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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 5:
Determination of iron content

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

Partie 5: Dosage du fer

Reference number
ISO 6101-5:1990(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 6101-5 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products.*

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*

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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 5:
Determination of iron content

1 Scope

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

It is applicable to raw rubber, rubber products and latex having iron contents of 5,0 mg/kg to 1 000 mg/kg. Higher concentrations may be determined, provided that suitable adjustments are made to the mass of the test portion and/or the concentrations of the solutions used.

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 247:1978, *Rubber — Determination of ash.*

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

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

ISO 1796:1982, *Rubber, raw — Sample preparation.*

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 and if any silicates are present they are decomposed with a mixture of sulfuric acid and hydrofluoric acid to remove them.

The solution obtained is aspirated into an atomic absorption spectrometer and the absorption is measured at a wavelength of 248,3 nm for concentrations up to 10 mg/kg or 0,001 % (m/m), or 372,0 nm for concentrations of 10 mg/kg to 1 000 mg/kg or 0,001 % (m/m) to 0,1 % (m/m).

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.

4.1 Sulfuric acid, ρ = 1,84 Mg/m^3.

4.2 Hydrochloric acid, ρ = 1,19 Mg/m^3.

4.3 Hydrochloric acid, 1 + 3 (V/V).

Dilute 1 volume of the concentrated hydrochloric acid (4.2) with 3 volumes of water.

4.4 Hydrofluoric acid, ρ = 1,13 Mg/m^3, 38 % (m/m) to 40 % (m/m).

4.5 Nitric acid, ρ = 1,42 Mg/m^3.

4.6 Iron, standard solution corresponding to 1 g of Fe per cubic decimetre.

Use either commercially available standard iron solutions, or prepare as follows:

Grind metallic iron, purity greater than 99 % (m/m). Weigh 1 g to the nearest 0,01 mg in a 250 cm^3 conical flask (5.11) and dissolve it in a mixture of 100 ml of the 1 + 3 hydrochloric acid (4.3) and 10 ml of the nitric acid (4.5). Transfer it to a 1 000 cm^3 one-mark volumetric flask (5.4), dilute to the mark with 1 + 3 hydrochloric acid (4.3) and mix thoroughly.

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

5 Apparatus

Use ordinary laboratory apparatus and the following, ensuring that all apparatus and laboratory implements are non-ferrous:

5.1 Balance, accurate to 0,01 mg.

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

5.3 Beaker, of capacity 250 cm^3.

5.4 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.

5.5 Filter funnel.

5.6 Crucible, of silica or porcelain, of capacity 150 cm^3.

5.7 Crucible, of platinum, of capacity 50 cm^3 to 150 cm^3.

5.8 Platinum rod, as stirrer.

5.9 Filter paper, ashless, of diameter 150 mm,

5.10 Electrical 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 hollow-cathode lamp capable of emitting radiation of the required wavelengths and a burner fed with acetylene and compressed air. 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.

5.13 Volumetric pipettes, of capacity 5 cm^3, 10 cm^3, 20 cm^3, 50 cm^3 and 100 cm^3, complying with the requirements of ISO 648, class A.

5.14 Watch glasses, for covering the crucibles (5.6 and 5.7).

5.15 Heated water bath.

6 Sampling

Carry out sampling as follows:

- raw rubber, in accordance with ISO 1796;
- latex, in accordance with ISO 123;
- products, to be representative of the whole sample.

7 Procedure

7.1 Preparation of test portion

7.1.1 Wash the test portion with the 1 + 3 hydrochloric acid (4.3) to remove surface contamination, wash with water and allow to dry in a desiccator.

7.1.2 Weigh, to the nearest 0,01 mg, 1,0 g of milled or cut rubber into a crucible (5.6 or 5.7), using a non-ferrous cutting implement. If the iron content is about 5 mg/kg, it may be necessary to increase the mass of the test portion to 5 g maximum to obtain more reliable absorbances.

7.1.3 If the rubber contains silicates, proceed in accordance with 7.1.2 but use the platinum crucible (5.7).

7.2 Preparation of test solution

7.2.1 Destruction of organic matter

Ash in accordance with method A or B of ISO 247, in the muffle furnace (5.2), maintained at 550 °C ± 25 °C. If the ash is black, caused by small amounts of carbon black, stir carefully with the platinum rod (5.8) and continue heating.

7.2.2 Dissolution of inorganic residue

After ashing, allow the crucible and its contents to cool to ambient temperature. Add carefully 20 cm^3 of the 1 + 3 hydrochloric acid (4.3) to the ash and heat for 30 min on a water bath (5.15). Cover with a watch glass (5.14) to avoid losses, for example due to carbonates, which cause splashing and foaming.

Transfer the solution and the residue to a beaker (5.3) with 50 cm^3 of the 1 + 3 hydrochloric acid (4.3) 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 1 + 3 hydrochloric acid (4.3) and proceed in accordance with 7.4.

If the ash is not totally dissolved, i.e. silicates are present, ash a new portion in accordance with 7.1.3 and 7.2.1. Add a few drops of the sulfuric acid (4.1) and heat to fuming. Cool and add a further 3 drops of the sulfuric acid and 5 cm^3 of the hydrofluoric acid (4.4). Heat on the electric heating plate or sand bath (5.10) in a fume cupboad and evaporate to dryness, while stirring with the platinum rod (5.8). Repeat this procedure twice.

Cool, and add 50 cm^3 of the 1 + 3 hydrochloric acid (4.3). Cover with a watch glass (5.14) and heat for 10 min. Filter and wash the filter with the 1 + 3 hydrochloric acid (4.3) and combine the filtrate and washings in a 100 cm^3 volumetric flask (5.4). Dilute to the mark with the 1 + 3 hydrochloric acid (4.3) and mix thoroughly. Proceed in accordance with 7.4.

7.3 Preparation of the calibration curves

7.3.1 Preparation of standard calibration solutions

7.3.1.1 Primary calibration solution

Pipette carefully 10 cm^3 of the iron standard solution (4.6) into a 1 dm^3 one-mark volumetric flask (5.4) and dilute to the mark with the 1 + 3 hydrochloric acid (4.3).

1 cm^3 of this primary calibration solution contains 10 µg of Fe.

7.3.1.2 Standard calibration solutions

Into a series of eight 100 cm^3 one-mark volumetric flasks (5.4), place the volumes of the primary calibration solution (7.3.1.1) as indicated in table 1, add 1 + 3 hydrochloric acid (4.3) to the mark and mix thoroughly.

Table 1 — Volume of primary calibration solution with corresponding concentration of iron

Volume of primary calibration solution (7.3.1.1) cm^3	Corresponding concentration of iron µg/100 cm^3
100	1 000
50	500
20	200
10	100
5	50
2 1)	20 1)
1 1)	10 1)
0 2)	0

1) Only if the sensitivity of the spectrometer is high enough for accurate results.

2) Calibration blank solution.

7.3.2 Spectrometric measurements

Switch on the spectrometer (5.12) sufficiently in advance to ensure stabilization. Adjust the wavelength to 248,3 nm or 372,0 nm, and the sensitivity and the slit aperture according to the characteristics of the instrument.

Adjust the pressure of the air and of the acetylene according to the characteristics of the aspirator/burner in order to obtain a clear, reducing flame.

Adjust the flow rate according to the characteristics of the instrument.

Aspirate the series of standard calibration solutions (7.3.1.2) 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. It should be ensured that at least one standard is at or below the level corresponding to the rubber being tested.

It is important that water be aspirated through the burner after each measurement.

7.3.3 Plotting the calibration curves

Plot two curves (one for each of the concentration ranges given below) having, for example, the masses, in micrograms, of iron contained in

100 cm^3 of the standard calibration solutions as abscissae from

a) 10 µg/100 cm^3 to 100 µg/100 cm^3 for 248,2 nm,

b) 100 µg/100 cm^3 to 1 000 µg/100 cm^3 for 372,0 nm,

and the corresponding values of absorbance, corrected for the absorbance of the calibration blank solution (see table 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 248,3 nm or 372,0 nm on the test solution (7.2.2), following the procedures specified in 7.3.2.

7.4.2 Dilution

If the instrument response for the test solution is greater than that found for the standard calibration solution having the highest iron content (see table 1), dilute as appropriate with the 1 + 3 hydrochloric acid (4.3), in accordance with the following procedure.

Pipette carefully a volume V of the test solution (7.2.2) into a 100 cm^3 one-mark volumetric flask so that the iron concentration lies within the range covered by the standard calibration solutions. Dilute to the mark with the 1 + 3 hydrochloric acid (4.3). Repeat the measurement.

7.4.3 Blank determination

Carry out a blank determination in parallel with the determination, using the 1 + 3 hydrochloric acid (4.3), but omitting the test portion.

If sulfuric acid and hydrofluoric acid were used for the test portion preparation, the same quantities of these acids shall be used in the preparation of the blank determination solution.

8 Expression of results

8.1 Read the iron content of the test solution directly from the appropriate calibration graph (see 7.3.3).

The iron content of the test portion, expressed in parts per million by mass, is given by the formula

$$\frac{\rho_{\mathrm{Fe,t}} - \rho_{\mathrm{Fe,b}}}{100m} \times f \times 10^4$$

where

$\rho_{\mathrm{Fe,t}}$ is the iron concentration, in micrograms per 100 cubic centimetres, of the test solution (7.2.2) read from the calibration graph;

$\rho_{\mathrm{Fe,b}}$ is the iron concentration, in micrograms per 100 cubic centimetres, of the blank determination solution (7.4.3) read from the calibration graph;

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

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 the test solution pipetted out in 7.4.2.

8.2 Report the results to three significant figures as parts per million by mass if the result is less than 1 000 ppm or as a percentage by mass if the result is greater than 1 000 ppm. Report results of less than 5 ppm as "less than 5 ppm".

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;

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.
