International Standard 6101/1

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Rubber — Determination of metal content — Flame atomic absorption spectrometric method — Part 1 : Determination of zinc content

Caoutchouc — Dosage du métal — Méthode par spectrométrie d'absorption atomique dans la flamme — Partie 1 : Dosage du zinc

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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.

International Standard ISO 6101/1 was developed by Technical Committee ISO/TC 45, *Rubber and rubber products*, and was circulated to the member bodies in March 1980.

It has been approved by the member bodies of the following countries :

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The member body of the following country expressed disapproval of the document on technical grounds :

Denmark

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Rubber — Determination of metal content — Flame atomic absorption spectrometric method — Part 1 : Determination of zinc content

1 Scope and field of application

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

The method is applicable to products having zinc contents in the range 0,1 to 3,0 % (m/m). Zinc contents outside this range may be determined, provided that suitable adjustments are made to the mass of the test portion and to the concentrations of the solutions used.

2 Reference

ISO 247, *Rubber — Determination of ash.*

3 Principle

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

If the rubber contains halogenated compounds, digestion of a test portion in sulphuric acid and nitric acid, removal of the acids by evaporation, and ashing of the residue at 550 ± 25 °C. Otherwise, direct ashing of a test portion at 550 ± 25 °C.

Dissolution of the ash obtained in hydrochloric acid. If any insoluble zinc silicates are present, decomposition with a mixture of sulphuric acid and hydrofluoric acid to convert them to zinc sulphate.

Aspiration of the solution obtained into an atomic absorption spectrometer and measurement of the absorbance at a wavelength of 213,8 nm, using a hollow-cathode tube for the zinc emission source.

4 Reagents

All recognized health and safety precautions shall be observed when carrying out the procedures specified in this International Standard.

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

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

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

4.3 Hydrochloric acid solutions.

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

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

4.3.2 Hydrochloric acid, 1 + 100 (V/V) solution.

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

4.4 Hydrofluoric acid (ϱ_{20} = 1,19 Mg/m^3) [38 to 40 % (m/m)].

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

4.6 Zinc, standard solution corresponding to 1 g of zinc per cubic decimetre.

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

Weigh, to the nearest 0,000 1 g, 1,000 g of pure zinc dust (purity 99,9 %) and dissolve in a minimum amount of the 1 + 2 hydrochloric acid solution (4.3.1). Dilute to 1 000 cm^3 with the 1 + 100 hydrochloric acid solution (4.3.2) and mix thoroughly.

1 cm^3 of this standard solution contains 1 mg (1 000 µg) of zinc.

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[1] At present at the stage of draft.

4.7 Zinc, standard solution corresponding to 0,01 g of zinc per cubic decimetre.

Carefully pipette 10 cm^3 of the standard zinc solution (4.6) into a 1 000 cm^3 one-mark volumetric flask. Dilute to the mark with the 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 zinc.

5 Apparatus[1]

5.1 Balance, accurate to 0,000 1 g.

5.2 Muffle furnace, capable of being controlled at 550 ± 25 °C.

5.3 Beaker, of capacity 250 cm^3.

5.4 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.

5.5 Filter funnel, of diameter 65 mm, and of 60° angle.

5.6 Crucible, of silica or porcelain, and of capacity 50 cm^3 (see ISO 1772).

5.7 Crucible, of platinum, and of capacity 50 cm^3.

5.8 Platinum rod, as stirrer.

5.9 Filter paper, ashless, of diameter 110 mm.

5.10 Electric heating plate or **gas burner with sand bath.**

5.11 Conical flask, of capacity 250 cm^3.

5.12 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air. The instrument shall be operated in accordance with the manufacturer's instructions for optimum performance.

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

6 Procedure

6.1 Test portion

6.1.1 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 (5.6 or 5.7).

6.1.2 If the rubber contains halogenated compounds (for example chloroprene rubber), weigh, to the nearest 0,1 mg, 0,1 g of milled or finely cut rubber into the 250 cm^3 conical flask (5.11).

6.2 Preparation of test solution

6.2.1 Ashing of test portion

6.2.1.1 Carry out ashing of the test portion (6.1.1) in accordance with method A or method B of ISO 247. Weighing of the ash is unnecessary.

6.2.1.2 If the rubber contains halogenated compounds, carry out ashing of the test portion (6.1.2) in accordance with the following alternative procedure.

Add to the test portion (6.1.2), 10 to 15 cm^3 of the sulphuric acid (4.1) and heat moderately until the test portion has disintegrated. Carefully add 5 cm^3 of the 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.

Transfer the reaction mixture quantitatively into the crucible (5.6), evaporate to dryness and ash at 550 ± 25 °C, until all the carbon has burned off.

6.2.2 Dissolution of the ash

6.2.2.1 Add carefully 20 cm^3 of the hydrochloric acid solution (4.3.1) to the ash. (Carbonates cause splashing and foaming.)

Transfer the solution and the residue to the beaker (5.3) with 50 cm^3 of the hydrochloric acid solution (4.3.1) and heat for 30 min.

If the residue dissolves completely, transfer to a 100 cm^3 volumetric flask (5.4), dilute to the mark with the hydrochloric acid solution (4.3.1), and proceed in accordance with 6.4.

6.2.2.2 If the ash is not totally dissolved when following the procedure described in 6.2.2.1, repeat the ashing in accordance with 6.2.1.1 or 6.2.1.2 using a new test portion and proceed as follows.

Transfer the ash from the new test portion to the crucible (5.7). Add a few drops of the sulphuric acid (4.1) and heat to fuming. Cool and add a further 3 drops of the sulphuric acid (4.1) and 5 cm^3 of the hydrofluoric acid (4.4). Heat on the electric heating plate or sand bath (5.10) and evaporate to dryness, while stirring with the platinum rod (5.8). Repeat this procedure twice.

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[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.

CAP [See ISO 31/0, subclause 2.3.3 + ISO 31/6(F)(page 2)]

Cool, and add 50 cm^3 of the hydrochloric acid solution (4.3.1) and filter. Wash the filter with the hydrochloric acid solution (4.3.1) and combine the filtrate and washings in a 100 cm^3 volumetric flask (5.4). Dilute to the mark with the hydrochloric acid solution (4.3.1) and mix thoroughly. Proceed in accordance with 6.4.

6.2.2.3 Test solutions should contain approximately 33 % of the hydrochloric acid (4.2). If evaporation or reaction with carbonates, etc., has reduced or increased this concentration, adjust it accordingly with the concentrated hydrochloric acid (4.2) or water.

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6.3 Preparation of calibration graph

6.3.1 Preparation of standard matching solutions

Into a series of five 100 cm^3 one-mark volumetric flasks (5.4), place the volumes of the standard zinc solution (4.7) indicated in the following table, dilute to the mark with the hydrochloric acid solution (4.3.1) and mix thoroughly.

Volume of standard zinc solution (4.7)	Corresponding mass of zinc contained in 1 cm^3
cm^3	µg
100	10
50	5
20	2
10	1
5	0,5

6.3.2 Spectrometric measurements

Switch on the spectrometer (5.12) 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 according to 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 matching solutions (6.3.1) in succession into the flame, and measure the absorbance of each solution twice. Take care to ensure that the rate of aspiration is constant throughout.

NOTE — Aspirate water through the burner after each measurement.

6.3.3 Blank test

Carry out a blank test in parallel with the calibration, using the hydrochloric acid solution (4.3.1).

6.3.4 Plotting the calibration curve

Plot a graph, having, for example, the masses, in micrograms, of zinc contained in 1 cm^3 of the standard matching solutions as abscissae, and the corresponding values of absorbance, corrected for the absorbance of the blank test solution (6.3.3), as ordinates.

6.4 Determination

6.4.1 Carry out duplicate spectrometric measurements at a wavelength of 213,8 nm on the test solution (6.2.2) and on the blank test solution (see 6.4.3), following the procedures specified in 6.3.2.

6.4.2 If the instrument response for the test solution is greater than that for the standard matching solution having the highest zinc content (see 6.3.1), dilute as appropriate with the hydrochloric acid solution as follows.

Pipette carefully *n* cm^3 of the test solution (6.2.2) into a 100 cm^3 one-mark volumetric flask (5.4) so that the zinc concentration lies within the range covered by the standard matching solutions. Dilute to the mark with the hydrochloric acid solution (4.3.1). Repeat the spectrometric measurements.

NOTE — To increase the reliability of the test method, it may be advisable to determine zinc by the "addition" method in which increasing amounts of standard matching solution (6.3.1) are added to the test solution and remeasured. The results obtained are plotted against the added zinc concentration and extrapolated to zero addition. The use of this method will reduce background interference due to the presence of any unknown interfering ash components.

6.4.3 Blank test

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

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

7 Expression of results

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

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

$$\frac{M_t - M_b}{m} \times 100 \times f \qquad 10\overset{4}{n}$$

where

M_t is the zinc content, in micrograms per cubic centimetre, of the test solution (6.2.2), read from the calibration graph;

M_b is the zinc content, in micrograms per cubic centimetre, of the blank test solution (6.4.3), read from the calibration graph;

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

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

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

where

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

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

7.2 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

$$\frac{M_t - M_b}{100 \times m} \times f$$

where

M_t is the zinc content, in micrograms per cubic centimetre, of the test solution :

$$M_t = \frac{A_t \times M_n}{A_n}$$

M_b is the zinc content, in micrograms per cubic centimetre, of the blank test solution :

$$M_b = \frac{A_b \times M_n}{A_n}$$

A_t is the absorbance of the test solution;

A_b is the absorbance of the blank test solution;

A_n is the absorbance of the standard matching solution having a zinc content closest to that of the test solution;

M_n is the zinc 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;

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

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

where

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

7.3 Report the result rounded to two decimal places.

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 result 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.