INTERNATIONAL STANDARD

ISO 6101-2

Second edition
1997-06-01

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 2:
Determination of lead content

Caoutchouc — Détermination de la teneur en métal par spectrométrie d'absorption atomique —

Partie 2: Dosage du plomb

Reference number
ISO 6101-2:1997(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 6101-2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products.*

This second edition cancels and replaces the first edition (ISO 6101-2:1986), which has been technically revised.

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.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 2:
Determination of lead content

WARNING — Persons using this part of ISO 6101 should be familiar with normal laboratory practice. This part of ISO 6101 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 ensure compliance with any national regulatory conditions.

1 Scope

This part of ISO 6101 specifies an atomic absorption spectrometric method for the determination of the lead content of rubbers.

The method is applicable to raw rubber and rubber products. There is no limit to the concentration of lead that can be determined. High or low concentrations may be determined, provided that suitable adjustments are made to the mass of the test portion and/or the concentration 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 1795:1992, *Rubber, raw, natural and synthetic — Sampling and further preparative procedures.*

3 Principle

If the rubber does not contain halogenated compounds, a test portion is directly ashed at 550 °C ± 25 °C as specified in ISO 247:1990, method A. If the rubber contains halogenated compounds, a test portion is first mineralized with sulfuric and nitric acids, the acids are removed by evaporation, and the portion is ashed at 550 °C ± 25 °C.

NOTE — The presence of even small amounts of halogens may lead to the loss of volatile lead salts during dry ashing.

The ash obtained is boiled with ammonium acetate solution to dissolve the lead. Insoluble lead silicates, if present, are converted to chloride by boiling with a mixture of hydrochloric acid, nitric acid and hydrogen peroxide.

The solution is aspirated into an atomic absorption spectrometer and the absorbance is measured at a wavelength of 283,3 nm, using a lead hollow-cathode lamp as the lead emission source.

NOTE — 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

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

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

4.2 Nitric acid, ρ_{20} = 1,40 Mg/m^3.

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

4.4 Hydrochloric acid, diluted 1 + 2.

Dilute 1 volume of concentrated hydrochloric acid (4.3) with 2 volumes of water.

4.5 Hydrogen peroxide, 30 % (*m*/*m*) solution.

4.6 Ammonium acetate, 180 g/dm^3 solution.

4.7 Standard lead stock solution, containing 1 g of Pb per cubic decimetre.

Either use a commercially available standard lead solution, or prepare as follows:

Weigh, to the nearest 0,1 mg, 1 g of metallic lead (purity ⩾ 99,95 %) and transfer to a 100 cm^3 beaker (5.12). Add 30 cm^3 of water and 20 cm^3 of nitric acid (4.2) and boil on a sand-bath (5.10). If the lead is dissolved, continue boiling until the solution is reduced to about 20 cm^3 or less. No nitrogen oxides should be observed. Otherwise, add water and continue boiling. Transfer to a 1 000 cm^3 one-mark volumetric flask (see 5.7) with 1 + 2 hydrochloric acid (4.4) and fill to the mark with 1 + 2 hydrochloric acid (4.4).

1 cm^3 of this standard stock solution contains 1 mg of Pb.

4.8 Standard lead solution, containing 10 mg of Pb per cubic decimetre.

Carefully pipette 10 cm^3 of the standard lead stock solution (4.7) into a 1 000 cm^3 one-mark volumetric flask (see 5.7) dilute to the mark with 1 + 2 hydrochloric acid (4.4), and mix thoroughly.

Prepare this solution on the day of use.

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

5 Apparatus

Ordinary laboratory apparatus, plus the following:

5.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air, compressed to at least 60 kPa and 300 kPa, respectively, and also fitted with a lead hollow-cathode lamp as the lead 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, during drying, ashing and volatilization of the test portion.

5.2 Balance, accurate to 0,1 mg.

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

5.4 Evaporating dish, of capacity about 100 cm^3, made of quartz glass, with a clock-glass cover.

5.5 Conical flask, of capacity 250 cm^3, made of silica or borosilicate glass.

5.6 Measuring cylinder, of capacity 25 cm^3, graduated in 0,5 cm^3 divisions.

5.7 One-mark volumetric flasks, glass-stoppered, of capacities 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.

5.8 Filter funnel, 65 mm diameter, 60° angle.

5.9 Volumetric pipettes, of capacities 5 cm^3, 10 cm^3, 20 cm^3 and 50 cm^3, complying with the requirements of ISO 648, class A.

5.10 Electric hotplate or **heated sand bath.**

5.11 Steam bath.

5.12 Beaker, of capacity 100 cm^3.

5.13 Crucible, of platinum, and of capacity 50 cm^3 to 150 cm^3 depending on the test portion size.

5.14 Crucible, of silica or borosilicate glass, of capacity 50 cm^3 to 150 cm^3 depending on the test portion size, complying with the requirements of ISO 1772.

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 the rubber does not contain halogenated compounds, weigh, to the nearest 0,1 mg, 0,5 g to 2,0 g (depending on the expected lead content) of milled or finely cut rubber into a crucible (5.13 or 5.14).

NOTE — It is advisable to run the Beilstein test on a preliminary test portion for halogen content, as volatile lead compounds are possibly formed in the presence of halogen-containing admixtures.

7.1.2 If the rubber contains halogenated compounds (for example, in the case of chloroprene rubber), weigh, to the nearest 0,1 mg, 0,5 g to 2,0 g (depending on the expected lead content) of milled or finely cut rubber into the conical flask (5.5).

7.2 Preparation of test solution

7.2.1 Destruction of organic matter

7.2.1.1 If the rubber does not contain halogenated compounds, ash the test portion in accordance with method A of ISO 247:1990.

7.2.1.2 If the rubber contains halogenated compounds (7.1.2), use the following alternative procedure:

To the flask containing the test portion, add 10 cm^3 to 15 cm^3 of sulfuric acid (4.1) and heat moderately on the electric hotplate or on the sand bath over a gas burner (5.10) until the rubber has disintegrated. Carefully add 5 cm^3 of nitric acid (4.2). Continue heating until the rubber has completely decomposed and white fumes are evolved.

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

Transfer the reaction mixture quantitatively into the evaporating dish (5.4), evaporate to dryness and ash in the muffle furnace (5.3), maintained at 550 °C ± 25 °C, until all the carbon has burned off.

7.2.2 Dissolution of inorganic residue

After cooling, boil the residue obtained in 7.2.1.1 or 7.2.1.2 with 15 cm^3 of ammonium acetate solution (4.6) and filter through a paper filter. Retain this filtrate (A) and ash the filter with the residue in the muffle furnace (5.3), maintained at 550 °C ± 25 °C, until all the carbon has burned off.

Cool to room temperature, add a mixture of 10 cm^3 of hydrochloric acid (4.3), 5 cm^3 of nitric acid (4.2) and 10 drops of hydrogen peroxide (4.5), then boil for about 10 min.

Cool and filter the reaction mixture. Evaporate the filtrate on the steam bath (5.11) to dryness and take up the residue with water. Add this to filtrate A. Transfer the combined solutions, quantitatively, to a 50 cm^3 one-mark volumetric flask (see 5.7) with hydrochloric acid (4.4). Dilute to the mark with hydrochloric acid (4.4) and proceed in accordance with 7.4.

Test solutions in hydrochloric acid shall be of the same concentration as in 4.4. If evaporation, etc., has reduced or increased this concentration, adjust it accordingly with concentrated hydrochloric acid (4.3) or with water.

7.3 Preparation of the calibration graph

7.3.1 Preparation of calibration solutions

7.3.1.1 Into a series of five 100 cm^3 one-mark volumetric flasks (see 5.7) introduce, using pipettes (see 5.9), the volumes of standard lead solution (4.8) indicated in table 1. Dilute to the mark with 1+2 hydrochloric acid (4.4) and mix thoroughly.

Table 1 — Standard calibration solutions

Volume of standard lead solution cm³	Mass of lead contained in 1 cm³ µg
50	5
20	2
10	1
5	0,5
0	0

7.3.1.2 Prepare the set of calibration solutions immediately prior to the determination.

7.3.1.3 If the test portion was prepared with sulfuric acid and ammonium acetate, use the same quantities in the calibration solutions and for the corresponding calibration blank.

7.3.2 Spectrometric measurements

Switch on the spectrometer (5.1) sufficiently in advance to ensure stabilization. With the lead hollow-cathode lamp suitably positioned, adjust the wavelength to 283,3 nm and the sensitivity and 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 blue, non-luminous, oxidizing flame, suited to the characteristics of the particular spectrometer being used.

Aspirate the set of calibration solutions in succession into the flame and measure the absorbance of each solution twice, averaging the readings. Take care that the aspiration rate is constant throughout this process. Ensure also that at least one calibration solution is at or below the analyte level found in the rubber being tested.

Aspirate water through the burner after each measurement.

If sulfuric acid has been used in the preparation of the test portion, it is advisable to use a background correction.

7.3.3 Plotting the calibration graph

Plot a graph, having, for example, the masses, in micrograms of lead contained in 1 cm³ of the calibration solutions, as abscissae and the corresponding values of absorbance, corrected for the absorbance of the calibration blank, as ordinates. Represent the points on the graph by the best straight line as judged visually or as calculated by the least-squares fit method.

7.4 Determination

7.4.1 Spectrometric measurements

Carry out duplicate spectrometric measurements at a wavelength of 283,3 nm on the test solution prepared in 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 found for the calibration solution having the highest lead content, dilute as appropriate with 1+2 hydrochloric acid (4.4) in accordance with the following procedure:

Pipette carefully a suitable volume (V cm^3) of the test solution prepared in 7.2.2 into a 100 cm^3 one-mark volumetric flask (see 5.7) so that the lead concentration lies within the range covered by the calibration solutions. Dilute to the mark with 1 + 2 hydrochloric acid (4.4). Repeat the spectrometric measurements.

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

7.5 Blank determination

Carry out a blank test in parallel with the determination, using 1 + 2 hydrochloric acid (4.4), but omitting the test portion.

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

7.6 Number of determinations

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

8 Expression of results

8.1 Read the lead content of the test solution directly from the calibration graph plotted in 7.3.3.

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

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

where

$\rho(\mathrm{Pb})_\mathrm{t}$ is the lead content, in micrograms per cubic centimetre, of the test solution, read from the calibration graph;

$\rho(\mathrm{Pb})_\mathrm{b}$ is the lead content, in micrograms per cubic centimetre, of the blank test solution, read from the calibration graph;

m is the mass, in grams, of the test portion;

f is the test solution dilution factor, if required (see 7.4.2), given by

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

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

8.2 Alternatively, the lead content, expressed as a percentage by mass, is given by the formula

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

where

$\rho(\mathrm{Pb})_\mathrm{t}$ is the lead content, in micrograms per cubic centimetre, of the test solution, given by

$$\rho(\mathrm{Pb})_\mathrm{t} = \frac{A_\mathrm{t} \times \rho(\mathrm{Pb})_\mathrm{n}}{A_\mathrm{n}}$$

$\rho(\mathrm{Pb})_b$ is the lead content, in micrograms per cubic centimetre, of the blank test solution, given by

$$\rho(\mathrm{Pb})_b = \frac{A_b \times \rho(\mathrm{Pb})_n}{A_n}$$

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 the lead content closest to that of the test solution,

$\rho(\mathrm{Pb})_n$ being the lead content, in micrograms per cubic centimetre, of the standard calibration solution having the absorbance closest to that of the test solution;

m is the mass, in grams, of the test portion;

f is the test solution dilution factor, if required (see 7.4.2), given by

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

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

8.3 The test result is the average of two determinations, rounded to two decimal places when the lead 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 lead content as a percentage if greater than or equal to 0,1 %, or as milligrams per kilogram if less than 0,1 %.

9 Test report

The test report shall include the following particulars:

a) a reference to this part of ISO 6101;

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

c) the method of sampling;

d) the method of ashing 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 operation not included in this part of ISO 6101, or in the International Standards to which reference is made, as well as any incident 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 accuracy of an atomic absorption analysis.

It is used with samples containing unknown concentrations of matrix materials, with samples which are difficult to duplicate with blanks and/or when it is necessary to lower the limits of detection.

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, and a different, but known, volume of standard lead 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 lead per cubic centimetre of solution, on the *x*-axis.

Extrapolate the straight line to intersect the *x*-axis (zero absorbance). At the point of intersection with the *x*-axis, read the concentration of lead in the test solution.

An example is given in figure A.1.

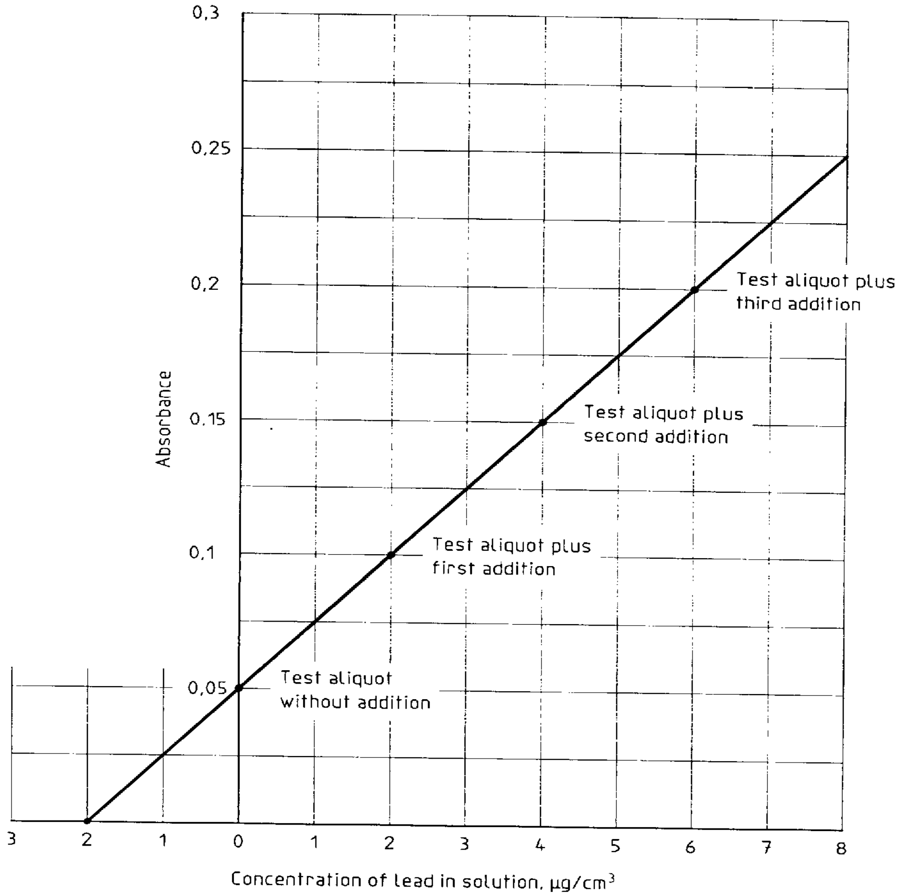

Figure A.1 — Example of graph obtained using the method of standard additions

ICS 83.060

Descriptors: rubber, chemical analysis, determination of content, lead, atomic absorption spectrometric method.

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