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Magnesium and magnesium alloys — Determination of nickel — Inductively coupled plasma optical emission spectrometric method

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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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For an explanation of 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 79, *Light metals and their alloys*, Subcommittee SC 5, *Magnesium and alloys of cast or wrought magnesium*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Magnesium and magnesium alloys are one kind of light metallic materials and show several advantageous properties, such as low density, high specific stiffness and strength, good damping capacity, castability, weldability and machinability, etc. Nickel, as one of the hazardous elements, can significantly reduce the corrosion resistance of magnesium and its alloys. Thus, the nickel content should be controlled and monitored in order to check if its content remains at trace level. Nickel contents are limited to values not greater than 0,1 %, even 0,000 3 %, according to the material standards ISO 3116, ISO 8287 and ISO 16220. Therefore, it is extremely important to determine nickel content accurately in magnesium and its alloys.

Magnesium and magnesium alloys — Determination of nickel — Inductively coupled plasma optical emission spectrometric method

1 Scope

This document specifies an inductively coupled plasma optical emission spectrometric method for the determination of nickel contents between 0,000 2 % (mass fraction) and 0,2 % (mass fraction) in magnesium and magnesium alloys.

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 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 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

After dissolution of a test sample with nitric acid and hydrochloric acid, the solution is nebulized into an inductively coupled plasma optical emission spectrometer and the intensity of the emitted light from nickel is measured. The concentrations of nickel in the test solutions are derived from magnesium-based calibration curves.

5 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.

5.1 Pure magnesium, purity ≥ 99,99 % (mass fraction), free from nickel.

5.2 Pure nickel, purity ≥ 99,99 % (mass fraction).

5.3 Hydrochloric acid, ρ about 1,19 g/ml.

5.4 Nitric acid, ρ about 1,42 g/ml.

5.5 Hydrochloric acid solution 1 + 1.

Add 500 ml of hydrochloric acid (5.3) to 500 ml of water and mix.

5.6 Nitric acid solution 1 + 1.

Add 500 ml of nitric acid (5.4) to 500 ml of water and mix.

5.7 Nickel standard solution (1 mg/ml), 1 g/l.

Weigh 1,000 0 g of pure nickel (5.2) and transfer into a 500 ml glass beaker. Add 50 ml of nitric acid solution (5.6). Cover with a watch glass and, if necessary, heat gently to complete the dissolution. Cool and transfer into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of nickel.

5.8 Nickel standard solution (100 µg/ml), 0,1 g/l.

Transfer 10,00 ml of nickel standard solution (5.7) into a 100 ml volumetric flask, add 10 ml of nitric acid solution (5.6), dilute to the mark with water, and mix well.

1 ml of this solution contains 0,1 mg of nickel.

5.9 Nickel standard solution (10 µg/ml), 0,01 g/l.

Transfer 10,00 ml of nickel standard solution (5.8) into a 100 ml volumetric flask, add 10 ml of nitric acid solution (5.6), dilute to the mark with water, and mix well.

1 ml of this solution contains 0,01 mg of nickel.

5.10 Nickel standard solution (1 µg/ml), 0,001 g/l.

Transfer 10,00 ml of nickel standard solution (5.9) into a 100 ml volumetric flask, add 10 ml of nitric acid solution (5.6), dilute to the mark with water, and mix well.

1 ml of this solution contains 0,001 mg of nickel.

6 Apparatus

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

6.1 Inductively coupled plasma optical emission spectrometer.

6.1.1 General

The instrument used first shall be optimized in accordance with the manufacturer's instructions and then shall meet the performance criteria given in 6.1.3 to 6.1.4.

6.1.2 Wavelengths

This method does not specify any particular wavelength. Each laboratory shall carefully investigate the wavelengths available on its own equipment to find the most suitable ones regarding the sensitivity and the absence of interferences.

Several suggestions are given in Table 1 together with possible interferences. These wavelengths have been carefully investigated. It is recommended to use Ni 231,604 nm or Ni 221,647 nm because of their high sensitivity.

Table 1 — Examples of wavelengths for nickel determination

Element	Wavelength nm	Possible interferences
Ni	231,604	Co, Fe
	221,647	Cu, Fe

6.1.3 Limit of detection

Calculate the limit of detection of nickel in accordance with Annex A. The limit of detection should be equal to or less than 0,001 mg/l.

6.1.4 Linearity of the calibration curve

The linearity of the calibration curve is checked by calculating the corresponding correlation coefficient. This coefficient shall be higher than 0,999.

7 Sampling and sample preparation

Sampling shall be carried out in accordance with an appropriate national standard for magnesium. 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 ethanol or acetone and then dried in air. The sample shall be in the form of fine drillings, chips or millings with a maximum thickness of 1 mm. Sampling position shall be selected so as to be representative of the sample. In order to avoid oxidation of the surface, the chips shall be taken from an inner part of a bulk sample just before starting the analytical procedure.

8 Procedure

8.1 General

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

8.2 Test sample

Mix the sample well so that any portion weighed represents the average composition.

8.3 Determination

8.3.1 Preparation of the test solution for nickel contents between 0,000 2 % (mass fraction) and 0,01 % (mass fraction)

Weigh, to the nearest 0,1 mg, 0,5 g of the test sample (see 8.2) and transfer into a 300 ml glass beaker.

Add about 50 ml of water, and, in small portions, 10 ml of nitric acid solution (5.6) and 3 ml of hydrochloric acid solution (5.5). Cover with a watch glass and, if necessary, heat gently to complete the dissolution.

Allow to cool at room temperature. Transfer the solution quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

For samples containing silicon or zirconium, add 1 to 2 drops of hydrofluoric acid (ρ about 1,13 g/ml) to assist the dissolution.

8.3.2 Preparation of the calibration solutions for nickel contents between 0,000 2 % (mass fraction) and 0,01 % (mass fraction)

Weigh, to the nearest 1 mg, 0,50 g of pure magnesium (5.1) and transfer into a series of 300 ml glass beakers. Add about 50 ml of water, and, in small portions, 10 ml of nitric acid solution (5.6) and 3 ml of hydrochloric acid solution (5.5). Cover with a watch glass and, if necessary, heat gently to complete the dissolution. Cool and transfer quantitatively into a series of 100 ml one-mark volumetric flasks.

In each volumetric flask, add the volumes of nickel standard solution (5.9 and 5.10) shown in Table 2. Dilute to the mark with water and mix well.

Table 2 — Calibration solutions for nickel contents between 0,000 2 % and 0,01 %

Calibration solution label	Volume of nickel standard solution (5.9) ml	Volume of nickel standard solution (5.10) ml	Concentration of nickel in the calibration solution µg/ml	Corresponding nickel mass fraction in the test sample %
S_0	0	0	0	0
S_1	—	1,00	0,01	0,000 2
S_2	—	2,00	0,02	0,000 4
S_3	—	5,00	0,05	0,001 0
S_4	2,50	—	0,25	0,005 0
S_5	5,00	—	0,50	0,010

8.3.3 Preparation of the test solution for nickel contents between 0,01 % (mass fraction) and 0,2 % (mass fraction)

Weigh, to the nearest 0,1 mg, 0,1 g of the test sample (see 8.2) and transfer into a 300 ml glass beaker.

Add about 50 ml of water and, in small portions, 10 ml of nitric acid solution (5.6) and 3 ml of hydrochloric acid solution (5.5). Cover with a watch glass and, if necessary, heat gently to complete the dissolution.

Allow to cool at room temperature. Transfer the solution quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

For samples containing silicon or zirconium, add 1 to 2 drops of hydrofluoric acid (ρ about 1,13 g/ml) to assist the dissolution.

8.3.4 Preparation of the calibration solutions for nickel contents between 0,01 % (mass fraction) and 0,2 % (mass fraction)

Weigh, to the nearest 1 mg, 0,10 g of pure magnesium (5.1) and transfer into a series of 300 ml glass beakers. Add about 50 ml of water, and, in small portions, 10 ml of nitric acid solution (5.6) and 3 ml of hydrochloric acid solution (5.5). Cover with a watch glass and, if necessary, heat gently to complete the dissolution. Cool and transfer quantitatively into a series of 100 ml one-mark volumetric flasks.

In each volumetric flask, add the volumes of nickel standard solution (5.9) shown in Table 3. Dilute to the mark with water and mix well.

Table 3 — Calibration solutions for nickel contents between 0,01 % and 0,2 %

Calibration solution label	Volume of nickel standard solution (5.9) ml	Concentration of nickel in the calibration solution µg/ml	Corresponding nickel mass fraction in the test portion %
S_0'	0	0	0
S_1'	1.00	0.10	0,010
S_2'	5,00	0,50	0,050
S_3'	10,00	1,00	0,10
S_4'	15,00	1,50	0,15
S_5'	20,00	2,00	0,20

8.4 Adjustment of the apparatus

Start the inductively coupled plasma optical emission spectrometer (6.1) and let it stabilize in accordance with the manufacturer's instructions before any measurement. Optimize the instrument according to the manufacturer's instructions. Prepare the software to measure the intensity, and for the calculation of the mean value and coefficient of variation corresponding to the appropriate wavelength.

8.5 Measurement of the calibration solutions

Measure the absolute intensities at the appropriate wavelength beginning with the lowest calibration solution S_0 and ending up with the highest calibration solution S_5.

Measure each of the calibration solutions three times and calculate the mean intensity.

Subtract the mean absolute intensity (I_{c0}) of the zero member from the mean absolute intensity (I_{ci}) of each calibration solution, in order to obtain the net absolute intensity (I_{cN}).

8.6 Calibration curve

Establish the calibration curve using the net intensities of nickel on the y-axis and the corresponding concentrations of nickel on the x-axis, expressed in micrograms per millilitre.

Calculate the correlation coefficient of the calibration curve. This shall meet the specification given in 6.1.4.

8.7 Measurements of the test solution

Measure the absolute intensity of the test solution three times and calculate the mean intensity.

9 Expression of results

9.1 Method of calculation

Using the calibration curve (see 8.6) and the net absolute intensity of the test solution obtained in 8.7, calculate the concentration of nickel in the test solution, expressed in micrograms per millilitre.

The mass fraction of nickel, expressed as a percentage, W_i, is given by Formula (1):

$$W_i = \frac{\rho_i \times V \times 10^{-6}}{m} \times 100 \tag{1}$$

where

ρ_i is the concentration of nickel in the test solution, in µg/ml;

V is the volume of the test solution, in ml;

m is the mass of the test sample, in g.

9.2 Precision

A planned trial of this method was carried out by seven laboratories in China at four levels of nickel, each laboratory making three determinations at each level.

Two of the three determinations were carried out 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 (on a different day) by the same operator as for the other two determinations, using the same apparatus with a new calibration.

The repeatability limit (r) and the reproducibility limits (R_w and R) were calculated using the procedure specified in ISO 5725-2.

The results obtained were treated statistically in accordance with ISO 5725-2. The relationships between the content of nickel and the repeatability limit (r) and reproducibility limits (R_w and R) of the test results are summarized in Annex B. A graphical representation of the data is shown in Annex C.

10 Test report

The test report shall include the following information:

a) the method used with a reference to this document, i.e. ISO 4155;

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

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

d) any unusual features noted during the determination;

e) any operation not specified in this document or any optional operation which can have influenced the results;

f) the signature of the responsible person.

Annex A
(normative)

Limit of detection

The limit of detection (L_{OD}) is used as a measure for instrument sensitivity, and can be calculated as follows:

a) measure 10 times, under repeatability conditions, the intensity of the zero member of the calibration curve and calculate the corresponding average (I_0) and standard deviation (σ_0);

b) measure 10 times, under repeatability conditions, the intensity of the lowest concentration (C_x) calibration solution and calculate the corresponding average (I_x).

Taking into account the statistical risks α and β, each at the 95 % level, the limit of detection is calculated according to Formula (A.1):

$$L_{OD} = (4{,}65 \times \sigma_0 \times C_x) / (I_x - I_0) \qquad \text{(A.1)}$$

Annex B
(informative)

Information on the precision test

Table B.1 shows the statistical results which are derived from an interlaboratory test carried out in 2020 involving seven laboratories in China on four magnesium alloy samples.

The precision data are presented in graphical form in Annex C.

Table B.1 — Results for repeatability limit and reproducibility limits

Sample no.	Average of nickel content	Repeatability limit	Reproducibility limits	
	(mass fraction %)	r (%)	R_w (%)	R (%)
1#	0,000 3	0,000 13	0,000 22	0,000 26
2#	0,003 4	0,000 26	0,000 31	0,000 40
3#	0,015	0,000 7	0,001 5	0,001 6
4#	0,14	0,006	0,018	0,019