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# Magnesium lithium alloys — Determination of lithium — 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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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 lithium alloys are the lightest metallic materials in the world and show several advantageous properties such as: excellent rigidity, high electric and thermal conductivity, good damping, electromagnetic, shielding, welding, matching and cold forming performances. Lithium is the most important element in magnesium lithium alloys, and can improve the deformation capability of alloys with further a decrease in weight. With the increasing demands of the world today for lightweight materials, energy saving, environmental protection and sustainable development, magnesium lithium alloys show broad application prospects in the fields of materials, transportation, electronics, medical products and so on.

Chemical compositions of magnesium and its alloys are widely standardized from major to trace contents in international and other national standards. However, there is no standard dealing with the determination of lithium content in magnesium lithium alloys.

# Magnesium lithium alloys — Determination of lithium — Inductively coupled plasma optical emission spectrometric method

## 1 Scope

This document specifies a method for the determination of lithium contents in magnesium lithium alloys by inductively coupled plasma (ICP) optical emission spectrometry.

The method is applicable to the determination of lithium content between 3,0 % and 16,0 % (mass fraction) in magnesium lithium 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 terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

## 4 Principle

Dissolution of a test portion in hydrochloric acid. Nebulization of the solution into an ICP optical emission spectrometer and measurement of the intensity of the emitted light from lithium.

Calibration based on a very close matrix matching of the calibration solutions to the sample shall be carried out. The advantage with this procedure is that all possible interferences from the matrix will be compensated, which will result in high accuracy. This is important to spectral interferences, which can be severe in highly alloyed matrixes.

All spectral interferences shall be kept at a minimum level. Therefore, it is essential to select the appropriate wavelengths. The wavelengths generally used for lithium are shown in Table 1 together with the possible interferences. Depending on the performance of each spectrometer, other wavelengths may be used, provided that interferences, sensitivity, resolution and linearity criteria have been carefully investigated.

## 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 lithium.

**5.2 Lithium carbonate,** purity ≥ 99,99 % (mass fraction).

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

**5.4 Hydrochloric acid solution 1 + 1,** add 500 ml of hydrochloric acid (5.3) to 500 ml of water.

**5.5 Hydrogen peroxide,** ρ about 1,13 g/ml.

**5.6 Magnesium base solution,** corresponding to 2,5 g of magnesium per litre.

Weigh, to the nearest of 1 mg, 0,5 g of pure magnesium (5.1) and transfer into a 300 ml glass beaker. Add about 50 ml of water and, in small portions, 25 ml of hydrochloric acid (5.4). Cover with a watch-glass and, if necessary, heat gently to complete the dissolution. Add a few drops of hydrogen peroxide (5.5) and boil for 5 min. Cool and transfer quantitatively into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 2,5 mg of magnesium.

**5.7 Magnesium base solution,** corresponding to 0,25 g of magnesium per litre.

Transfer 10 ml of the solution (5.6) to a 100 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (5.4). Dilute to the mark with water and mix.

1 ml of this solution contains 0,25 mg of magnesium.

**5.8 Lithium standard solution,** corresponding to 1,0 g of lithium per litre.

Dry several grams of lithium carbonate (5.2) in an oven at 100 °C ± 5 °C for at least 1 h and cool to room temperature in a desiccator. Weigh, to the nearest 0,1 mg, 5,322 8 g of the dried lithium carbonate, transfer into a 500 ml glass beaker, add 60 ml of hydrochloric acid (5.4), cover with a watch-glass and, if necessary, heat gently to complete the dissolution. 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 1,0 mg of lithium.

**5.9 Lithium standard solution,** corresponding to 0,1 g of lithium per litre.

Transfer 10,00 ml of the lithium standard solution (5.8) to a one-mark 100 ml volumetric flask. Add 10 ml of hydrochloric acid (5.4). Dilute to the mark with water and mix.

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

## 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 will be satisfactory if, after optimizing in accordance with the manufacturer's instructions, it meets the performance criteria given in 6.1.3 to 6.1.5.

#### 6.1.2 Wavelengths

This method does not specify any particular emission line. It is mandatory that each laboratory carefully investigates the wavelengths available on its own equipment to find the most suitable one regarding sensitivity and absence of interferences.

In Table 1, however, several suggestions are given together with possible interferences. These wavelengths have been carefully investigated. It is recommended to use Li 670,784 nm or Li 610,362 nm because of their high sensitivity.

**Table 1 — Examples of wavelengths for lithium determination**

| Element | Wavelength<br>nm | Possible interferences |
|---|---|---|
| Li | 670,784 | V, Ti, Sc |
| | 610,362 | Ca, Fe |

#### 6.1.3 Minimum resolution of the spectrometer

Calculate the bandwidth, according to A.1, for the wavelength used. The bandwidth shall be less than 0,030 nm.

#### 6.1.4 Minimum short-term precision

Calculate the short-term precision according to A.2. The relative standard deviation (RSD) should not exceed 1 %.

#### 6.1.5 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 the inner portion of a bulk sample just before starting an analytical procedure.

## 8 Procedure

### 8.1 General

For each set of determinations, all reagents, including water, calibration and test solutions, shall be from the same batch.

## 8.2 Test portion

Mix the sample well so that any portion weighed represents the average composition. Weigh, to the nearest 0,1 mg, 0,5 g of the test sample.

## 8.3 Determination

### 8.3.1 Preparation of the test solution

a) Place the test portion (8.2) into a 300 ml glass beaker.

b) Add about 50 ml of water, and, in small portions, 25 ml of hydrochloric acid (5.4). Cover with a watch-glass and, if necessary, heat gently to complete the dissolution. Add a few drops of hydrogen peroxide (5.5) and boil for 5 min.

c) Cool the solution from b) to room temperature. Transfer quantitatively into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix.

d) Transfer 10,00 ml of the solution from c) to a 100 ml one-mark volumetric flask, add 10 ml of hydrochloric acid (5.4). Dilute to the mark with water and mix.

e) Transfer 10,00 ml of the solution from d) to a 100 ml one-mark volumetric flask, add 10 ml of hydrochloric acid (5.4). Dilute to the mark with water and mix.

### 8.3.2 Preparation of the calibration solutions

Transfer 10 ml of magnesium base solution (5.7) and 10 ml of hydrochloric acid (5.4) into a series of 100 ml one-mark volumetric flasks. Add the volumes of lithium standard solution (5.9) shown in Table 2. Dilute to the mark with water and mix.

**Table 2 — Calibration solution for lithium in magnesium**

| Calibration solution label | Volume of lithium standard solution (5.9)<br>ml | Concentration of lithium in the calibration solution<br>µg/ml | Corresponding lithium mass fraction in the test portion<br>% |
|---|---|---|---|
| $S_0$ | 0 | 0 | 0 |
| $S_1$ | 0,50 | 0,5 | 2,0 |
| $S_2$ | 1,00 | 1,0 | 4,0 |
| $S_3$ | 3,00 | 3,0 | 12,0 |
| $S_4$ | 5,00 | 5,0 | 20,0 |

## 8.4 Adjustment of the apparatus

Start the inductively coupled plasma optical emission spectrometer 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 RSD 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 $S_4$.

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

Subtract the mean absolute intensity ($I_{c0}$) of the calibration solution $S_0$ 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 lithium on the y-axis and the corresponding concentrations of lithium on the x-axis, expressed in micrograms per millilitre.

Prepare a software for linear regression and calculate the correlation coefficient of the calibration curve. This shall meet the specification given in 6.1.5.

### 8.7 Measurements of the test solution

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

## 9 Expression of results

### 9.1 Method of calculation

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

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

$$W_\mathrm{i} = \frac{\rho_\mathrm{i} \times V \times R \times 10^{-6}}{m} \times 100 \qquad (1)$$

where

$\rho_\mathrm{i}$ is the concentration of lithium in the test solution, in µg/ml;

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

$R$ is the dilution factor;

$m$ is the mass of the test portion, in g.

### 9.2 Precision

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

NOTE 1 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.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in Note 1, using the same apparatus with a new calibration.

NOTE 3 The repeatability limit (r) and reproducibility limits ($R_W$ and R) were calculated using the procedure specified in ISO 5725-3.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3. The relationship between the content of lithium 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 by reference to this document, i.e. ISO 20258;

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 might have influenced the results;

f) signature of the responsible person.

# Annex A
(normative)

# Inductively coupled plasma optical emission spectrometer — 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 assessment.

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).

$$\text{FWHM} = \frac{\left(\dfrac{d\lambda}{dX}\right)\left(W_\text{i} + W_0\right)}{2} \tag{A.1}$$

where

$W_\text{i}$ and $W_0$ 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).

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

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;

$\beta$ 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 Minimum short-term precision

An important parameter for assessing the performance of an instrument is the short-term stability of an emission signal. This is defined as the closeness of the agreement between the values obtained from the highest calibration solution by repeating measurements in rapid succession.

The minimum short-term precision is expressed as the RSD of the signals measured.

Carry out ten consecutive measurements on the highest calibration solution and calculate the corresponding RSD.