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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Rubber — Determination of metal content by atomic absorption spectrometry —

Part 4:
Determination of manganese content

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

Partie 4: Dosage du manganèse

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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.

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 6101-4 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*

Annex A forms an integral part of this part of ISO 6101.

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Rubber — Determination of metal content by atomic absorption spectrometry —

Part 4:
Determination of manganese content

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1 Scope

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

The method is applicable to raw rubber and rubber products having manganese contents above 0,5 ppm. Manganese contents below this limit may be determined, provided that suitable adjustments are made to the mass of the test portion and/or to the concentrations of the solutions used. The use of the standard additions method may further decrease the lower 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 listed 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 1772 : 1975, *Laboratory crucibles in porcelain and silica.*

ISO 4793 : 1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO 6955 : 1982, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary.*

ISO 6956 : —[1], *Atomic absorption spectrometry — Introduction to use.*

3 Principle

NOTE — For the terminology used, see ISO 6955, and for further information on the use of atomic absorption spectrometry, see ISO 6956.

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. The solution is aspirated into an atomic absorption spectrometer and the absorption is measured at a wavelength of 279,5 nm, using a manganese hollow-cathode lamp as the manganese emission source. Any silicates are volatilized by sulfuric and hydrofluoric acid.

4 Reagents

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

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

4.1 Hydrochloric acid, $\varrho_{20} = 1{,}19$ Mg/m^3.

4.2 Hydrochloric acid, 1 + 2 (V/V).

Dilute 1 volume of the concentrated hydrochloric acid (4.1) with 2 volumes of water.

4.3 Sulfuric acid, $\varrho_{20} = 1{,}84$ Mg/m^3.

4.4 Sulfuric acid, 1 + 3 (V/V).

Add carefully 1 volume of the concentrated sulfuric acid (4.3) to 3 volumes of water.

4.5 Hydrofluoric acid, $\varrho_{20} = 1{,}13$ Mg/m^3, 38 % (m/m) to 40 % (m/m).

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[1] To be published.

4.6 Manganese, standard solution corresponding to 1 g of Mn per cubic decimetre.

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

Using electrolytic manganese of purity ⩾ 99,9 %, free the surface of any manganese oxides by placing a few grams of the metal in a beaker containing 60 cm^3 to 80 cm^3 of the 1 + 3 sulfuric acid (4.4) with about 100 cm^3 of water. Stir and, after a few minutes, decant the acid solution and pour water into the beaker. Repeat the decantation and washing with water several times. Then place the manganese metal in acetone and stir. Decant the acetone, dry the metal in a hot-air oven (5.13), maintained at 100 °C ± 5 °C, for about 2 min and allow it to cool in a desiccator.

In a 600 cm^3 tall-form beaker, weigh, to the nearest 0,1 mg, 1 g of this purified manganese metal, and dissolve it with 40 cm^3 of the 1 + 3 sulfuric acid solution (4.4) and about 80 cm^3 of water. Boil the solution for several minutes. Allow to cool and transfer to a 1 000 cm^3 one-mark volumetric flask (5.5). Dilute to the mark and mix thoroughly.

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

4.7 Manganese, standard solution corresponding to 10 mg of Mn per cubic decimetre.

Using a pipette (5.6), carefully introduce 10 cm^3 of the standard manganese solution (4.6) into a 1 000 cm^3 one-mark volumetric flask (5.5), dilute to the mark with the 1 + 2 hydrochloric acid solution (4.2) and mix thoroughly.

Prepare this solution on the day of use.

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

5 Apparatus

Ordinary laboratory apparatus and

5.1 Atomic absorption spectrometer, fitted with a burner fed with acetylene and air, compressed respectively to at least 60 kPa and 300 kPa, and also fitted with a manganese hollow-cathode lamp as the manganese 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, using the test solution as prepared in 7.2.

5.2 Balance, accurate to 0,1 mg.

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

5.4 Glass filter crucible, filter pore size 16 µm to 40 µm (porosity grade P 40 — see ISO 4793).

5.5 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.

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

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

5.8 Steam bath.

5.9 Platinum rod, for use as stirrer.

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

5.11 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.

5.12 Ashless filter paper.

5.13 Oven, capable of being maintained at a temperature of 100 °C ± 5 °C.

6 Sampling

Carry out sampling as follows:

- raw rubber: in accordance with ISO 247;
- latex: in accordance with ISO 123;
- products: to be representative of the whole sample.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,1 mg, approximately 10 g of milled or finely cut rubber into an appropriate crucible (5.10 or 5.11). The size of the test portion shall be judged by prior knowledge of the approximate amount of manganese present.

7.2 Preparation of test solution

7.2.1 Destruction of organic matter

Ash the test portion (7.1) in accordance with method A or B of ISO 247, in the muffle furnace (5.3), maintained at 550 °C ± 25 °C. If the ash is black, caused by small amounts of carbon black, stir carefully with the platinum rod (5.9) and continue heating.

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7.2.2 Dissolution of inorganic residue

After ashing, allow the crucible and its contents to cool to ambient temperature. Add 20 cm^3 of concentrated hydrochloric acid (4.1). Heat the mixture on the steam bath (5.8) for at least 10 min. Do not let the reaction mixture boil. Allow to cool to ambient temperature and transfer the solution, with the aid of water, to a 50 cm^3 one-mark volumetric flask (5.5). If the ash is not totally dissolved, proceed as follows.

Transfer the solution and the undissolved ash, with the aid of water, to a platinum crucible (5.10). Add a few drops of concentrated sulfuric acid (4.3) and 5 cm^3 of hydrofluoric acid (4.5). Heat on the electric heating plate or sand bath (5.7) in a fume cupboard and evaporate to dryness, while stirring with the platinum rod (5.9). Repeat this digestion with the same quantities of sulfuric and hydrofluoric acids two more times.

Allow to cool to ambient temperature, add 20 cm^3 of concentrated hydrochloric acid (4.1), heat for 10 min and transfer, with the aid of water, to a 50 cm^3 one-mark volumetric flask.

Dilute to the mark with water and mix thoroughly. Insoluble matter may settle and, if so, shall be filtered off using a filter crucible (5.4) just before making spectrometric measurements in accordance with 7.3.

Test solutions should contain approximately 12 % hydrochloric acid. If evaporation, etc., has reduced or increased this concentration, adjust accordingly with concentrated hydrochloric acid (4.1) or water.

7.3 Preparation of the calibration graph

7.3.1 Preparation of standard calibration solutions

7.3.1.1 Into a series of five 100 cm^3 one-mark volumetric flasks (5.5), introduce, using pipettes (5.6), the volumes of standard manganese solution (4.7) indicated in table 1. Dilute to the mark with 1 + 2 hydrochloric acid solution (4.2) and mix thoroughly.

Table 1 — Standard calibration solutions

Volume of standard manganese solution (4.7) cm^3	Mass of manganese contained in 1 cm^3 µg
25	2,5
10	1,0
5	0,5
2	0,2
0	0

7.3.1.2 Prepare standard calibration solutions (7.3.1.1) daily.

7.3.2 Spectrometric measurements

Switch on the spectrometer (5.1) sufficiently in advance to ensure stabilization. With the manganese hollow-cathode tube suitably positioned, adjust the wavelength to 279,5 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 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 series of standard calibration solutions (7.3.1.1) 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. It should be ensured that at least one calibration solution 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 graph

Plot a graph having, for example, the masses, in micrograms, of manganese contained in 1 cm^3 of the calibration solutions as abscissae and the corresponding values of absorbance, corrected for the absorbance of the calibration blank solution (see 7.3.1.1), 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 279,5 nm on the test solution (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 standard calibration solution having the highest manganese content (see 7.3.1.1), dilute, as appropriate, with 1 + 2 hydrochloric acid solution (4.2), in accordance with the following procedure.

Pipette carefully a suitable volume (V cm^3) of the test solution (7.2.2) into a 100 cm^3 one-mark volumetric flask (5.5) so that the manganese concentration lies within the range covered by the standard calibration solutions. Dilute to the mark with 1 + 2 hydrochloric acid solution (4.2). Carry out the spectrometric measurements in accordance with 7.4.1.

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

7.4.3 Blank determination

Carry out a blank determination in parallel with the determination, using 1 + 2 hydrochloric acid solution (4.2), 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 test solution.

8 Expression of results

8.1 Read the manganese content of the test solution directly from the calibration graph (7.3.3).

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

$$\frac{\varrho(\mathrm{Mn})_t - \varrho(\mathrm{Mn})_b}{200\, m} \times f$$

where

$\varrho(\mathrm{Mn})_t$ is the manganese content, in micrograms per cubic centimetre, of the test solution (7.2.2), read from the calibration graph;

$\varrho(\mathrm{Mn})_b$ is the manganese content, in micrograms per cubic centimetre, of the blank test solution (7.4.3), read from the calibration graph;

m is the mass, in grams, of the test portion (7.1);

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 taken in 7.4.2.

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

$$\frac{\varrho(\mathrm{Mn})_t - \varrho(\mathrm{Mn})_b}{200\, m} \times f$$

where

$\varrho(\mathrm{Mn})_t$ is the manganese content, in micrograms per cubic centimetre, of the test solution:

$$\varrho(\mathrm{Mn})_t = \frac{A_t \times \varrho(\mathrm{Mn})_n}{A_n}$$

$\varrho(\mathrm{Mn})_b$ is the manganese content, in micrograms per cubic centimetre, of the blank test solution:

$$\varrho(\mathrm{Mn})_b = \frac{A_b \times \varrho(\mathrm{Mn})_n}{A_n}$$

in which

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 calibration solution having the manganese content closest to that of the test solution;

$\varrho(\mathrm{Mn})_n$ is the manganese content, in micrograms per cubic centimetre, of the standard calibration solution having an absorbance closest to that of the test solution;

m is the mass, in grams, of the test portion (7.1);

f is the dilution factor, if appropriate (see 7.4.2), of the test solution:

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

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

8.3 Carry out the procedure in duplicate, using separate test portions cut from the same homogenized sample. The test result is the average of two determinations rounded to two decimal places when the manganese 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 manganese content as a percentage if greater than or equal to 0,1 %, or in milligrams per kilogram if less than 0,1 %.

9 Test report

The test report shall include the following information:

a) the type and the 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 (flame or graphite furnace spectrometer);

f) the results obtained and the units in which they are expressed;

g) any unusual features noted during the determination;

h) any operations not included in this part of ISO 6101, or in the International Standards to which reference is made, which might have affected the results.

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