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Third edition
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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

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This third edition cancels and replaces the second edition (ISO 6101-5:2006), which has been technically revised as follows:

- nitric acid has been added as a digestion acid;
- the concentration for sulphuric acid has been specified;
- the procedure for the destruction of organic matter has been further detailed;
- the volume for final solution following dissolution using hydrochloric acid (8.2.2) has been changed to 50 cm^3 to ensure consistency of the formulae used throughout the ISO 6101 series;
- Formulae 1 and 2 in Clause 9 have been corrected for the iron content expressed as percentage by mass and milligram per kilogram, respectively;
- Annex A and Annex B have been added to include method of standard addition and precision statement of the method.

A list of all parts in the ISO 6101 series can be found on the ISO website.

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 5:
Determination of iron content

1 Scope

This document specifies an atomic absorption spectrometric method for the determination of the iron content of rubbers.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 247-1, *Rubber — Determination of ash — Combustion method*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp/

4 Principle

A test portion is ashed at 550 °C ± 25 °C in accordance with ISO 247-1. The ash is dissolved in hydrochloric acid or nitric 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 % (by mass), or 372,0 nm for concentrations of 10 mg/kg to 1 000 mg/kg or 0,001 % (by mass) to 0,1 % (by mass).

5 Reagents

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

5.1 Sulfuric acid, ρ_{20} = 1,84 Mg/m^3, 95 % (m/m) to 97 % (m/m).

5.2 Hydrochloric acid, ρ_{20} = 1,19 Mg/m^3, 37 % (m/m).

5.3 Hydrochloric acid diluted 1 + 3, dilute 1 volume of concentrated hydrochloric acid (5.2) with 3 volumes of water.

5.4 Hydrofluoric acid, ρ_{20} = 1,13 Mg/m^3, 38 % (m/m) to 48 % (m/m).

5.5 Concentrated nitric acid, ρ_{20} = 1,42 Mg/m^3, 69 % (m/m).

5.6 Dilute nitric acid, 1,6 % (by mass), carefully pipette 11,5 cm^3 of concentrated nitric acid (5.5) into a 1 000 cm^3 one-mark volumetric flask, making up to the mark with water, and mix thoroughly.

5.7 Standard iron stock solution, containing 1 g of Fe per cubic decimetre.

Either use a commercially available standard iron solutions, or prepare as follows:

Grind metallic iron, purity greater than 99 % (by mass). Weigh 1 g to the nearest 0,1 mg in a 250 cm^3 conical flask (6.11) and dissolve it in a mixture of 100 cm^3 of 1 + 3 hydrochloric acid (5.3) and 10 cm^3 of concentrated nitric acid (5.5). Transfer it to a 1 000 cm^3 one-mark volumetric flask (6.4), dilute to the mark with 1 + 3 hydrochloric acid (5.3) and mix thoroughly.

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

5.8 Standard iron solution, containing 10 mg of Fe per 1 000 cm^3.

Carefully pipette 10 cm^3 of the standard iron stock solution (5.7) using volumetric pipette (6.13) into a 1 000 cm^3 one-mark volumetric flask (6.4) and dilute to the mark with 1 + 3 hydrochloric acid (5.3) or diluted nitric acid (5.6).

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

6 Apparatus

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

6.1 Balance, accurate to 0,1 mg.

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

6.3 Beaker, of capacity 250 cm^3.

6.4 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.

6.5 Filter funnel.

6.6 Crucible (silica or porcelain), of capacity 150 cm^3 depending on the test portion size.

6.7 Crucible (platinum), of capacity 50 cm^3 to 150 cm^3 depending on the test portion size.

6.8 Platinum rod or borosilicate-glass rod, as stirrer.

6.9 Ashless filter paper, of diameter 150 mm.

6.10 Electrical heating plate or **sand bath**.

6.11 Conical flask, of capacity 250 cm^3.

6.12 Atomic absorption spectrometer, fitted with a burner fed with acetylene and compressed air and also fitted with an iron hollow-cathode lamp capable of emitting radiation of the required wavelengths. 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.

6.13 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.

6.14 Watch glasses, for covering the crucibles (6.6 and 6.7).

6.15 Steam bath.

6.16 Non-ferrous cutting implement.

7 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 sample.

8 Procedure

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

8.1 Preparation of test portion

8.1.1 Weigh, to the nearest 0,1 mg, approximately 1 g to 5 g of rubber product and 5 g to 10 g of raw rubber, milled or finely cut, into an appropriate crucible (6.6 or 6.7), using a non-ferrous cutting implement (6.16). The size of the test portion shall be judged by prior knowledge of the approximate amount of iron present.

8.1.2 If the rubber contains silicates, proceed in accordance with 8.1.1 but use the platinum crucible (6.7).

8.1.3 For natural rubber latex concentrate, take a portion of thoroughly mixed latex containing about 10 g of total solids, make into a thin film by pouring the portion onto a glass plate, dry to constant mass as specified in ISO 124 and cut into small pieces.

8.1.4 For raw, natural rubber, take the test portion from a test sample prepared in accordance with ISO 1795.

8.2 Preparation of test solution

8.2.1 Destruction of organic matter

Ash in accordance with ISO 247-1 in the muffle furnace (6.2) maintained at 550 °C ± 25 °C. After ashing, allow the crucible and its contents to cool to ambient temperature.

If the ash is black, caused by small amounts of carbon black, add 1 cm^3 of concentrated nitric acid (5.5) to the ash, evaporate to dryness on an electrical heating plate or gas burner with sand bath (6.10) and return to the muffle furnace and ashed for 10 min to 15 min.

8.2.2 Dissolution of inorganic residue using hydrochloric acid

Add carefully 20 cm^3 of 1 + 3 hydrochloric acid (5.3) to the ash and heat for 30 min on a steam bath (6.15). Cover with a watch glass (6.14) to avoid losses, for example due to carbonates, which cause splashing and foaming.

Transfer the solution and the residue to a beaker (6.3) with 50 cm^3 of 1 + 3 hydrochloric acid (5.3) and heat for 30 min.

If the residue dissolves completely, transfer to a 50 cm^3 volumetric flask (6.4), dilute to the mark with 1 + 3 hydrochloric acid (5.3) and proceed in accordance with 8.4.

If the ash is not totally dissolved, i.e. silicates are present, ash a new portion in accordance with 8.1.2 and 8.2.1. Add a few drops of sulfuric acid (5.1) and heat to fuming. Cool and add a further three drops of sulfuric acid and 5 cm^3 of hydrofluoric acid (5.4). Heat on the electric heating plate or sand bath (6.10) in a fume cupboard and evaporate to dryness, while stirring with the platinum rod or borosilicate-glass rod (6.8). Repeat this procedure twice.

Allow to cool to ambient temperature, add 20 cm^3 of 1 + 3 hydrochloric acid (5.3), cover with a watch glass (6.14) and heat for 10 min. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask (6.4) through an ashless filter paper (6.9) and rinse the contents with 1 + 3 hydrochloric acid (5.3). Dilute to the mark using 1 + 3 hydrochloric acid (5.3) and mix thoroughly. Proceed in accordance with 8.4.

8.2.3 Dissolution of inorganic residue using nitric acid — Alternative method

Add 10 cm^3 of dilute nitric acid (5.6) to the cooled residue. Cover with a watch glass and heat on a steam bath (6.16) or electrical heating plate (6.10) for at least 30 min. Allow to cool to ambient temperature. Filter the contents of the crucible into a 50 cm^3 one-mark volumetric flask (6.4) through an ashless filter paper (6.9). Rinse the crucible and mix thoroughly, before making up with dilute nitric acid (5.6) to the mark. Proceed in accordance with 8.4.

8.3 Preparation of the calibration curves

8.3.1 Preparation of standard calibration solutions

8.3.1.1 Into a series of eight 100 cm^3 one-mark volumetric flasks (6.4), place the volumes of the standard iron solution (5.8) as indicated in Table 1, add 1 + 3 hydrochloric acid (5.3) or dilute nitric acid (5.6) to the mark and mix thoroughly.

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

Table 1 — Standard calibration solutions

Volume of standard iron solution cm^3	Mass of iron contained in 1 cm^3 µg
100	10
50	5
20	2
10	1
5	0,5
2[a]	0,2[a]
1[a]	0,1[a]

[a] Only if the sensitivity of the spectrometer is high enough for accurate results.

8.3.2 Spectrometric measurements

Switch on the spectrometer (6.12) sufficiently in advance to ensure stabilization. With the iron hollow-cathode tube suitably positioned, 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 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 series of standard calibration solutions 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 standard is at or below the level corresponding to the rubber being tested.

Aspirate water through the burner after each measurement.

8.3.3 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 248,3 nm,

b) 100 µg/100 cm^3 to 1 000 µg/100 cm^3 for 372,0 nm (recommended flame for wavelength 372,0 nm is nitrous oxide-acetylene)

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.

8.4 Determination

8.4.1 Spectrometric measurements

Carry out duplicate spectrometric measurements at a wavelength of 248,3 nm or 372,0 nm on the test solution (8.2.2 or 8.2.3), following the procedures specified in 8.3.2.

8.4.2 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 1 + 3 hydrochloric acid (5.3) or dilute nitric acid (5.6) in accordance with the following procedure.

Pipette carefully a volume, *V*, of the test solution (8.2.2 or 8.2.3) 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 1 + 3 hydrochloric acid (5.3) or dilute nitric acid (5.6). Repeat the measurement.

NOTE To increase the reliability of the test method, the standard-addition method can be used (see Annex A).

8.4.3 Blank determination

Carry out a blank determination in parallel with the determination, using 1 + 3 hydrochloric acid (5.3) or dilute nitric acid (5.6), 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.

8.4.4 Number of determinations

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

9 Expression of results

9.1 Read the iron content of the test solution directly from the calibration graph plotted in 8.3.3. The iron content of the test portion, expressed as percentage by mass, is given by the Formula (1):

$$\frac{\rho(Fe)_{\mathrm{t}} - \rho(Fe)_{\mathrm{b}}}{200m} \times f \qquad (1)$$

where

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

$\rho(Fe)_{\mathrm{b}}$ is the iron content, in micrograms per cubic centimetre, of the blank 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 8.4.2), given by:

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

where *V* is the volume, in cubic centimetres, of the test solution pipetted out.

9.2 The iron content of the test portion can also be calculated, in milligram per kilogram, of the test solution, by Formula (2):

$$\frac{50\left[\rho(Fe)_{\mathrm{t}} - \rho(Fe)_{\mathrm{b}}\right]}{m} \times f \qquad (2)$$

9.3 The test result is the average of two determinations, rounded to two decimal places when the iron concentration is expressed as a percentage and to the nearest whole number when the concentration is expressed in milligrams per kilogram.

9.4 Report the iron content as a percentage if greater than or equal to 0,1 % or as milligrams per kilogram if less than 0,1 %.

10 Precision

See Annex B.

11 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 document, i.e. ISO 6101-5:2018;

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 are expressed;

g) any unusual features noted during the determination;

h) details of any operations not specified in this document, or in the International Standards to which reference is made, which might have affected the results.

Annex A
(informative)

Method of standard addition

The method of standard addition is used with samples containing unknown concentration 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 addition can be found in any standard text book on atomic absorption spectroscopy 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 8.2, take four aliquots of the same size. To three of these aliquots, add a different, but known, volume of standard iron 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 iron 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 off the concentration of iron in the test solution.

An example is given in Figure A.1.