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

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

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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.

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

It cancels and replaces International Standards ISO 1397 : 1975 and ISO 1655 : 1975, of which it constitutes a technical revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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

0 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 concerning 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* (section one), 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* (section two), 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 provided chlorine is also absent.

1 Scope and field of application

This International Standard specifies photometric methods for the determination of manganese, after oxidation with sodium periodate, in rubbers and rubber latices.

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

Section two specifies a method for raw rubber, latex and compounded rubber which does 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. The method can be applied to natural and synthetic rubbers which do not contain chlorine.

2 References

- ISO 123, *Rubber latex — Sampling.*
- ISO 124, *Rubber latices — Determination of total solids content.*
- ISO 1795, *Raw rubber in bales — Sampling.*
- ISO 1796, *Rubber, raw — Sample preparation.*
- ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

Section one : Determination of manganese — General method

3 Principle

Ashing of the rubber in a platinum crucible followed by fusion of the ash with sodium fluoroborate. After treatment with dilute sulfuric and nitric acids, removal of the insoluble matter and oxidation of the manganese to permanganate by boiling with sodium periodate solution. Photometric measurement at approximately 525 nm of this solution gives the absorbance, which is proportional to the concentration of manganese.

WARNING — All recognized health and safety precautions shall be in effect when carrying out this procedure.

4 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 4.5).

4.1 Sodium fluoroborate.

If analytical grade is not available, this reagent shall be prepared 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 while 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.

4.2 Sodium periodate.

4.3 Sulfuric acid, $\rho = 1,84 \text{ g/cm}^3$.

4.4 Nitric acid, $\rho = 1,42 \text{ g/cm}^3$.

4.5 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.

4.6 Potassium permanganate, solution, approximately 0,03 g/dm³.

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

Either of the following solutions 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 (4.3). 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 (4.3). 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 either of these standard solutions contains 0,01 mg of manganese.

Prepare either solution just before use.

5 Apparatus

Ordinary laboratory apparatus and

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

5.2 Platinum crucible, 30 cm³ nominal capacity is suitable.

5.3 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.

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

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

6 Sampling

6.1 Raw rubber

Carry out the sampling in accordance with ISO 1795.

6.2 Latex

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

6.3 Compounded rubber

Cut a 10 g test portion from the sample, if necessary from more than one piece, so that proper representation of the whole sample is achieved.

7 Procedure

WARNING — All precautions and safeguards required for the carrying out of trace metal analysis shall be observed.

7.1 Preparation of test portion

7.1.1 Raw rubber

Prepare a test portion from the piece or pieces (6.1) in accordance with ISO 1796 or by cutting the rubber into small portions each weighing approximately 0,1 g. Weigh a 10 g test portion to the nearest 10 mg.

7.1.2 Latex

Take a portion of the thoroughly mixed latex (6.2) containing about 10 g of total solids, dry to constant mass as specified in ISO 124, and cut into small pieces.

7.1.3 Vulcanized rubber

Sheet or crumble on a mill, or comminute by hand a 10 g test portion (6.3).

NOTE — At all stages of sample preparation, take care to avoid contamination of the rubber.

7.2 Preparation of test solution

7.2.1 Ashing of test portion

Choose the mass of test portion so that it contains not more than 1 g of titanium dioxide. Transfer the test portion to a weighed platinum crucible (5.2) which is supported in the hole in the heat-resistant, thermally insulating board (5.3).

Commence the preparation of a blank solution at the same time using a similar crucible (5.2) 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 (5.4) maintained at a temperature of 550 ± 25 °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 concentrated sulfuric acid (4.3) 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 °C for a few minutes. Repeat the treatment of the ash with the sulfuric acid (4.3), adding the acid as before from a fine pipette, heating gently until fuming ceases, and then again at about 550 °C for a few minutes. After cooling again to room temperature, add to the crucible 8 parts by mass of sodium fluoroborate (4.1), 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.

7.2.2 Dissolution

Cool the crucible to room temperature, and add 12 cm³ of stabilized water (4.5) and 4 cm³ of sulfuric acid (4.3). After warming very gently to dissolve the solidified mass, rinse the contents into a 100 cm³ conical flask and treat the contents of the platinum crucible with a further 10 cm³ of stabilized water (4.5) and 2 cm³ of sulfuric acid (4.3) which should also be added to the conical flask.

Add 5 cm³ of nitric acid (4.4) to the flask and then pour the contents through the cleaned sintered glass filter (5.5), washing the filter once with 5 cm³ of hot stabilized water (4.5). 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 (4.2) 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 centrifugation or by passing through the porosity grade P 40 filter.

Quantitatively transfer the solution to a 50 cm³ volumetric flask and dilute to the mark with stabilized water (4.5) 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 7.2.1.

Proceed in accordance with 7.4.

7.3 Preparation of calibration graph

7.3.1 Preparation of standard matching solutions

Prepare a series of standard matching solutions each containing 25 cm³ of stabilized water (4.5), 6 cm³ of sulfuric acid (4.3) and 5 cm³ of nitric acid (4.4). To these solutions, add portions of the standard manganese solution (4.7) ranging from 0 (compensation solution) to 10 cm³, followed in each case by 0,3 g of sodium periodate (4.2). Boil the solutions for 10 min to ensure full development of the colour; finally cool and dilute with stabilized water (4.5) to 50 cm³ in volumetric flasks.

7.3.2 Spectrometric measurements

Rinse the cell of the photometer or spectrophotometer (5.1) first with the potassium permanganate solution (4.6) then with stabilized water (4.5) and finally with the appropriate standard matching solution. 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.

7.3.3 Plotting the calibration graph

Plot the reading thus obtained for each solution against the appropriate concentration of manganese to give the calibration graph. The graph shall be checked periodically according to local conditions and the type of instrument used.

7.4 Determination

Rinse the cell of the photometer or spectrophotometer (5.1) first with potassium permanganate solution (4.6), then with stabilized water 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 (see 7.2.1) 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.

8 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.

9 Test report

The test report shall include the following information :

- a) type and identification of the test sample ;
- b) a reference to the method used : i.e. ISO 7780 general method ;
- c) the result as described in clause 8 ;
- d) any unusual features noted during the determination ;
- e) any operation not included in this International Standard, or regarded as optional.

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