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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 6101-1:1991(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 6101-1 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 6101-1:1981), of which it constitutes a technical revision.

ISO 6101 consists of the following parts, under the general title *Rubber — Determination of metal content by atomic absorption spectrometry*:

- *Part 1: Determination of zinc content*
- *Part 2: Determination of lead content*
- *Part 3: Determination of copper content*
- *Part 4: Determination of manganese content*
- *Part 5: Determination of iron content*

Annex A forms an integral part of this part of ISO 6101.

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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 1:
Determination of zinc content

1 Scope

This part of ISO 6101 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 % (m/m). Zinc contents below this limit may 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 may lower the bottom limit of detection.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 6101. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6101 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 123:1985, *Rubber latex — Sampling.*

ISO 247:1990, *Rubber — Determination of ash.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1772:1975, *Laboratory crucibles in porcelain and silica.*

ISO 1795:—[1], *Rubber, raw, natural and synthetic — Sampling and further preparative procedures (Combined revision of ISO 1795:1974 and ISO 1796:1982, also incorporating ISO/TR 2630:1978).*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Principle

A test portion is ashed at 550 °C ± 25 °C in accordance with ISO 247, method A or B. The ash is dissolved in hydrochloric 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.

NOTE 1 ISO 6955:1982, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary*, defines the spectrometric terms used in this part of ISO 6101.

4 Reagents

WARNING — All recognized health and safety precautions shall be observed when carrying out the procedures specified in this part of ISO 6101.

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

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[1] To be published. (Revision of ISO 1795:1974)

4.1 Sulfuric acid, $\varrho_{20} = 1{,}84\ \mathrm{Mg/m^3}$.

4.2 Hydrochloric acid, $\varrho_{20} = 1{,}18\ \mathrm{Mg/m^3}$.

4.3 Hydrochloric acid solutions.

4.3.1 Hydrochloric acid, diluted 1 + 2.

Dilute 1 volume of the concentrated hydrochloric acid (4.2) with 2 volumes of water.

4.3.2 Hydrochloric acid, diluted 1 + 100.

Dilute 1 volume of the concentrated hydrochloric acid (4.2) with 100 volumes of water.

4.4 Hydrofluoric acid,
$\varrho_{20} = 1{,}13\ \mathrm{Mg/m^3}$, 38 % (m/m) to 40 % (m/m).

4.5 Nitric acid, $\varrho_{20} = 1{,}42\ \mathrm{Mg/m^3}$.

4.6 Zinc, standard stock solution containing 1 g of Zn per cubic decimetre.

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 (4.3.1). Allow to cool and transfer quantitatively to a 1 000 cm^3 one-mark volumetric flask (5.5). Make up to the mark with 1 + 100 hydrochloric acid solution (4.3.2) and mix thoroughly.

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

4.7 Zinc, standard solution corresponding to 10 mg of Zn per cubic decimetre.

Using a pipette (5.6), carefully introduce 10 cm^3 of the standard stock zinc solution (4.6) into a 1 000 cm^3 one-mark volumetric flask (5.5). Dilute to the mark with 1 + 2 hydrochloric acid solution (4.3.1) and mix thoroughly.

Prepare this solution on the day of use.

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

5 Apparatus

Ordinary laboratory apparatus and

5.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air compressed respectively to at least 60 kPa and 300 kPa, and also fitted with a zinc hollow-cathode lamp as the zinc emission source. 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, using the test solution as prepared in 7.2.

5.2 Balance, accurate to 0,1 mg.

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

5.4 Beaker, of capacity 250 cm^3.

5.5 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, complying with the requirements of ISO 1042, class A.

5.6 One-mark volumetric pipettes, of capacity 5 cm^3, 10 cm^3, 20 cm^3 and 50 cm^3, complying with the requirements of ISO 648, class A.

5.7 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).

5.8 Silica or porcelain crucible, of capacity 50 cm^3, complying with the requirements of ISO 1772.

5.9 Platinum crucible, of capacity 50 cm^3.

5.10 Platinum rod, for use as stirrer.

5.11 Filter paper, ashless, acid-resistant or glass-fibre, of diameter 110 mm.

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

5.13 Conical flask, of capacity 250 cm^3.

6 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.

7 Procedure

7.1 Test portion

7.1.1 If ashing is to be carried out by method A or method B of ISO 247, weigh, to the nearest 0,1 mg, 0,1 g of milled or finely cut rubber into the appropriate crucible (5.8 or 5.9).

7.1.2 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 a 250 cm³ conical flask (5.13).

7.2 Preparation of test solution

7.2.1 Destruction of organic matter

7.2.1.1 Ash the test portion (7.1.1) in accordance with method A or method B of ISO 247, using the muffle furnace (5.3) maintained at 550 °C ± 25 °C. Weighing of the ash is unnecessary.

7.2.1.2 If the rubber contains halogenated compounds, carry out destruction of the organic matter in the test portion (7.1.2) in accordance with the following alternative procedure.

Add to the test portion (7.1.2), 10 cm³ to 15 cm³ of sulfuric acid (4.1) and heat moderately until the test portion has disintegrated. Carefully add 5 cm³ of nitric acid (4.5). 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.

7.2.2 Dissolution of inorganic residue

7.2.2.1 Add carefully 20 cm³ of 1 + 2 hydrochloric acid (4.3.1) to the residue. (Carbonates cause splashing and foaming.)

Transfer the solution and the residue to a beaker (5.4) with 50 cm³ of 1 + 2 hydrochloric acid solution (4.3.1) and heat for 30 min.

If the residue dissolves completely, transfer to a 100 cm³ volumetric flask (5.5), dilute to the mark with 1 + 2 hydrochloric acid solution (4.3.1), and proceed in accordance with 7.4.

7.2.2.2 If the ash is not totally dissolved when following the procedure described in 7.2.2.1, repeat the ashing in accordance with 7.2.1.1 or 7.2.1.2 using a new test portion, and proceed as follows.

Transfer the ash from the new test portion to a platinum crucible (5.9). Add a few drops of sulfuric acid (4.1) and heat to fuming. Cool and add a further 3 drops of sulfuric acid (4.1) and 5 cm³ of hydrofluoric acid (4.4). Heat on the electric heating plate or sand bath (5.12) in a fume cupboard and evaporate to dryness, while stirring with the platinum rod (5.10). Repeat this digestion with the same quantities of sulfuric and hydrofluoric acids two more times.

Cool, add 50 cm³ of 1 + 2 hydrochloric acid solution (4.3.1) and filter. Wash the filter with 1 + 2 hydrochloric acid solution (4.3.1) and combine the filtrate and washings in a 100 cm³ volumetric flask (5.5). Dilute to the mark with 1 + 2 hydrochloric acid solution (4.3.1) and mix thoroughly. Proceed in accordance with 7.4.

7.2.2.3 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 (4.2) or water.

7.3 Preparation of the calibration graph

7.3.1 Preparation of standard calibration solutions

7.3.1.1 Into a series of five 100 cm³ one-mark volumetric flasks (5.5), introduce, using pipettes (5.6), the volumes of the standard zinc solution (4.7) indicated in table 1. Dilute to the mark with 1 + 2 hydrochloric acid solution (4.3.1) and mix thoroughly.

Table 1 — Standard calibration solutions

Volume of standard zinc solution (4.7) cm³	Mass of zinc contained in 1 cm³ µg
50	5
20	2
10	1
5	0,5
0	0

7.3.1.2 Prepare fresh standard calibration solutions daily.

7.3.2 Spectrometric measurements

Switch on the spectrometer (5.1) 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 (7.3.1.1) 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.

7.3.3 Plotting the calibration graph

Plot a graph having, for example, the masses, in micrograms, 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 7.3.1.1), as ordinates. Represent the points on the graph by the best straight line as judged visually, or calculated by the least-square fit method.

7.4 Determination

7.4.1 Spectrometric measurements

Carry out duplicate spectrometric measurements at a wavelength of 213,8 nm on the test solution (7.2.2), following the procedure specified in 7.3.2.

7.4.2 Dilution

If the instrument response for the test solution is greater than that for the standard calibration solution having the highest zinc content (see 7.3.1.1), dilute as appropriate with 1 + 2 hydrochloric acid solution (4.3.1) in accordance with the following procedure.

Pipette carefully a suitable volume (V cm^3) of the test solution (7.2.2) into a 100 cm^3 one-mark volumetric flask (5.5) 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 (4.3.1). Repeat the spectrometric measurements.

NOTE 2 To increase the reliability of the test method, the standard additions method may be used (see annex A).

7.4.3 Blank determination

Carry out a blank test in parallel with the determination, using 1 + 2 hydrochloric acid solution (4.3.1), 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.

8 Expression of results

8.1 Read the zinc content of the test solution directly from the calibration graph (7.3.3).

The zinc content, expressed as a percentage by mass, of the test portion is given by the formula

$$\frac{\varrho(\mathrm{Zn}) - \varrho(\mathrm{Zn})_\mathrm{b}}{m} \times 100 \times f$$

where

$\varrho(\mathrm{Zn})$ is the zinc content, in micrograms per cubic centimetre, of the test solution (7.2.2), read from the calibration graph;

$\varrho(\mathrm{Zn})_\mathrm{b}$ is the zinc content, in micrograms per cubic centimetre, of the blank test solution (7.4.3), read from the calibration graph;

m is the mass, in micrograms, of the test portion (7.1);

f is the dilution factor, if required (see 7.4.2), of the test solution:

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

V being the volume, in cubic centimetres, of test solution taken in 7.4.2.

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

8.2 Alternatively, providing that the absorbance of the test solution lies within the linear section of the calibration curve, the zinc content, expressed as a percentage by mass, is given by the formula

$$\frac{\varrho(\mathrm{Zn}) - \varrho(\mathrm{Zn})_\mathrm{b}}{100 \times m} \times f$$

where

$\varrho(\mathrm{Zn})$ is the zinc content, in micrograms per cubic centimetre, of the solution:

$$\varrho(\mathrm{Zn}) = \frac{A_\mathrm{t} \times \varrho(\mathrm{Zn})_\mathrm{n}}{A_\mathrm{n}}$$

$\varrho(\mathrm{Zn})_\mathrm{b}$ is the zinc content, in micrograms per cubic centimetre, of the blank test solution:

$$\varrho(\mathrm{Zn})_\mathrm{b} = \frac{A_\mathrm{b} \times \varrho(\mathrm{Zn})_\mathrm{n}}{A_\mathrm{n}}$$

A_t being the absorbance of the test solution;

A_b being the absorbance of the blank test solution;

A_n being the absorbance of the standard calibration solution having a zinc content closest to that of the test solution;

$\varrho(\mathrm{Zn})_\mathrm{n}$ being the zinc content, in micrograms per cubic centimetre, of the standard calibration solution having an absorbance closest to that of the test solution;

m is the mass, in grams, of the test portion (7.1);

f is the dilution factor, if required (see 7.4.2), of the test solution:

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

V being the volume, in cubic centimetres, of test solution taken in 7.4.2.

8.3 Carry out the procedure in duplicate, using separate test portions cut from the same homogenized sample. 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 milligrams per kilogram.

8.4 Report the zinc content as a percentage if greater than or equal to 0,1 % (*m*/*m*), or in milligrams per kilogram if less than 0,1 % (*m*/*m*).

9 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 part of ISO 6101;

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 part of ISO 6101, or in the International Standards to which reference is made, which might have affected the results.

Annex A

(normative)

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 7.2, 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 micrograms of zinc per cubic centimetre 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.

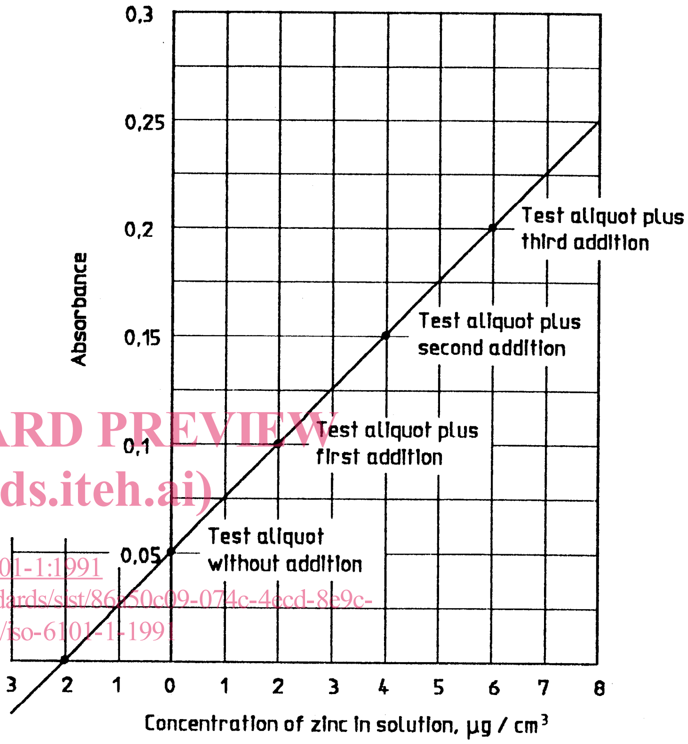

Figure A.1 — Example of graph obtained using the method of standard additions

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