with nickel concentrations in $T_{l,Ni}$ slightly below and in $T_{h,Ni}$ slightly above the nickel concentration in the unknown test solution as follows.

7.5.1 Add the suitable volume, $K_{l,Ni}$, of the nickel standard solutions (4.7 or 4.8) in a 250 ml PTFE or PFA beaker (5.1) marked $T_{l,Ni}$ so that the mass of nickel, expressed as $K_{l,Ni}$ %, is approximately 2 % below the estimated mass content of nickel, expressed as K_{Ni} %, in the sample.

The selected volume, $K_{l,Ni}$, shall be easy to pipette.

7.5.2 Add the suitable volume, $K_{h,Ni}$, of the nickel standard solutions (4.7 or 4.8) in a 250 ml PTFE or PFA beaker (5.1) marked $T_{h,Ni}$ so that the mass of nickel, expressed as $K_{h,Ni}$ %, is approximately 2 % above the estimated mass content of nickel, expressed as K_{Ni} %, in the sample.

The selected volume, $K_{h,Ni}$, shall be easy to pipette.

7.5.3 Add to the calibration solutions, $T_{l,Ni}$ and $T_{h,Ni}$, all matrix elements having mass fractions above 1 % in the test solution using the appropriate volumes of standard solutions (4.9) to match the equivalent matrix composition to the nearest percent.

NOTE The calibration solutions, $T_{l,Ni}$ and $T_{h,Ni}$, are specific for each sample.

7.5.4 Add in each beaker, $T_{l,Ni}$ and $T_{h,Ni}$, 2,5 ml H_3PO_4 (4.4), 7,5 ml $HClO_4$ (4.5) and heat until the perchloric acid starts to fume. Continue to fume for two to three minutes.

7.5.4 Continue as specified from 7.3.3 to 7.3.5.

7.6 Adjustment of the apparatus

7.6.1 Start the inductively coupled plasma optical emission spectrometer and let it stabilize in accordance with the manufacturer's instructions.

7.6.2 At one of the wavelengths listed in Table 1, adjust all appropriate instrumental parameters, as well as the pre-spraying and the integrating times, according to the instrument manufacturer's instructions while aspirating the highest concentration calibration solution.

Depending on the instrument configuration, these parameters may include the outer, intermediate or central gas flow-rates, the torch position, the entrance slits, the exit slits and the photomultiplier tubes voltage.

NOTE Other wavelengths can be used provided that interferences, sensitivity, resolution, and linearity criteria have been carefully investigated.

7.6.3 Prepare the software for measurements of the intensity at the appropriate analytical line and for the calculation of the mean value and relative standard deviation.

7.6.4 If an internal reference element is used, prepare the software to calculate the ratio between the analyte intensity and the internal reference element intensity. The intensity of the internal reference element shall be measured simultaneously with the analyte intensity.

7.6.5 Where relevant, check the instrument performance requirements given in 5.3.1 to 5.3.3.

7.7 Measurement of the solutions

Measure the absolute or ratioed intensity of the analytical line of T_0, firstly (for rinsing the nebulisation device), then the lowest calibration solution, $T_{l,Ni}$, then the test solution, T_{Ni}, and, finally, the highest calibration solution, $T_{h,Ni}$. Repeat this sequence three times and calculate the mean intensities, $I_{l,Ni}$ and $I_{h,Ni}$ for the low and high calibration solutions and I_{Ni} for the test solution, respectively.

The pre-spraying and the integrating times should be optimized in order to carry out the measurements under stabilized instrumental conditions.

8 Expression of the results

8.1 Method of calculation

Calculate the nickel content in the sample, K_{Ni} in %, corresponding to the test solution, T_{Ni}, by means of Formula (1).

$$K_{Ni} = K_{l,Ni} + \frac{\left(I_{Ni} - I_{l,Ni}\right)\left(K_{h,Ni} - K_{l,Ni}\right)}{I_{h,Ni} - I_{l,Ni}} \qquad (1)$$

8.2 Precision

Thirteen laboratories in six countries participated in an inter laboratory validation test programme under the auspices of ISO/TC 155 involving three determinations of nickel at 15 content levels (samples).

Each laboratory carried out two determinations 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. The third determination was carried out at a different time using the same apparatus with a different calibration.

The results provided by four laboratories were not taken into account for the statistical evaluation as they have shown systematic inconsistencies: wide within laboratory spread or excessive bias or both.

The remaining data were statistically evaluated in accordance with ISO 5725 (all parts) and CEN/TR 10345 and the results of this evaluation are reported in Table 2. Some of the precision parameters in Table 2 are discrepant, as, for six samples, CV (R) is higher than Max CV (R) and, for five samples, r is higher than R_w.

In addition, the precision data obtained have no consistent relationship with the related nickel content mean values as the correlation coefficients are the following:

- 0,81 for the logarithmic relation between the repeatability (r) and the content mean value;
- 0,81 for the logarithmic relation between the intra-laboratory reproducibility (R_w) and the content mean value;
- 0,76 for the logarithmic relation between the reproducibility (R) and the content mean value.

In these conditions, only the experimental precision data are shown (see Table 2).

The compositions of the samples used are given in Annex B.

Table 2 — Results obtained from the precision test (1 of 2)

SAMPLE	**155-Ni-1**	**155-Ni-2**	**155-Ni-3**	**155-Ni-4**	**155-Ni-5**	**155-Ni-6**	**155-Ni-7**	**155-Ni-8**
Mean (%)	20,58	34,84	40,93	45,51	50,70	53,16	55,11	58,50
σ (r), %	0,068	0,113	0,128	0,119	0,166	0,145	0,181	0,154
σ (R_W), %	0,045	0,173	0,108	0,143	0,185	0,144	0,271	0,218
σ (R), %	0,107	0,493	0,218	0,336	0,277	0,555	0,436	0,262
r, %	0,191	0,317	0,358	0,333	0,465	0,407	0,508	0,430
R_W, %	0,126	0,483	0,303	0,399	0,519	0,404	0,760	0,609
R, %	0,300	1,379	0,609	0,941	0,776	1,554	1,221	0,733
CV (R)	0,52	1,41	0,53	0,74	0,55	1,04	0,79	0,45
Aim CV (R)	0,52	0,43	0,41	0,39	0,38	0,37	0,37	0,36
Max CV (R)	1,14	0,95	0,90	0,86	0,83	0,82	0,81	0,79

Table 2 — Results obtained from the precision test (2 of 2)

SAMPLE	**155-Ni-9**	**155-Ni-10**	**155-Ni-11**	**155-Ni-12**	**155-Ni-13**	**155-Ni-14**	**155-Ni-15**
Mean (%)	59,76	61,52	65,19	71,35	74,27	75,89	79,58
σ (r), %	0,239	0,281	0,239	0,162	0,133	0,275	0,234
σ (R_W), %	0,281	0,305	0,425	0,393	0,182	0,238	0,208
σ (R), %	0,584	0,535	0,484	0,790	0,421	0,393	0,932
r, %	0,669	0,787	0,670	0,454	0,373	0,771	0,654
R_W, %	0,787	0,854	1,190	1,100	0,510	0,666	0,583
R, %	1,636	1,498	1,355	2,213	1,178	1,100	2,609
CV (R)	0,98	0,87	0,74	1,11	0,57	0,52	1,17
Aim CV (R)	0,36	0,35	0,35	0,34	0,33	0,33	0,32
Max CV (R)	0,79	0,78	0,76	0,74	0,73	0,72	0,71

9 Test report

The test report shall include the following information:

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

b) the method used by reference to this Technical Specification, i.e. ISO/TS 18223;

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

d) any unusual features noted during the determination;

e) any operation not specified in this Technical Specification or any optional operation which may influence the results.

Annex A
(informative)

Plasma optical emission spectrometer — Suggested performance criteria to be checked

A.1 Resolution of a spectrometer

The resolution of a spectrometer can be defined as the wavelength difference, $d\lambda$, between two lines which can still just be observed separately. In practice, the parameter FWHM (full width at half maximum) is used as a resolution measure.

Ideally, the resolution should be of the same order as the physical line width in plasma emission spectra, i.e. 2 pm to 5 pm (1 pm = 10^{-12} m). In practice, however, the observed width of the emission lines and, consequently, the resolution will often be determined by the bandwidth of the spectrometer being used. As long as broadening resulting from aberrations can be neglected, this bandwidth is given by Formula (A.1).

$$\mathrm{FWHM} = \frac{\left(\dfrac{d\lambda}{dX}\right)\left(Wi + Wo\right)}{2} \tag{A.1}$$

where

Wi and Wo are the widths of the entrance slit and exit slit, respectively;

$\left(\dfrac{d\lambda}{dX}\right)$ is the reciprocal linear dispersion which is given by Formula (A.2).

$$\left(\frac{d\lambda}{dX}\right) = \frac{d\left(\cos\beta\right)}{nL} \tag{A.2}$$

where

L is the focal length of the spectrometer;

n is the order number;

d is the reciprocal of the grove density of the grating;

β is the diffraction angle.

Commercial spectrometers normally present resolutions in the range of 4 pm to 30 pm. A good resolution is of great importance to cope with the spectral interferences which occur in inductively coupled plasma optical emission spectrometry. Since a line with a wavelength in the second order will have the same diffraction angle, β, as a line with a wavelength 2λ in the first order, a spectrometer should have either an order-sorting possibility or an optical filter to avoid an order overlap.

A.2 Short-term stability

The evaluation of the short-term stability consists on the calculation of the repeatability standard deviation of a series of measurements carried out with the spectrometer.

A series of 10 consecutive intensity measurements of the highest calibration solution is carried out using the typical integration time for the system. The average of the intensity measurement, I_{avrg}, and the standard deviation, Si, of the 10 measurements are calculated, as well as the relative standard deviation, RSD_{I}, according to Formula (A.3).

$$RSD_{\mathrm{I}} = \left(\frac{\mathrm{Si}}{I_{\mathrm{avrg}}} \right) \times 100 \text{ (in \%)} \qquad \text{(A.3)}$$

In inductively coupled plasma optical emission spectrometry, for solutions with concentrations at least twice the background equivalent concentration (BEC), RSD_{I}, values between 0,3 % and 1,0 % are generally accepted. For concentrations solutions, RSD_{I}, values should be below 0,2 %.

A.3 Evaluating the background equivalent

The background equivalent concentration (BEC) is used as an evaluation of the instrument sensitivity. Since the analyte signal has usually a relatively high background, its correction by the background intensity is recommended. It is therefore calculated by using Formula (A.4).

$$\mathrm{BEC} = \left(\frac{I_{\mathrm{BG}}}{I_{\mathrm{net}}} \right) \times C_{\mathrm{Analyte}} \qquad \text{(A.4)}$$

where

I_{BG} is the intensity of the background;

I_{net} is the intensity of the analyte (overall intensity minus intensity of the background);

C_{Analyte} is the concentration of analyte that gives I_{net}.

Background equivalent concentration values can be found in wavelength tables (usually part of the instrument software). The background equivalent concentration is better the smaller its numerical value is.