
Magnesium and magnesium alloys — Determination of mercury

Magnésium et alliages de magnésium — Dosage du mercure

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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.

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 is the lightest of all the common metals and has been prepared for industry use as metal ingots and alloys since these have the best strength-to-weight ratio of any of the commonly used structural alloys. Chemical compositions of magnesium and its alloys are widely standardized from major to trace quantities. Mercury has generally been a non-analysing element to monitor because it seems to be volatilized on heating due to its low boiling point. Thus, mercury has not been prescribed solely in standards, but has been included as impurities in standards. ISO 8287 for unalloyed magnesium specifies that the sum of hazardous elements, including mercury, in all materials should be less than 0,01 % mass fraction. ISO 16220 for magnesium alloy ingots and casting denotes the impure elements should not be less than 0,01 % separately.

However, there exists no standardized analytical methods for determination of mercury in magnesium and magnesium alloys. Moreover, a new global mercury treaty called the Minamata Convention that came into effect in 2020, which regulates and controls mercury globally, has encouraged the development of the analysis of mercury on some trading materials and products.

This document specifies the methods for determination of trace levels of mercury in magnesium and magnesium alloys.

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Magnesium and magnesium alloys — Determination of mercury

1 Scope

This document specifies the methods for the determination of mercury in magnesium and magnesium alloys by inductively coupled plasma (ICP) atomic mass spectrometric analysis and by atomic absorption spectrometric analysis.

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 384, *Laboratory glass and plastics ware — Principles of design and construction of volumetric instruments*

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*

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

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 Classification of methods for determination

The method for the determination of tin shall be in accordance with any one of the following methods.

- a) ICP mass spectrometric analysis (Method A).

This method is applicable to magnesium and magnesium alloy of 0,000 01 % (mass fraction) or over up to and including 0,01 % (mass fraction) in mercury content.

- b) Atomic absorption spectrometric analysis (Method B).

This method is applicable to magnesium and magnesium alloy of 0,000 02 % (mass fraction) or over up to and including 0,001 % (mass fraction) in mercury content.

5 Sampling, storing and weighing of analytical samples

5.1 Sampling

Sampling shall be carried out as follows.

- a) When the chips are sampled from a casting sample (A) or a product sample (B), select the sampling position so as to represent the quality of the sample, and penetrate the sample by boring at right angles to its surface. In the case of a sample with a thickness not penetrable from one direction, another suitable method (e.g. boring from two directions) shall be used.
- b) Prior to boring for chipping, clean the drill (which is not more than 10 mm in diameter) using ethanol. Remove the adhered matters on the surface of the sampling position, and then carry out the boring, without using any sort of oils or lubricant and with just enough force to drill without oxidizing the sample chips. At this time, adjust the pressure exerted or the revolution frequency of the drill so that no excessive heat is generated. Do not attempt to cool off or stop the temperature from rising by pouring water or another liquid over the sample.

The use of cutting tools other than a drill, such as a lathe, is permissible.

- c) Collect all of the sample chips (which shall be no larger than 10 mm), and remove iron powder, etc., using a strong magnet. Then, mix the chips together thoroughly to create the analytical sample and leave them in a desiccator to cool to room temperature.
- d) If the sampling from specimens such as thin sheets, pipes, etc., cannot be in accordance with the specifications given in a) to c), the sampling method shall be as agreed by the purchaser and the supplier.

5.2 Storing of analytical sample

The analytical sample shall be stored as follows.

- a) Store the sample in a glass container with a lid sealed hermetically to prevent contamination.
- b) If there is the possibility that substances (e.g. oil) have adhered on the surface, clean the analytical sample using a product (e.g. ethanol, acetone) and dry it before using.

5.3 Weighing of the analytical sample

The analytical sample shall be weighed as follows.

- a) Mix the sample thoroughly so that any portion weighed out represents the average composition.
- b) Weigh out 0,1 g (method A) or 0,5 g (method B) of the sample to a digit of 1 mg by using an analytical balance described in [6.3](#).

6 Apparatus

Use normal laboratory apparatus and, in particular, the following.

6.1 Volumetric glassware, of Class A in accordance with ISO 384, ISO 648 and ISO 1042, and used in accordance with ISO 4787.

6.2 Analytical balance, sensitive to 0,1 mg.

6.3 ICP mass spectrometer, to measure the ion intensities of mercury with separate masses from the inductively coupled plasma.

6.4 Atomic absorption spectrometer, to measure the light absorption of specific wavelength arising from mercury in the quartz cell.

7 ICP mass spectrometric analysis (Method A)

7.1 Summary

The aqueous solution including the chipped magnesium sample is added with solution of permanganate ion prior to dissolution. The solution is then decomposed with nitric acid, thus suppressing volatilization of mercury in the sample. Precipitates of manganese(IV) oxide generated during decomposition are reduced with hydroxyl ammonium chloride. The prepared solution is sprayed into the argon plasma of the ICP mass spectrometer and the ion intensities of mercury are measured.

7.2 Reagents

During the analysis, use only reagents of recognized analytical grade and water that conforms to grade 1 or 2 of ISO 3696.

7.2.1 Hydrochloric acid, 1+1.

Dilute hydrochloric acid [35 % to 37 % (mass fraction)] of analytical grade twice with water.

7.2.2 Nitric acid, 1+1.

Dilute nitric acid [60 % to 61 % (mass fraction)] of analytical grade twice with water.

7.2.3 Potassium permanganate solution, Mn(VII): 50 g/l.

Weigh out 14,5 g of potassium permanganate [not less than 99,3 % (mass fraction)] and transfer it into a beaker (100 ml). Add 50 ml of water to dissolve, then transfer it into a 100 ml brown coloured volumetric flask by using water, and dilute it up to the mark with water.

7.2.4 Hydroxyl ammonium chloride solution, 200 g/l.

Weigh out 20 g of hydroxyl ammonium chloride [not less than 98,0 % (mass fraction)] and transfer it into a beaker (100 ml). Add 50 ml of water to dissolve, then prepare it as a 100 ml solution in a volumetric flask with water.

7.2.5 L-Cysteine solution, 1 g/l.

Weigh out 0,20 g of L-cysteine [not less than 98,0 % (mass fraction)] and transfer it into a beaker (100 ml). Add 50 ml of water to dissolve, then prepare it as a 200 ml solution in a volumetric flask with water.

7.2.6 Magnesium solution, Mg(II): 40 mg/ml.

Weigh out 33,2 g of magnesium oxide [not less than 99,99 % (mass fraction)] and transfer it into a beaker (500 ml). Add 50 ml of water, cover it with a watch glass and add 280 ml of nitric acid (1+1). After the reaction has stopped, decompose it completely by heating. After cooling it down to a normal temperature, prepare it as a 500 ml solution in a volumetric flask with water.

7.2.7 Aluminium solution, Al(III): 1,0 mg/ml.

Weigh out 0,20 g of aluminium [not less than 99,99 % (mass fraction)], transfer it into a beaker (300 ml) and cover it with a watch glass. Add 10 ml of water and then decompose it by adding the premixed acid solution from 10 ml of hydrochloric acid (1+1) and 30 ml of nitric acid (1+1). When the reaction has stopped, decompose it completely by heating. After cooling it down to a normal temperature, wash the

lower surface of the watch glass and the inner wall of the beaker with water, remove the watch glass, then prepare it as a 200 ml solution in a volumetric flask with water.

7.2.8 Zinc solution, Zn(II): 0,5 mg/ml.

Weigh out 0,10 g of zinc [not less than 99,99 % (mass fraction)], transfer it into a beaker (300 ml) and cover it with a watch glass. After adding 10 ml of water, decompose zinc by adding 25 ml of nitric acid (1+1) little by little. When the reaction has stopped, decompose it completely by heating. After cooling it down to a normal temperature, wash the lower surface of the watch glass and the inner wall of the beaker with water, remove the watch glass, then prepare it as a 200 ml solution in a volumetric flask with water.

7.2.9 Mercury standard solution, Hg(II): 0,1 µg/ml.

Weigh out 0,0677 g of mercury(II) chloride [not less than 99,9 % (mass fraction)], transfer it into a beaker (300 ml) and cover it with a watch glass. Add 50 ml of water and then decompose it with 50 ml of nitric acid (1+1). Prepare it as a 500 ml stock solution in a volumetric flask with water (Hg: 100 µg/ml). Alternatively, dilute a mercury standard solution [1 000 µg/ml] that is commercially available 10-folds with a volumetric pipette to make a stock solution of identical concentration (Hg: 100 µg/ml). Dilute only the necessary amount of this stock solution 1 000-folds with water stepwise using volumetric pipettes and flasks just prior to measurement, and take it as the mercury standard solution for measurement. The compound and stock solution are both highly toxic; handle with care.

7.3 Amount of sample to be weighed out

The amount of sample to be weighed out shall be 0,1 g to a digit of 1 mg.

7.4 Operation

7.4.1 Preparation of the sample solution

The preparation of the sample solution shall be carried out in accordance with the following procedures.

- Weigh out the sample, transfer it into a beaker (300 ml) and cover it with a watch glass. Add 50 ml of water and 5,0 ml of potassium permanganate solution (7.2.3) in order, prior to dissolution by acid.
- Observe the sample chips settled into the solution, then dissolve them by adding 12,0 ml of nitric acid (1+1) (7.2.2). Manganese dioxide is precipitated during the dissolution.
- Add several drops of hydroxyl ammonium chloride solution (7.2.4) and shake the beaker until the brown precipitate of manganese dioxide has vanished.
- Transfer the solution in the beaker to a 250 ml volumetric flask, wash the lower surface of the watch glass and the inner wall of the beaker with water. Add 10,0 ml of nitric acid (1+1) (7.2.2) and 8,0 ml of hydrochloric acid (1+1) (7.2.1). L-cysteine solution (7.2.5) is also added to an amount of 10,0 ml to prevent any adhesion onto the inner surface of the introduction tube of the instrument. Dilute it up to the mark with water.

7.4.2 Measurement of ion intensity

Spray a portion of the solution obtained in 7.4.1 d) into the argon plasma of the ICP mass spectrometer, then measure the ion intensity of mercury at a mass number of 200 or 202.

7.5 Blank test

Place 25,0 ml of magnesium solution (7.2.6) in a beaker (300 ml), and carry out the same operation as for the sample but without the sample, in parallel with the operation on the sample following the procedure given in 7.4.1 a) to 7.4.2.

7.6 Preparation of the working curve

The preparation of the working curve shall be carried out in accordance with the following procedures.

- Take magnesium solution (7.2.6) in each of three separate 250 ml volumetric flasks so that the amount of magnesium is the same as that contained in the sample weighed out in the procedure in 7.4. Then, add 10,0 ml of nitric acid (1+1) (7.2.2), 8,0 ml of hydrochloric acid (1+1) (7.2.1) and 5,0 ml of potassium permanganate solution (7.2.3) to the flask, add stepwise amounts of 0 ml to 10,0 ml (0 ng ml⁻¹ to 4,0 ng ml⁻¹ as the concentrations of mercury) of mercury standard solution (7.2.9), and dilute up to the mark with water. The concentration of the assay standard solutions should be varied corresponding to the mercury content in the sample. If the sample contains aluminium and zinc as components, match its concentrations up to that of the sample, using aluminium solution (7.2.7) and zinc solution (7.2.8).
- Spray a portion of the solutions into the argon plasma of the ICP mass spectrometer and measure the ion intensity of mercury at a mass number of 200 or 202 in parallel with the sample solution. Prepare the relation curve between the ion intensity and the amount of mercury added as the mercury standard solutions. Translate the relation curve so that it passes through the origin, and take it as the working curve.

7.7 Calculation

Note the amounts of mercury from the ion intensities obtained in 7.4.2 and 7.5 using the working curve prepared in 7.6, and calculate the content of mercury in the sample according to Formula (1):

$$Hg = \frac{A_1 - A_2}{m} \times 100 \quad (1)$$

where

Hg is the content of mercury in the sample, in mass fraction (%);

A_1 is the amount of mercury detected in sample solution, in g;

A_2 is the amount of mercury detected in blank solution, in g;

m is the amount of sample weighed out, in g.

7.8 Reporting analytical data

The precision of this method is 5 % (RSD) or better. Its trueness lies within 24 %, considering that the analytical results of the certified reference materials (CRMs) of magnesium alloys have a coincidence within their uncertainties of the certified values, 11 % to 24 %. Consequently, the analytical data should be reported, showing the reliability of 5 % in precision after several runs of measurement.

8 Atomic absorption spectrometric analysis (Method B)

8.1 Summary

The sample is decomposed by the same procedure as the one described in method A. After adding sulfuric acid, tin(II) chloride solution is used for reduction of Hg(II), and mercury is vaporized by passing air into the solution. The absorbance of a gas cell filled with evaporated mercury vapour is measured with an atomic absorption photometer. This technique is often called cold vapour generation-atomic absorption spectrometry (CVAAS).

8.2 Reagents

During the analysis, use only reagents of recognized analytical grade and water that conforms with grade 1 or 2 of ISO 3696.

8.2.1 Hydrochloric acid, 1+1.

Prepare in accordance with [7.2.1](#).

8.2.2 Nitric acid, 1+1.

Prepare in accordance with [7.2.2](#).

8.2.3 Sulfuric acid, 1+20.

Dilute sulfuric acid [96 % or more (mass fraction)] of analytical grade 21-fold with water, by mixing sulfuric acid and water in a volume ratio of 1 and 20.

8.2.4 Potassium permanganate solution, Mn (VII): 50 g/l.

Prepare in accordance with [7.2.3](#).

8.2.5 Hydroxyl ammonium chloride solution, 200 g/l.

Prepare in accordance with [7.2.4](#).

8.2.6 Magnesium solution, Mg: 40 mg/ml.

Prepare in accordance with [7.2.6](#).

8.2.7 Aluminium solution, Al: 1,0 mg/ml.

Prepare in accordance with [7.2.7](#).

8.2.8 Zinc solution, Zn: 0,5 mg/ml.

Prepare in accordance with [7.2.8](#).

8.2.9 Tin(II) chloride solution, Sn(II): 0,1 g/ml.

Take 19,0 g of tin(II) chloride dihydrate [97 % or more (mass fraction)] and add 60 ml of sulfuric acid (1+20), which is prepared by dilution of sulfuric acid (1+1) ([8.2.3](#)) 10-folds with water. After heating to dissolve, prepare it as a 100 ml solution in a volumetric flask with water. It should be prepared just before use.

8.2.10 Mercury standard solution, Hg: 0,1 µg/ml.

Prepare in accordance with [7.2.9](#).

8.3 Amount of sample to be weighed out

The amount of sample to be weighed out shall be 0,5 g to a digit of 1 mg.

8.4 Apparatus and implements

8.4.1 Mercury vapour generator of closed circulating system or open air-supply system. Examples of the composition of such apparatus are shown in [Figures 1](#) and [2](#). The absorption cell, drying tube and mercury trap constituting the apparatus shall be in accordance with [8.4.2](#) to [8.4.4](#).

8.4.2 Absorption cell, 8 mm to 30 mm in diameter, 100 mm to 300 mm in length, made of quartz glass or made of plastics (without mercury vapour absorbed) and provided with quartz glass windows at both ends.

8.4.3 Drying tube, consisting of a glass tube or a U-tube packed with silica gel or anhydrous calcium chloride for drying.

8.4.4 Mercury trap, of a gas-washing bottle filled with a sulfuric acid (1+4) solution containing potassium permanganate (50 g/l) or any reagent which is equivalent in performance.

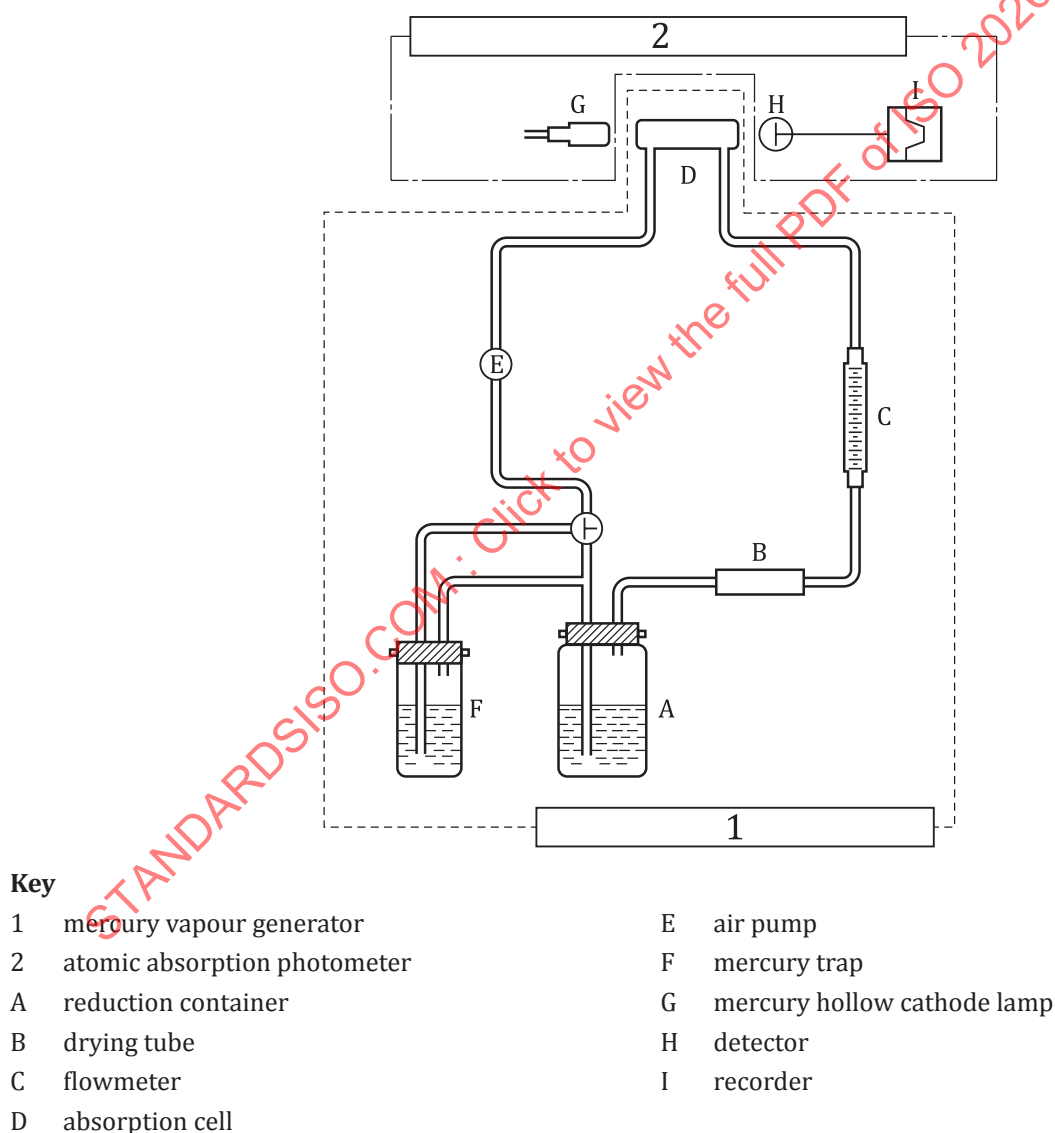
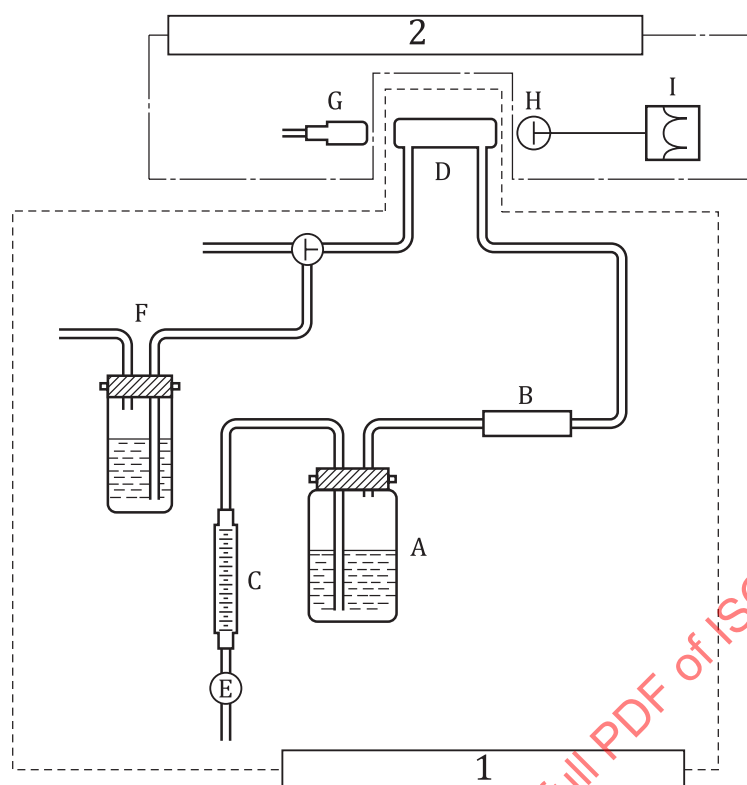


Figure 1 — Example of a closed circulating system for the measurement of mercury



Key

1	mercury vapour generator	E	air pump
2	atomic absorption photometer	F	mercury trap
A	reduction container	G	mercury hollow cathode lamp
B	drying tube	H	detector
C	flowmeter	I	recorder
D	absorption cell		

Figure 2 — Example of an opened air supply system for the measurement of mercury

8.5 Operation

8.5.1 Preparation of the sample solution

The preparation of the sample solution shall be carried out in accordance with the following procedures.

- Weigh out the sample, transfer it into a beaker (300 ml), and cover it with a watch glass. Add 50 ml of water and 20,0 ml of potassium permanganate solution (8.2.4) in order, prior to dissolution by acid.
- Observe the sample chips settled into the solution, then dissolve them by adding 15,0 ml of nitric acid (1+1) (8.2.2). Manganese dioxide is precipitated during the dissolution.
- Drop hydroxyl ammonium chloride solution (8.2.5) and shake the beaker until the brown precipitate of manganese dioxide has vanished.
- Transfer the solution into a reduction container, wash the lower surface of the watch glass and the inner wall of the beaker with water. Add 10,0 ml of sulfuric acid (1+1) (8.2.3) and make the solution volume from 150 ml to 200 ml with water.

When the content of mercury is 0,000 1 % (mass fraction) or over up to 0,001 0 % (mass fraction), carry out the following procedures.