INTERNATIONAL STANDARD

ISO 6101-1

Third edition
2019-11

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 1:
Determination of zinc content

Caoutchouc — Dosage du métal par spectrométrie d'absorption atomique —

Partie 1: Dosage du zinc

Reference number
ISO 6101-1:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This third edition cancels and replaces the second edition (ISO 6101-1:1991), which has been technically revised.

The main changes compared to the previous edition are as follows.

- The procedure for the destruction of organic matter is further detailed.
- Formula (2) in 9.2 has been changed to zinc content being expressed as milligram per kilogram.
- Precision data have been updated in Annex B.

A list of all parts in the ISO 6101 series can be found on the ISO website.

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.

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 1:
Determination of zinc content

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies an atomic absorption spectrometric method for the determination of the zinc content of rubbers.

The method is applicable to raw rubber and rubber products having zinc contents at a minimum of 0,05 % (mass fraction). Zinc contents below this limit can be determined, provided that suitable adjustments are made to the mass of the test portion and/or to the concentrations of the solutions used. The use of the standard additions method might lower the bottom limit of detection.

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 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 247-1, *Rubber — Determination of ash — Part 1: Combustion method*

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

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

ISO 1772, *Laboratory crucibles in porcelain and silica*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

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

A test portion is ashed at 550 °C ± 25 °C in accordance with ISO 247-1. The ash is dissolved in hydrochloric or nitric acid. The solution is aspirated into an atomic absorption spectrometer and the absorption is measured at a wavelength of 213,8 nm, using a zinc hollow-cathode lamp as the zinc emission source. Any silicates are volatilized by sulfuric acid and hydrofluoric acid.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

5.1 Sulfuric acid, ϱ_{20} = 1,84 Mg/m^3.

5.2 Hydrochloric acid, ϱ_{20} = 1, 18 Mg/m^3.

5.3 Hydrochloric acid solutions.

5.3.1 Hydrochloric acid, diluted 1 + 2.

Dilute 1 volume of the concentrated hydrochloric acid (5.2) with 2 volumes of water.

5.3.2 Hydrochloric acid, diluted 1 + 100.

Dilute 1 volume of the concentrated hydrochloric acid (5.2) with 100 volumes of water.

5.4 Hydrofluoric acid, ϱ_{20} = 1, 12 Mg/m^3.

5.5 Nitric acid, ϱ_{20} = 1,42 Mg/m^3.

5.5.1 Dilute nitric acid, 1,6 % (by mass), carefully pipette 11,5 cm^3 of concentrated nitric acid (5.5) into a 1 000 cm^3 one-mark volumetric flask (6.5), making up to the mark with water, and mix thoroughly.

5.6 Zinc standard stock solution (1mg/ml).

Either use a commercially available standard zinc solution, or prepare as follows.

Weigh, to the nearest 0,1 mg, 1 g of pure zinc dust (minimum purity 99,9 %) and dissolve in a minimum amount of the 1 + 2 hydrochloric acid solution (5.3.1). Allow to cool and transfer quantitatively to 1 000 cm^3 one-mark volumetric flask (6.5). Make up to the mark with 1 + 100 hydrochloric acid solution (5.3.2) and mix thoroughly.

1 cm^3 of this standard stock solution contains 1 000 µg of Zn.

5.7 Zinc standard solution (10 µg/ml).

Using a pipette (6.6), carefully introduce 10 cm^3 of the zinc standard stock solution (5.6) into 1 000 cm^3 one-mark volumetric flask (6.5). Dilute to the mark with 1 + 2 hydrochloric acid solution (5.3.1) or dilute nitric acid (5.5.1) and mix thoroughly.

Prepare this solution on the day of use.

1 cm^3 of this standard solution contains 10 µg of Zn.

6 Apparatus

Use ordinary laboratory apparatus and the following.

6.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and compressed air and also fitted with a zinc hollow-cathode lamp capable of emitting radiation of the required wavelengths. A high-brightness lamp is advisable.

The instrument shall be operated in accordance with the manufacturer's instructions for optimum performance.

Alternatively, an **electrothermal atomization device** (graphite furnace) may be used. It shall be operated by a competent person in accordance with the manufacturer's instructions for optimum performance.

6.2 Balance, accurate to 0,1 mg.

6.3 Muffle furnace, capable of being maintained at a temperature of 550 °C ± 25 °C.

6.4 Beaker, of capacity 250 cm^3.

6.5 One-mark volumetric flasks, glass-stoppered, of capacity 50 cm^3, 100 cm^3, 200 cm^3, 500 cm^3 and 1 000 cm^3, in accordance with the requirements of ISO 1042, class A.

6.6 One-mark volumetric pipettes, of capacity 0,5 cm^3, 1,0 cm^3, 5 cm^3, 10 cm^3, 20 cm^3 and 50 cm^3, in accordance with the requirements of ISO 648, class A.

6.7 Filter funnel, of diameter 65 mm and angle 60°, fitted with a sintered-glass disc of pore size 16 µm to 40 µm (porosity grade P 40 — see ISO 4793).

6.8 Silica or porcelain crucible, of capacity 50 cm^3 to 150 cm^3 depending on the test portion size, in accordance with the requirements of ISO 1772.

6.9 Platinum crucible, of capacity 50 cm^3 to 150 cm^3 depending on the test portion size.

6.10 Platinum or borosilicate-glass rod, for use as stirrer.

NOTE Platinum rod is used to stir samples digested with hydrofluoric acid.

6.11 Ashless filter paper, diameter 150 mm.

6.12 Electric heating plate or **sand bath heated by a gas burner**.

6.13 Conical flask, of capacity 250 cm^3.

6.14 Steam bath.

6.15 Watch glass.

7 Sampling

Carry out sampling as follows:

- raw rubber: in accordance with ISO 1795;

- latex: in accordance with ISO 123;
- products: to be representative of the whole batch.

8 Procedure

8.1 Preparation of test portion

8.1.1 Weigh, to the nearest 0,1 mg, approximately 1 g to 5 g of rubber product and 5 g to 10 g of raw rubber, milled or finely cut into the appropriate crucible (6.8 or 6.9).

8.1.2 If the rubber contains halogenated compounds (for example, in the case of chloroprene rubber), weigh, to the nearest 0,1 mg, 0,1 g of milled or finely cut rubber into 250 cm^3 conical flask (6.13).

8.1.3 For natural rubber latex concentrate, take a portion of thoroughly mixed latex containing about 10 g of total solids, make into a thin film by pouring the portion onto a glass plate, dry to a constant mass as specified in ISO 124 and cut into small pieces.

8.1.4 For raw, natural rubber, take the test portion from a test sample prepared in accordance with ISO 1795.

8.2 Preparation of test solution

8.2.1 Destruction of organic matter

8.2.1.1 Ash the test portion (8.1.1) in accordance with method A or method B of ISO 247-1, using the muffle furnace (6.3) maintained at 550 °C ± 25 °C. After ashing, allow the crucible and its content to cool to ambient temperature.

If the ash is black, caused by a small amount of carbon black, add 1 cm^3 of concentrated nitric acid (5.5) to the ash, evaporate to dryness on an electrical heating plate or sand bath heated by a gas burner (6.12) and return to the muffle furnace and ash for 10 min to 15 min.

8.2.1.2 If the rubber contains halogenated compounds, carry out destruction of the organic matter in the test portion (8.1.2) in accordance with the following alternative procedure.

Add to the test portion (8.1.2), 10 cm^3 to 15 cm^3 of sulfuric acid (5.1) and heat moderately until the test portion has disintegrated. Carefully add 5 cm^{3}of nitric acid (5.5). Continue heating until the test portion has completely decomposed and white fumes are evolved.

Some rubber formulations cause considerable splashing; in this case, use a larger conical flask.

8.2.2 Dissolution of inorganic matter using hydrochloric acid

8.2.2.1 Add carefully 20 cm^3 of 1 + 2 hydrochloric acid (5.3.1) to the residue and heat for 30 min on a steam bath (6.14). Cover with a watch glass (6.15) to avoid losses, for example due to carbonates, which cause splashing and foaming.

Transfer the solution and the residue to a beaker (6.4) with 50 cm^3 of 1 + 2 hydrochloric acid solution (5.3.1) and heat for 30 min.

If the residue dissolves completely, transfer to 50 cm^3 volumetric flask (6.5), dilute to the mark with 1 + 2 hydrochloric acid solution (5.3.1), and proceed in accordance with 8.4.

8.2.2.2 If the ash is not totally dissolved when following the procedure described in 8.2.2.1, repeat the ashing in accordance with 8.2.1.1 or 8.2.1.2 using a new test portion, and proceed as follows.

Transfer the ash from the new test portion to a platinum crucible (6.9). Add a few drops of sulfuric acid (5.1) and heat to fuming. Cool and add a further 3 drops of sulfuric acid (5.1) and 5 cm^3 of hydrofluoric acid (5.4). Heat on the electric heating plate or sand bath (6.12) in a fume cupboard and evaporate to dryness, while stirring with the platinum rod (6.10). Repeat this digestion with the same quantities of sulfuric and hydrofluoric acids twice.

NOTE Borosilicate-glass rod is not suitable to stir samples digested with hydrofluoric acid.

Allow to cool to ambient temperature, add 20 cm^3 of 1 + 2 hydrochloric acid solution (5.3.1), cover with a watch glass and heat for 10 min. Filter the contents of the crucible into a 50 cm^3 volumetric flask (6.5) through an ashless filter paper (6.11) and rinse the contents with 1+2 hydrochloric acid (5.3.1). Dilute to the mark with 1 + 2 hydrochloric acid solution (5.3.1) and mix thoroughly. Proceed in accordance with 8.4.

8.2.2.3 Test solutions should contain approximately 12 % hydrochloric acid. If evaporation or reaction with carbonates, etc., has reduced or increased this concentration, adjust it accordingly with concentrated hydrochloric acid (5.2) or water.

8.2.3 Dissolution of inorganic matter using nitric acid — Alternative method

Add 10 cm^3 of dilute nitric acid (5.5.1) to the cooled residue. Cover with a watch glass and heat on a steam bath (6.14) or electrical heating plate (6.10) for at least 30 min. Allow to cool to ambient temperature. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask (6.5) through an ashless filter paper (6.11). Rinse the crucible and mix thoroughly, before making up with dilute nitric acid (5.5.1) to the mark. Proceed in accordance with 8.4.

8.3 Preparation of the calibration graph

8.3.1 Preparation of standard calibration solutions

8.3.1.1 Into a series of five 100 cm^3 one-mark volumetric flasks (6.5), introduce, using pipettes (6.6), the volumes of the standard zinc solution (5.7) indicated in Table 1. Dilute to the mark with 1 + 2 hydrochloric acid solution (5.3.1) or dilute nitric acid (5.5.1) and mix thoroughly.

Table 1 — Standard calibration solutions

Volume of standard zinc solution (5.7) cm^3	Mass of zinc contained in 1 cm^3 µg
50	5
20	2
10	1
5	0,5
0	0

8.3.1.2 Prepare fresh standard calibration solutions daily.

8.3.2 Spectrometric measurements

Switch on the spectrometer (6.1) sufficiently in advance to ensure stabilization. With the zinc hollow-cathode lamp suitably positioned, adjust the wavelength to 213,8 nm and the sensitivity and the slit aperture according to the characteristics of the instrument.

Adjust the pressures and flow rates of the air and of the acetylene in accordance with the manufacturer's instructions so as to obtain a clear, non-luminous, oxidizing flame, suited to the characteristics of the particular spectrometer being used.

Aspirate the series of standard calibration solutions (8.3.1.1) in succession into the flame, and measure the absorbance of each solution twice, averaging the readings. Take care to ensure that the rate of aspiration is constant throughout this process. Ensure also that at least one calibration solution is at or below the level of the zinc concentration in the test solution.

Aspirate water through the burner after each measurement.

8.3.3 Plotting the calibration graph

Plot a graph having, for example, the masses, in µg, of zinc contained in 1 cm^3 of the standard calibration solutions as abscissae, and the corresponding values of absorbance, corrected for the absorbance of the calibration blank solution (see 8.3.1.1), as ordinates. Represent the points on the graph by the best straight line as judged visually, or calculated by the least-square fit method.

8.4 Determination

8.4.1 Spectrometric measurements

Carry out duplicate spectrometric measurements at a wavelength of 213,8 nm on the test solution (8.2.2), following the procedure specified in 8.3.2.

8.4.2 Dilution

If the instrument response for the test solution is greater than that for the standard calibration solution having the highest zinc content (see 8.3.1.1), dilute as appropriate with 1 + 2 hydrochloric acid solution (5.3.1) or dilute nitric acid (5.5.1) in accordance with the following procedure.

Pipette carefully a suitable volume (V cm^3) of the test solution (8.2.2) into a 100 cm^3 one-mark volumetric flask (6.5) so that the zinc concentration lies within the range covered by the standard calibration solutions. Dilute to the mark with the 1 + 2 hydrochloric acid solution (5.3.1) or dilute nitric acid (5.5.1). Repeat the spectrometric measurements.

NOTE To increase the reliability of the test method, the standard additions method is found useful (see Annex A).

8.4.3 Blank determination

Carry out a blank test in parallel with the determination, using 1 + 2 hydrochloric acid solution (5.3.1) or dilute nitric acid (5.5.1), but omitting the test portion.

If the preparation of the test solution involved the use of sulfuric acid and hydrofluoric acid, prepare the blank test solution by repeating that procedure, but omitting the test portion.

9 Expression of results

9.1 Read the zinc content of the test solution directly from the calibration graph (8.3.3).

The zinc content, expressed as a percentage by mass, is given by Formula (1):

$$\frac{\rho(\mathrm{Zn})_\mathrm{t} - \rho(\mathrm{Zn})_\mathrm{b}}{200m} \times f \qquad (1)$$

where

$\rho(\mathrm{Zn})_t$ is the zinc content, in µg/cm^3, of the test solution (8.2.2), read from the calibration graph;

$\rho(\mathrm{Zn})_b$ is the zinc content, in µg/cm^3, of the blank test solution (8.4.3), read from the calibration graph;

m is the mass, in µg, of the test portion (8.1);

f is the dilution factor, if required (see 8.4.2), of the test solution:

$$f = \frac{100}{V}$$

V being the volume, in cm^3, of test solution taken in 8.4.2.

To express the zinc content as zinc oxide content, multiply the result by 1,245.

9.2 The zinc content of the test portion can also be calculated, in mg/kg, of the test solution, by Formula (2):

$$\frac{50\left[\rho(\mathrm{Zn})_t - \rho(\mathrm{Zn})_b\right]}{m} \times f \qquad (2)$$

9.3 The test result is the average of two determinations, rounded to two decimal places when the zinc concentration is expressed as a percentage and to the nearest whole number when the concentration is expressed in mg/kg.

9.4 Report the zinc content as a percentage if greater than or equal to 0,1 % (mass fraction), or as mg/kg if less than 0,1 % (mass fraction).

10 Precision

See Annex B.

11 Test report

The test report shall include the following information:

a) all details necessary for the complete identification of the product tested;

b) the method of sampling;

c) a reference to this document, i.e. ISO 6101-1:2019;

d) the method of ashing and the method of dissolution used;

e) the type of instrument used (flame or graphite furnace spectrometer);

f) the results obtained and the units in which they have been expressed;

g) any unusual features noted during the determination;

h) any operations not specified in this document, or in the International Standards to which reference is made, which might have affected the results.

Annex A

(informative)

Method of standard additions

The method of standard additions provides the analyst with a powerful tool for increasing the reliability and accuracy of an atomic absorption analysis.

It is used when samples contain unknown concentrations of matrix materials, which are difficult to duplicate with blanks, or where the analyst desires to increase the accuracy of the determination.

The method of standard additions can be found in any standard text-book on atomic absorption and is usually described in the user's manual supplied with the atomic absorption spectrometer.

The following example illustrates the method.

From a test solution prepared as described in 8.2, take four aliquots of the same size. To three of these aliquots, add a different, but known, volume of standard zinc solution. Make up the volumes to the same total for all four aliquots. Use concentrations which fall on the linear portion of the calibration graph.

Measure the absorbance of each of the four solutions so obtained.

Plot absorbance on the y-axis and the concentration, in µg of zinc per cm^3 of solution, on the x-axis.

Extrapolate the straight line to cut the x-axis (zero absorbance). At this point, read the concentration of zinc in the test solution. An example is given in Figure A.1.