International Standard 6101/2

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Rubber — Determination of metal content — Flame atomic absorption spectrometric method — Part 2: Determination of lead content

Caoutchouc — Détermination de la teneur en métal — Méthode par spectrométrie d'absorption atomique dans la flamme — Partie 2: Dosage du plomb

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6101/2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products.*

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Rubber — Determination of metal content — Flame atomic absorption spectrometric method — Part 2: Determination of lead content

1 Scope and field of application

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

The method is applicable to raw rubber and rubber products having lead contents from 5 to 1000 mg/kg [0,0005 to 0,1 % (m/m)].

NOTE — Higher or lower concentrations may be determined, provided that suitable adjustments are made to the mass of the test portion and to the concentration of solutions used. The use of the standard additions method may further decrease the lower limit of detection.

2 References

ISO 247, *Rubber — Determination of ash.*

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

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

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

NOTE — For the terminology used, see ISO 6955, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary*, and, for further information on the use of flame atomic absorption spectrometry, see ISO 6956, *Atomic absorption spectrometry — Introduction to use*[1].

3 Principle

Mineralization of a test portion with sulfuric and nitric acids, removal of the acids by evaporation, and ashing at 550 ± 25 °C. Alternatively, direct ashing of a test portion at 550 ± 25 °C as specified in ISO 247, method A or B.

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

Boiling of the ash obtained with ammonium acetate solution to dissolve the lead. Conversion of insoluble lead silicates, if present, to chloride by boiling with a mixture of hydrochloric acid, nitric acid and hydrogen peroxide.

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

4 Reagents

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

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

4.1 Sulfuric acid, ϱ_{20} = 1,84 g/cm³.

4.2 Nitric acid, ϱ_{20} = 1,40 g/cm³.

4.3 Hydrochloric acid, ϱ_{20} = 1,18 g/cm³.

4.4 Hydrochloric acid, 1 + 2 (V/V) solution.

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

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

4.6 Ammonium acetate, 180 g/dm³ solution.

4.7 Lead, standard solution containing 1 g of Pb per cubic decimetre.

Use either commercially available standard lead solutions, or prepare as follows.

Weigh, to the nearest 0,1 mg, 1 g of metallic lead [purity 99,95 % (m/m)] and transfer to a 100 cm³ beaker (5.12). Add 30 cm³ water and 20 cm³ 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 cm³ or less. No nitrogen oxides should be observed. Otherwise, add water and continue boiling. Transfer to a 1000 cm³ one-mark volumetric flask (5.7) with hydrochloric acid (4.4) and fill to the mark with hydrochloric acid (4.4).

1 cm³ of this standard solution contains 1 mg of Pb.

4.8 Lead, standard solution containing 10 mg of Pb per cubic decimetre.

Carefully pipette 10 cm³ of the standard lead solution (4.7) into a 1000 cm³ one-mark volumetric flask (5.7), dilute to the mark with hydrochloric acid (4.4), and mix thoroughly.

1) At present at the stage of draft.

Prepare this solution on the day of use.

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

5 Apparatus[1)]

Ordinary laboratory apparatus and

5.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air, with a lead hollow-cathode lamp for a 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 ± 25 °C.

5.4 Evaporating dish, of capacity about 100 cm^3, made of quartz glass, with 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 capacity 50; 100; 200; 500 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 capacity 5; 10; 20; and 50 cm^3, complying with the requirements of ISO 648, class A.

5.10 Electric heating plate, or **sand-bath heated by a gas burner**.

5.11 Steam-bath.

5.12 Beaker, of capacity 100 cm^3.

5.13 Crucible, of silica or borosilicate glass, platinum or porcelain of capacity 50 cm^3 (See ISO 1772).

6 Procedure

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.

6.1 Test portion

6.1.1 If the rubber does not contain halogenated compounds and if ashing is to be carried out by method A or method B of ISO 247, weigh, to the nearest 0,1 mg, 0,5 to 2,0 g (depending on the expected lead content) of milled or finely cut rubber into a crucible (5.13). If using method B of ISO 247, wrap the rubber in ashless filter paper before placing it in the crucible.

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

6.2 Preparation of test solution

6.2.1 Ashing of the test portion

6.2.1.1 If the rubber does not contain halogenated compounds, carry out ashing of the test portion (6.1.1) in accordance with method A or method B of ISO 247.

6.2.1.2 If the rubber contains halogenated compounds (6.1.2) use the following alternative procedure.

To the flask containing the test portion (6.1.2), add 10 to 15 cm^3 of sulfuric acid (4.1) and heat moderately on the electric heating plate or on the sand-bath over a gas burner (5.10) until the rubber has disintegrated. Carefully add 5 cm^3 of the 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 ± 25 °C, until all the carbon has burned off.

6.2.2 Dissolution of the ash

After cooling, boil the residue obtained according to 6.2.1.1 or 6.2.1.2 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), 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.

1) The term millilitre (ml) is commonly used as a special name for the cubic centimetre (cm^3), in accordance with a decision of the 12th Conférence Générale des Poids et Mesures. The term millilitre is acceptable, in general, for references in International Standards to capacities of volumetric glassware and to liquid volumes. Glassware with either marking is satisfactory for use with the procedure described in this International Standard.

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 (5.7) with hydrochloric acid (4.4). Dilute to the mark with hydrochloric acid (4.4) and proceed in accordance with 6.4.

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

6.3 Preparation of the calibration graph

6.3.1 Preparation of the set of calibration solutions

6.3.1.1 Into a series of 100 cm^3 one-mark volumetric flasks (5.7), pipette the volumes of standard lead solution (4.8) indicated in the table, dilute to the mark with hydrochloric acid (4.4) and mix thoroughly.

Table

Volume of standard lead solution (4.8)	Corresponding mass of Pb contained in 1 cm^3
cm^3	µg
50	5
20	2
10	1
5	0,5
0*	0

* Calibration blank.

6.3.1.2 Prepare the set of calibration solutions (6.3.1.1) immediately prior to the determinations.

6.3.1.3 If the test portion was prepared with sulfuric acid and ammonium acetate, the same quantities shall be used in the calibration solutions and for the corresponding calibration blank.

6.3.2 Spectrometric measurement

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 the slit aperture according to the characteristics of the instrument.

Adjust the pressures and flow rates of the air and of the acetylene according to 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 (6.3.1) 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.

NOTE — 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 employ background correction.

6.3.3 Electrothermal atomization

If using an electrothermal atomization device (graphite furnace), follow the manufacturer's instructions for drying, ashing and atomization (see 5.1).

6.3.4 Plotting the calibration graph

Plot a graph, having, for example, the masses, in micrograms, of lead contained in 1 cm^3 of the calibration solutions on the abscissa and the corresponding values of absorbance, corrected for the absorbance of the calibration blank (6.3.1), on the ordinate.

Represent the points on the graph by the best straight line as judged visually, or calculated by the least squares fit.

Non-acceptable curvature would result when the mid-point calibration absorption exceeds 0,55 times the absorption of the maximum calibration solution. If this solution is encountered, the calibration solutions should be diluted to the minimum standard volume needed to attain the curvature criterion stated.

6.4 Determination

6.4.1 Carry out duplicate spectrometric measurements at a wavelength of 283,3 nm on the test solution (6.2.2) following the procedures specified in 6.3.2.

6.4.2 If the instrument response for the test solution is greater than that found for the calibration solution having the highest lead content (see 6.3.1) dilute as appropriate with hydrochloric acid (4.4) as follows.

Pipette carefully a volume, V_t, in cubic centimetres, of the test solution (6.2.2) into a 100 cm^3 one-mark volumetric flask (5.7) so that the lead concentration lies within the range covered by the calibration solutions. Dilute to the mark with hydrochloric acid (4.4). Repeat the spectrometric measurement twice, averaging the readings.

NOTE — To increase the reliability of the test method, the standard addition method may be used. (See the annex.)

6.5 Blank test

Carry out a blank test in parallel with the determination, using the hydrochloric acid (4.4), but without a test portion.

If sulfuric acid and ammonium acetate solutions were used for the test portion preparation, the blank test solution shall contain the same quantities of these.

7 Expression of results

7.1 Read the lead content of the test solution directly from the calibration graph.

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

$$\frac{(c_t - c_b) \times f}{200 \times m}$$

If a volumetric flask other than 50 cm³ is used (6.2.2), use the following formula:

$$\frac{(c_t - c_b) \times V_f \times f \times 100}{m}$$

where

c_t is the lead content, in micrograms per cubic centimetre, of the test solution (6.4.1) as read from the calibration graph;

c_b is the lead content, in micrograms per cubic centimetre, of the blank test solution (6.5) as read from the calibration graph;

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

V_f is the volume, in cubic centimetres, of the volumetric flask used (6.2.2);

f is the dilution factor, if required (6.4.2), of the test solution:

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

in which V_t is the volume, in cubic centimetres, of the test solution (6.4.2).

7.2 Alternatively, provided that the absorbance of the test solution lies within the linear section of the calibration graph, the lead content, expressed as a percentage by mass, is given by the formula

$$\frac{(c_t - c_b) \times f}{200 \times m}$$

If a volumetric flask other than 50 cm³ is used (6.2.2), use the following formula:

$$\frac{(c_t - c_b) \times V_f \times f \times 100}{m}$$

where

c_t is the lead content, in micrograms per cubic centimetre, of the test solution

$$c_t = \frac{A_t \times c_n}{A_n}$$

c_b is the lead content, in micrograms per cubic centimetre, of the blank test solution

$$c_b = \frac{A_b \times c_n}{A_n}$$

in which

A_t is the absorbance of the test solution,

A_b is the absorbance of the blank determination solution,

A_n is the absorbance of the standard matching solution having a lead content closest to that of the test solution,

c_n is the lead content, in micrograms per cubic centimetre, of the standard matching solution having the absorbance closest to that of the test solution,

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

V_f is the volume, in cubic centimetres, of the volumetric flask used (6.2.2);

f is the dilution factor, if appropriate (6.4.2), of the test solution

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

in which V_t is the volume, in cubic centimetres, of test solution diluted in 6.4.2.

7.3 Report lead content as a percentage by mass if more than or equal to 0,1 % (m/m), or as milligrams per kilogram if less than 0,1 % (m/m).

7.4 A test result is the average of two acceptable determinations, rounded to two decimal places when concentrations are expressed as percentages by mass and to the nearest whole number when concentrations are expressed in milligrams per kilogram.

8 Test report

The test report shall include the following information:

a) the type and the identification of the product tested;

b) a reference to this part of ISO 6101;

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

d) the results obtained and the method of expression used;

e) any unusual features noted during the determination;

f) any operations not included in this part of ISO 6101 which might have affected the results.