
**Rubber and rubber latices — Determination
of manganese content — Sodium periodate
photometric methods**

*Caoutchoucs et latex de caoutchouc — Dosage du manganèse —
Méthodes photométriques au periodate de sodium*



Foreword

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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 7780 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 7780:1987) which has been technically revised.

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Introduction

Manganese in certain forms is known to catalyse the oxidative breakdown of natural rubber, although the mechanism by which degradation is brought about is not fully understood. It is recognized also that other forms of manganese can be present, even in relatively large amounts, without degradation taking place. However, there is always the possibility in the case of compounded rubbers that, under the influence of some constituents of the compound (notably the unsaturated acids), the manganese could assume a more aggressive role.

Clearly, it would be an advantage to distinguish analytically between catalytically active and inactive forms, but no generally accepted method has yet been put forward for doing so. There is therefore no alternative to determining the total amount of manganese in the rubber.

Little is known about the influence of manganese on the catalytic oxidation of synthetic rubbers, although it is widely accepted that its effect may be less severe than is the case with natural rubber. Possibly for this reason, the determination of manganese in synthetic rubbers and in compounds based on synthetic rubbers is less frequently carried out; nevertheless, the methods specified in this International Standard are applicable to all the commonly used elastomers.

The first of the two specified methods, referred to as the *general method*, is believed to be applicable to all rubbers and compounded rubbers in all forms. In this method, the ash from the rubber is taken through a fusion stage in order to obtain the manganese in soluble form; it is most suited to rubber compounds containing heavy loadings of inert fillers such as clay, or materials which form insoluble phosphates, for example titanium dioxide. The second method, referred to as the *restricted method*, is shorter and suitable for raw rubbers, their corresponding latices, and rubber compounds not containing a heavy loading of the fillers referred to above. It is expected that the second method would be used more frequently.

For those equipped with atomic absorption equipment, ISO 6101-4:1997, *Rubber — Determination of metal content by atomic absorption spectrometry — Part 4: Determination of manganese content*, may be used in place of ISO 7780. Both standards should be consulted because there may be some background material in each which could be useful before choosing the most desirable method for the determination of manganese in raw and vulcanized rubbers and latices.

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Rubber and rubber latices — Determination of manganese content — Sodium periodate photometric methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies photometric methods for the determination of manganese, after oxidation with sodium periodate, in rubbers and rubber latices. Both methods contain provisions for analysis of chlorine-containing rubber.

Clause 3 specifies a method for compounded or vulcanized rubbers which is not affected by heavy loadings of fillers such as synthetic and natural silicates or calcium carbonates in various forms, or by the presence of compounding ingredients which form an insoluble phosphate under the conditions of the test.

Clause 4 specifies a method for raw and compounded natural and synthetic rubbers and latices which do not contain heavy loadings (more than about 10 %) of inert silicate fillers or any ingredient such as titanium dioxide which under the conditions of test will form an insoluble phosphate.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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:—¹⁾, *Rubber latex — Sampling*.

ISO 124:1997, *Latex, rubber — Determination of total solids content*.

ISO 1795:1992, *Rubber, raw, natural and synthetic — Sampling and further preparative procedures*.

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

¹⁾ To be published. (Revision of ISO 123:1985)

3 General method (for samples not affected by heavy loadings of fillers)

3.1 Principle

In the presence of chlorine, digestion with sulfuric acid is required, followed by reaction with nitric acid. This procedure is carried out in a Kjeldahl flask. If silicates are present, the digested test portion is treated with sulfuric and hydrofluoric acids to volatilize any silicon as silicon tetrafluoride. In the absence of chlorine, the rubber is ashed in a platinum crucible and treated with sodium fluoroborate. After either procedure, the manganese is oxidized to permanganate by boiling with sodium periodate. The manganese concentration is determined by spectrophotometric measurement at 525 nm.

3.2 Reagents

During the analysis, wherever possible, use only reagents of recognized analytical grade, suitable for use in trace-metal analysis, and only stabilized water (see 3.2.5).

3.2.1 Sodium fluoroborate.

If analytical grade is not available, prepare this reagent as follows. Dissolve 110 g of technical-grade sodium fluoroborate in 100 cm³ of water warmed to about 35 °C. After filtering through a filter paper, cool the solution to room temperature and add 100 cm³ of 96 % (V/V) ethanol whilst stirring. Filter off the crystalline precipitate on to a filter paper in a Buchner funnel and drain thoroughly under slight vacuum, then transfer to a shallow porcelain or glass dish and dry at about 50 °C under vacuum.

3.2.2 Sodium periodate.

3.2.3 Sulfuric acid, $\rho = 1,84 \text{ Mg/m}^3$.

3.2.4 Nitric acid, $\rho = 1,42 \text{ Mg/m}^3$.

3.2.5 Stabilized water.

To approximately 1 dm³ of water, add about 0,1 g of potassium permanganate together with a few drops of sulfuric acid. Distil the water through an effective spray trap, discarding the first and last 50 cm³ of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

3.2.6 Potassium permanganate solution, approximately 30 g/dm³.

3.2.7 Manganese, standard solution, corresponding to 10 mg of manganese per cubic decimetre.

A solution prepared in either of the following ways may be used:

a) Weigh 0,720 g of potassium permanganate (KMnO₄) into a small beaker and dissolve in water containing 2 cm³ of sulfuric acid (3.2.3). Add water saturated with sulfur dioxide until the solution is colourless. Boil the solution for 15 min, cool, transfer to a 500 cm³ volumetric flask and dilute to the mark with water.

b) Weigh 0,770 g of manganese sulfate (MnSO₄·H₂O) into a small beaker and dissolve in water containing 2 cm³ of sulfuric acid (3.2.3). Transfer the solution to a 500 cm³ volumetric flask and dilute to the mark with water. This solution should be stable for at least a month.

Pipette 10 cm³ of either solution a) or solution b) into a second 500 cm³ volumetric flask and again dilute to the mark with water.

1 cm³ of this standard solution contains 0,01 mg of manganese.

Prepare the solution just before use.

3.2.8 Hydrogen peroxide, 30 % (V/V) solution in water.

3.2.9 Hydrofluoric acid, $\rho = 1,12 \text{ Mg/m}^3$.

3.3 Apparatus

Ordinary laboratory apparatus, plus the following:

3.3.1 Photometer or spectrophotometer, capable of measuring absorbance at approximately 525 nm, and **matched cells**.

3.3.2 Platinum crucible (30 cm³ nominal capacity is suitable).

3.3.3 Heat-resistant, thermally insulating board, approximately 100 mm square and 6 mm thick, with a hole in the centre to support the crucible so that approximately two-thirds projects below the board.

3.3.4 Muffle furnace, capable of being maintained at a temperature of $550 \text{ }^\circ\text{C} \pm 25 \text{ }^\circ\text{C}$.

3.3.5 Sintered-glass filter, porosity grade P 40 (see ISO 4793).

3.3.6 Electrical heating plate or gas burner with sandbath.

3.3.7 Kjeldahl flask, of capacity 250 cm³.

3.3.8 Platinum rod, as stirrer.

3.4 Sampling

At all stages of sampling and sample preparation, take care to avoid contamination of the rubber.

3.4.1 Raw rubber

Perform sampling in accordance with ISO 1795.

3.4.2 Latex

Perform sampling in accordance with one of the methods specified in ISO 123.

3.4.3 Compounded and vulcanized rubbers

Cut out a 50 g sample, if necessary from more than one piece so that proper representation is achieved.

3.5 Procedure

3.5.1 Preparation of test portion

3.5.1.1 Raw rubber

From the sample taken in 3.4.1, weigh out a 10 g test portion to the nearest 10 mg.

3.5.1.2 Latex

Thoroughly mix the latex obtained in 3.4.2, take a portion containing about 10 g of total solids, dry to constant mass as specified in ISO 124, and cut into small pieces.

3.5.1.3 Compounded and vulcanized rubbers

From the sample taken in 3.4.3, weigh out a 10 g test portion to the nearest 10 mg.

3.5.2 Preparation of test solution

3.5.2.1 Ashing the test portion in the absence of chlorine

Transfer the test portion to a weighed platinum crucible (3.3.2) which is supported in the hole in the heat-resistant, thermally insulating board (3.3.3).

Start the preparation of a blank solution at the same time, using a similar crucible but omitting the test portion, and continue by treating the test portion and the blank in an identical manner.

Heat the crucible and contents with a gentle gas flame until a dry carbonaceous residue remains and then transfer the crucible to the muffle furnace (3.3.4) maintained at a temperature of $550\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ and heat until all carbon has been oxidized.

Allow the crucible to cool in a desiccator, weigh it to determine the mass of ash and then, from a fine pipette, add an amount of sulfuric acid (3.2.3) drop by drop round the walls of the crucible just sufficient to moisten the ash. Heat gently until fuming ceases and then again at about $550\text{ }^{\circ}\text{C}$ for a few minutes.

Repeat the treatment of the ash with the sulfuric acid, adding the acid as before from a fine pipette, heating gently until fuming ceases, and then again at about $550\text{ }^{\circ}\text{C}$ for a few minutes. After cooling again to room temperature, add to the crucible 8 parts by mass of sodium fluoroborate (3.2.1), up to a maximum of 8 g, to 1 part by mass of the ash. Gently heat the crucible in a fume cupboard until fusion is complete, and then more strongly until the molten material becomes clear, or until no further reaction takes place and any insoluble matter is dispersed in the melt.

3.5.2.2 Ashing the test portion in the presence of chlorine

Place the test portion in a Kjeldahl flask (3.3.7), add 10 cm^3 of sulfuric acid (3.2.3) and heat moderately until the test portion has disintegrated. Carefully add 5 cm^3 of nitric acid (3.2.4). If the reaction becomes too vigorous, cool the flask in a beaker of cold water and store at room temperature for at least two hours before reheating.

As soon as the initial reaction has subsided, heat the mixture gently until the reaction has ceased, and then more strongly until the mixture darkens. Add a 1 cm^3 portion of nitric acid and heat until darkening takes place again. Repeat the nitric acid addition and heating until the solution becomes colourless or pale yellow and fails to darken on further heating.

If the digestion is prolonged, it may be necessary to add about 1 cm^3 of sulfuric acid to prevent the contents of the flask from solidifying.

If the digest is free from insoluble matter, cool, add $0,5\text{ cm}^3$ of hydrogen peroxide (3.2.8) and 2 drops of nitric acid and heat to fuming. Repeat the addition and heating until there is no further reduction in the colour of the solution. Cool, dilute with 10 cm^3 of water and heat to fuming.

Transfer the solution, and any residue present, to the crucible, evaporate to dryness and ignite until all of the carbon has burned off.

If insoluble material is present in the digest at this stage, cool, add a few drops of sulfuric acid and 5 cm^3 of hydrofluoric acid (3.2.9). Evaporate to dryness on the heating device (3.3.6) while stirring with the platinum rod (3.3.8). Repeat this procedure twice.

If insoluble material is absent, evaporate to dryness on the heating device.

3.5.2.3 Dissolution

Cool the crucible to room temperature, and add 12 cm³ of stabilized water (3.2.5) and 4 cm³ of sulfuric acid. After warming very gently to dissolve the solidified mass, pour the contents into a 100 cm³ conical flask. Repeat with a further 10 cm³ of stabilized water and 2 cm³ of sulfuric acid, again pouring into the conical flask.

Add 5 cm³ of nitric acid (3.2.4) to the flask and then pour the contents through the cleaned sintered-glass filter (3.3.5), washing the filter once with 5 cm³ of hot stabilized water. Transfer the filtrate to another conical flask, washing with stabilized water, and make up the volume to a total of 40 cm³, add 0,3 g of sodium periodate (3.2.2) and heat the solution to boiling. Continue boiling gently for 10 min to ensure full development of the colour. After cooling, any cloudiness due to precipitated potassium periodate may be cleared by centrifuging or by passing through the sintered-glass filter.

Quantitatively transfer the solution to a 50 cm³ volumetric flask and dilute to the mark with stabilized water at 20 °C. After mixing, the colour should be stable for several hours. Any tendency to fade indicates the incomplete removal of organic matter or chlorides. If this is the case, repeat the determination, but use an extra sulfuric acid treatment in 3.5.2.1.

Proceed in accordance with 3.5.4.

3.5.3 Preparation of calibration graph

3.5.3.1 Preparation of standard matching solutions

Prepare a series of standard matching solutions each containing 25 cm³ of stabilized water (3.2.5), 6 cm³ of sulfuric acid (3.2.3) and 5 cm³ of nitric acid (3.2.4). To these solutions, add portions of the standard manganese solution (3.2.7) ranging from 0 (compensation solution) to 10 cm³, followed in each case by 0,3 g of sodium periodate (3.2.2). Boil the solutions for 10 min to ensure full development of the colour. Finally, cool and make up to 50 cm³ with stabilized water in volumetric flasks.

3.5.3.2 Spectrometric measurements

Rinse the cell of the photometer or spectrophotometer (3.3.1) first with potassium permanganate solution (3.2.6), then with stabilized water and finally with the appropriate standard matching solution. Then fill with the standard matching solution and measure the absorbance at the wavelength of maximum absorption (about 525 nm).

Correct the reading by subtracting the absorbance of the compensation solution.

3.5.3.3 Plotting the calibration graph

Plot the reading thus obtained for each solution against the appropriate concentration of manganese to give the calibration graph. Check the graph periodically (the intervals will depend on local conditions and the type of instrument used).

3.5.4 Determination

Rinse the cell of the photometer or spectrophotometer (3.3.1) first with potassium permanganate solution (3.2.6), then with stabilized water (3.2.5) and finally with the test solution. Then fill with the test solution and measure the absorbance at the wavelength used in preparing the calibration graph.

Correct the reading by subtracting the absorbance of the blank solution treated similarly.

By means of the calibration graph, determine the concentration of manganese corresponding to the corrected reading, and from this calculate the manganese content of the test portion.

3.6 Expression of results

Take as the result the mean value of the individual results of two determinations.

Express the result as milligrams of manganese per kilogram of sample.

3.7 Test report

The test report shall include the following particulars:

- a) a reference to this International Standard;
- b) all details necessary for complete identification of the test sample;
- c) the method used, i.e. the general method;
- d) the result, calculated as described in 3.6;
- e) any unusual features noted during the determination;
- f) any operation not included in this International Standard, or regarded as optional.

4 Restricted method (limited to samples with filler loadings < 10 %)

4.1 Principle

In the absence of chlorine, rubber is ashed in a silica crucible. In the presence of chlorine, a sulfuric acid digestion is required, followed by reaction with nitric acid. This procedure is carried out in a Kjeldahl flask. If silicates are present, the digested test portion is treated with sulfuric and hydrofluoric acids to volatilize any silicon as silicon tetrafluoride. After either procedure the manganese is oxidized to permanganate by boiling with sodium periodate. The manganese concentration is determined by spectrophotometric measurement at 525 nm.

4.2 Reagents

During the analysis, wherever possible, use only reagents of recognized analytical grade, suitable for use in trace-metal analysis, and only stabilized water (see 4.2.6).

4.2.1 Potassium hydrogen sulfate.

4.2.2 Sodium periodate.

4.2.3 Sulfuric acid, $\rho = 1,84 \text{ Mg/m}^3$.

4.2.4 Sulfuric acid, 1 + 19 solution.

Dilute 1 volume of concentrated sulfuric acid (4.2.3) with 19 volumes of stabilized water (4.2.6).

4.2.5 Orthophosphoric acid, 85 % (V/V) to 90 % (V/V) H_3PO_4 .

4.2.6 Stabilized water.

See 3.2.5.

4.2.7 Potassium permanganate solution.

See 3.2.6.

4.2.8 Manganese, standard solution, corresponding to 10 mg of manganese per cubic decimetre.

See 3.2.7.

4.2.9 Nitric acid, $\rho = 1,42 \text{ Mg/m}^3$.

4.2.10 Hydrogen peroxide, 30 % (V/V) solution in water.

4.2.11 Hydrofluoric acid, $\rho = 1,12 \text{ Mg/m}^3$.

4.3 Apparatus

Ordinary laboratory apparatus, plus the following:

4.3.1 Photometer or spectrophotometer, capable of measuring absorbance at approximately 525 nm, and matched cells.

4.3.2 Silica crucibles, of capacity about 50 cm^3 , for use in 4.5.2.1, or platinum crucibles, of capacity about 80 cm^3 , for use in 4.5.2.2.

4.3.3 Heat-resistant, thermally insulating board, approximately 100 mm square and 6 mm thick, with a hole in the centre to support the crucible so that approximately two-thirds projects below the board.

4.3.4 Muffle furnace, capable of being maintained at a temperature of $550 \text{ }^\circ\text{C} \pm 25 \text{ }^\circ\text{C}$.

4.3.5 Sintered-glass filter, porosity grade P 40 (see ISO 4793).

4.3.6 Electrical heating plate or gas burner with sandbath.

4.3.7 Kjeldahl flask, of capacity 250 cm^3 .

4.3.8 Platinum rod, as stirrer.

4.4 Sampling

See 3.4.

4.5 Procedure

4.5.1 Preparation of test portion

See 3.5.1.

4.5.2 Preparation of test solution

4.5.2.1 Ashing the test portion in the absence of chlorine

Cut the test portion into small pieces of not more than 0,1 g (if not already done), and place in a 50 cm^3 silica crucible (see 4.3.2) which is supported in the hole in the heat-resistant, thermally insulating board (4.3.3).

Start the preparation of a blank solution at the same time, using a similar crucible but omitting the test portion, and continue by treating the test portion and the blank in an identical manner.

Heat the crucible and contents with a gentle gas flame until a dry carbonaceous residue remains and then transfer the crucible to the muffle furnace (4.3.4) maintained at a temperature of $550\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ and heat until all carbon has been oxidized.

Remove the crucible, allow it to cool and, from a fine pipette, add an amount of concentrated sulfuric acid (4.2.3) drop by drop round the walls of the crucible just sufficient to moisten the ash. Heat gently until fuming ceases and then place the crucible in the muffle furnace again at $550\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ to remove the last traces of carbon.

Repeat the treatment of the ash with the concentrated sulfuric acid, adding the acid as before from a fine pipette, but heating only until fuming ceases in order to retain the ash as far as possible in the form of sulfate. Allow the crucible to cool, add 2 g to 3 g of potassium hydrogen sulfate (4.2.1) and, supporting the crucible on the heat-resistant, thermally insulating board, apply strong heat from a burner until a clear melt is obtained. Cool the crucible and contents.

4.5.2.2 Ashing the test portion in the presence of chlorine

Place the test portion in the Kjeldahl flask (4.3.7), add 10 cm^3 of concentrated sulfuric acid (4.2.3) and heat moderately until the test portion has disintegrated. Carefully add 5 cm^3 of nitric acid (4.2.9). If the reaction becomes too vigorous, cool the flask in a beaker of cold water and store at room temperature for at least two hours before reheating.

As soon as the initial reaction has subsided, heat the mixture gently until the reaction has ceased, and then more strongly until the mixture darkens. Add a 1 cm^3 portion of nitric acid and heat until darkening takes place again. Repeat the nitric acid addition and heating until the solution becomes colourless or pale yellow and fails to darken on further heating.

If the digestion is prolonged, it may be necessary to add about 1 cm^3 of concentrated sulfuric acid to prevent the contents of the flask from solidifying.

If the digest is free from insoluble matter, cool, add $0,5\text{ cm}^3$ of hydrogen peroxide (4.2.10) and 2 drops of nitric acid and heat to fuming. Repeat the addition and heating until there is no further reduction in the colour of the solution. Cool, dilute with 10 cm^3 of water and heat to fuming.

Transfer the solution, and any residue present, to an 80 cm^3 platinum crucible (see 4.3.2), evaporate to dryness and ignite until all of the carbon has burned off.

If insoluble material is present in the digest at this stage, cool, add a few drops of concentrated sulfuric acid and 5 cm^3 of hydrofluoric acid (4.2.11). Evaporate to dryness on the heating device (4.3.6) while stirring with the platinum rod (4.3.8). Repeat this procedure twice.

If insoluble material is absent, evaporate to dryness on the heating device.

4.5.2.3 Dissolution

To the ash obtained in 4.5.2.1 or 4.5.2.2, add 20 cm^3 of dilute sulfuric acid (4.2.4) and heat the crucible on a steam bath until the solid material is dissolved or loosened from the walls of the crucible. Wash the contents into a small beaker, using a glass rod to dislodge undissolved solid, and gently boil the solution until no more will dissolve. Pass the solution through the cleaned sintered-glass filter (4.3.5) into a small conical flask, and wash the filter and insoluble material with two or three portions of water. Add to the solution in the flask 3 cm^3 of orthophosphoric acid (4.2.5), further additions of 1 cm^3 being made as necessary to remove any yellow colour due to iron.

Add to the solution 0,3 g of sodium periodate (4.2.2), heat the solution to boiling and maintain at the boiling point for 10 min. Hold the temperature above $90\text{ }^{\circ}\text{C}$ for a further 10 min to ensure full development of the permanganate colour. After cooling, any cloudiness due to precipitated potassium periodate may be cleared by centrifuging or by passing through the sintered-glass filter.