INTERNATIONAL STANDARD ISO 1397

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Compounded rubber — Determination of manganese content — Sodium periodate photometric method

Mélanges à base de caoutchoucs — Dosage du manganèse — Méthode photométrique au periodate de sodium

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 45 has reviewed ISO Recommendation R 1397 and found it technically suitable for transformation. International Standard ISO 1397 therefore replaces ISO Recommendation R 1397-1970 to which it is technically identical.

ISO Recommendation R 1397 was approved by the Member Bodies of the following countries :

Australia
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The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

Germany

The Member Body of the following country disapproved the transformation of ISO/R 1397 into an International Standard :

Germany

Printed in Switzerland

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Compounded rubber – Determination of manganese content – Sodium periodate photometric method

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 in the rubber compound, even in relatively large amounts, without degradation taking place, but in these cases there is always the possibility 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 compound.

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

Of the two specified procedures, the first, known as the general method, is believed to be applicable to all compounded rubbers not containing chlorine. In this method, the ash from the rubber is taken through a fusion stage in order to obtain the manganese in a soluble form; it is most suited to those rubber compounds which contain heavy loadings of inert fillers such as clay, or materials which form insoluble phosphates, for example titanium dioxide. The second, known as the restricted method, is shorter and suitable for all other rubber compounds and will probably be more frequently used.

SECTION ONE : DETERMINATION OF MANGANESE – GENERAL METHOD

1 SCOPE AND FIELD OF APPLICATION

Section one of this International Standard specifies a photometric method using sodium periodate for the determination of trace amounts of manganese in compounded or vulcanized rubbers which do not contain chlorine. The method is not intended for compounded rubber latex. It 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.

2 REFERENCES

ISO 1795, *Raw rubber in bales – Sampling.*

ISO 1796, *Raw rubber – Sample preparation.*

3 PRINCIPLE

Ashing of the rubber in a platinum crucible. Fusion of the ash with sodium fluoroborate, After treatment with dilute sulphuric and nitric acids, removal of the insoluble matter and oxidation of the manganese to permanganate by boiling with sodium periodate. Photometric measurement of the absorbance of this solution, which is proportional to the concentration of manganese.

4 REAGENTS

All reagents shall be of recognized analytical reagent quality suitable for use in trace metal analysis. Distilled water shall be used whenever water is specified, unless otherwise stated.

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 cm^3* of water warmed to about 35 °C. After filtering through paper, cool the solution to room temperature and add 100 cm^3 of 96 % ethanol while stirring. Filter the crystalline precipitate onto 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 Sulphuric acid, concentrated, ρ 1,84 g/cm^3.

4.4 Nitric acid, concentrated, ρ 1,42 g/cm^3.

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* The term millilitre (ml) is commonly used as a special name for the cubic centimetre (cm^3), in accordance with a decision of the Twelfth Conférence Générale des Poids et Mesures. The term millilitre is acceptable, in general, for references in International Standards to capacities of volumetric glassware and to liquid volumes.

4.5 Stabilized water

To approximately 1 dm³ of water add about 0,1 g of potassium permanganate together with a few drops of sulphuric 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, approximately 0,001 N solution.

4.7 Standard manganese solution

Either of the following solutions may be used :

a) Weigh 0,720 g of potassium permanganate ($KMnO_4$) into a small beaker and dissolve in water containing 2 cm³ of sulphuric acid. Add sulphur dioxide-saturated water until the solution is colourless. Boil the solution for 15 min, cool, transfer to a 500 cm³ volumetric flask and dilute to the mark. Pipette 10 cm³ of this solution into a second 500 cm³ volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0,01 mg of manganese per cubic centimetre and must be freshly prepared from the stock solution when required.

b) Weigh 0,770 g of manganese sulphate ($MnSO_4.H_2O$) into a small beaker and dissolve in water containing 2 cm³ of sulphuric acid. Transfer the solution to a 500 cm³ volumetric flask and dilute to the mark. This solution should be stable for at least a month. Pipette 10 cm³ of this solution into a second 500 cm³ volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0,01 mg of manganese per cubic centimetre and must be freshly prepared from the stock solution when required.

5 APPARATUS

Ordinary laboratory apparatus and

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

5.2 Platinum crucible (30 cm³ capacity is suitable).

5.3 Asbestos board, approximately 100 mm square and 6 mm thick, with a hole in the centre to support the crucible so that approximately two-thirds project below the board.

5.4 Muffle furnace, capable of maintaining a temperature of 550 ± 25 °C.

6 SAMPLING

Carry out the sampling in accordance with ISO 1795.

7 PROCEDURE

7.1 Preparation of test portion

Cut a 10 g test portion from the sample, if necessary from more than one place, so that proper representation of the whole sample is achieved. Treat the piece or pieces comprising the test portion in accordance with ISO 1796. Alternatively, prepare the test portion by cutting the rubber into small portions each weighing approximately 0,1 g.

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

7.2 Preparation of calibration curve

Prepare a series of standard matching solutions each containing 25 cm³ of stabilized water (4.5), 6 cm³ of sulphuric 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 to 10 cm³ followed in each case by 0,3 g of sodium periodate (4.2). Boil the solutions and treat exactly as described for the test solution; finally cool and dilute to 50 cm³ in volumetric flasks. Rinse the cell of the electrophotometer or spectrophotometer first with approximately 0,001 N potassium permanganate solution (4.6) then with stabilized water 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 solution containing no added manganese. If the absorbance is measured on a double-beam or null-point instrument, place the cell containing the blank solution in the reference beam and measure the absorbance of each standard matching solution against that of the solution containing no added manganese.

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

7.3 Determination[1]

Weigh, to the nearest 10 mg, a test portion of the rubber not exceeding 10 g, the mass chosen being such as to contain not more than 1 g of titanium dioxide. Transfer the test portion to the platinum crucible (5.2) which is supported in the hole in the asbestos board (5.3).

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[1] All precautions and safeguards for the carrying out of trace metal analysis must be observed.

Commence a blank determination using a similar crucible at the same time and give identical treatment throughout to the test and blank determination. 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, and from a fine pipette add sulphuric acid (4.3) drop by drop round the walls of the crucible in amount just sufficient to moisten the ash. Then heat gently until fuming ceases and again at about 550 °C for a few minutes. After cooling again to room temperature, add to the crucible 8 parts of sodium fluoroborate (4.1), up to a maximum of 8 g, for each part 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.

Then cool the crucible to room temperature, and add 12 cm^3 of water and 4 cm^3 of sulphuric acid. After warming very gently to dissolve the solidified mass, rinse the contents into a 100 cm^3 conical flask and give the platinum crucible a further treatment with 10 cm^3 of water and 2 cm^3 of sulphuric acid which should also be added to the conical flask. Add to the flask 5 cm^3 of nitric acid (4.4) and pass through a sintered glass filter (porosity grade 3), washing the filter once with 5 cm^3 of hot water. Transfer the filtrate to another conical flask with washings made up to about 40 cm^3, 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, transfer the solution to a 50 cm^3 volumetric flask and dilute to the mark with stabilized water (4.5) at room temperature. After mixing, the colour should be stable for several hours; any tendency to fade indicates the incomplete removal of organic matter or chloride.

Rinse the cell of the electrophotometer or spectrophotometer (5.1) first with approximately 0,001 N 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 curve. Correct the reading by subtracting the absorbance of the blank solution treated similarly. If the absorbance is measured on a double-beam or a null-point instrument, place the cell containing the blank solution in the reference beam and measure the absorbance of the test solution against that of the blank.

8 EXPRESSION OF RESULTS

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

Express the result as parts per million (ppm) of manganese (Mn) calculated by mass.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

SECTION TWO : DETERMINATION OF MANGANESE – RESTRICTED METHOD

10 SCOPE AND FIELD OF APPLICATION

Section two of this International Standard specifies a method suitable for the determination of manganese in 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. It is not intended for compounded rubber latex.

11 REFERENCES

ISO 1795, *Raw rubber in bales – Sampling.*

ISO 1796, *Raw rubber – Sample preparation.*

12 PRINCIPLE

Ashing of the rubber, in a silica crucible. Treatment of the ash with sulphuric acid and potassium hydrogen sulphate to convert the manganese to the soluble form. After dissolution of the sulphated ash in dilute sulphuric acid, complexing of any iron present with orthophosphoric acid, and oxidation of the manganese to permanganate by boiling with sodium periodate. Photometric measurement of the colour of the solution, which is proportional to the concentration of manganese.

13 REAGENTS

All reagents shall be of recognized analytical reagent quality suitable for use in trace metal analysis. Distilled water shall be used whenever water is specified, unless otherwise stated.

13.1 Potassium hydrogen sulphate.

13.2 Sodium periodate.

13.3 Sulphuric acid, concentrated, ρ 1,84 g/cm^3.

13.4 Sulphuric acid, dilute.

Mix 1 volume of concentrated sulphuric acid (13.3) with 19 volumes of water.

13.5 Orthophosphoric acid, 85 to 90 % H_3PO_4.

13.6 Stabilized water

To approximately 1 dm^3 of water add about 0,1 g of potassium permanganate together with a few drops of sulphuric acid. Distil the water through an effective spray trap, discarding the first and last 50 cm^3 of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

13.7 Potassium permanganate, approximately 0,001 N solution.

13.8 Standard manganese solution

Either of the following solutions may be used :

a) Weigh 0,720 g of potassium permanganate ($KMnO_4$) into a small beaker and dissolve in water containing 2 cm^3 of sulphuric acid. Add sulphur dioxide-saturated water until the solution is colourless. Boil the solution for 15 min, cool, transfer to a 500 cm^3 volumetric flask and dilute to the mark. Pipette 10 cm^3 of this solution into a second 500 cm^3 volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0,01 mg of manganese per cubic centimetre and shall be freshly prepared from the stock solution when required.

b) Weigh 0,770 g of manganese sulphate ($MnSO_4.H_2O$) into a small beaker and dissolve in water containing 2 cm^3 of sulphuric acid. Transfer the solution to a 500 cm^3 volumetric flask and dilute to the mark. This solution should be stable for at least a month. Pipette 10 cm^3 of this solution into a second 500 cm^3 volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0,01 mg of manganese per cubic centimetre and shall be freshly prepared from the stock solution when required.

14 APPARATUS

Ordinary laboratory apparatus and

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

14.2 Silica crucibles, nominal capacity 50 or 80 cm^3, depending on the method of ashing.

14.3 Asbestos board, approximately 100 mm square and 6 mm thick, with a hole in the centre to support the crucible so that approximately two-thirds project below the board.

14.4 Muffle furnace, capable of maintaining a temperature of 550 ± 25 °C.

15 SAMPLING

Carry out the sampling in accordance with ISO 1795.

16 PROCEDURE

16.1 Preparation of test portion

Cut a test portion from the sample, if necessary from more than one place, so that proper representation of the whole sample is achieved, treat the piece or pieces comprising the test portion in accordance with ISO 1796. Alternatively, prepare the test portion by cutting the rubber into small portions each weighing approximately 0,1 g.

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

16.2 Preparation of calibration curve

Prepare a series of standard matching solutions each containing 20 cm^3 of dilute sulphuric acid (13.4), 3 cm^3 of orthophosphoric acid (13.5) and 25 cm^3 of stabilized water (13.6). To these solutions add portions of the standard manganese solution (13.8) ranging from 0 to 10 cm^3 followed in each case by 0,3 g of sodium periodate (13.2). Boil the solutions and treat exactly as described for the test solution; finally cool and dilute to 50 cm^3 in volumetric flasks. Rinse the cell of the electrophotometer or spectrophotometer first with approximately 0,001 N potassium permanganate solution (13.7), then with stabilized water (13.6) 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 solution containing no added manganese. If the absorbance is measured on a double-beam or null-point instrument, place the cell containing the blank solution in the reference beam and measure the absorbance of each standard matching solution against that of the solution containing no added manganese. Plot the reading thus obtained for each solution against the appropriate concentration of manganese to give the calibration curve which shall be checked periodically according to local conditions and the type of instrument used.

16.3 Determination[1]

Cut the milled rubber into small pieces of not more than 0,1 g, weigh a 10 g test portion to the nearest 10 mg and place in a crucible (14.2) which is supported in the hole cut in the asbestos board (14.3). Commence a blank determination using a similar crucible at the same time and give identical treatment throughout to the test and blank determinations.

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 (14.4) maintained at a temperature of 550 ± 25 °C and heat until all carbon has been oxidized.

Remove the crucible and allow it to cool, and from a fine pipette add concentrated sulphuric acid (13.3) drop by drop round the sides of the crucible in amount just sufficient to moisten the ash. Fume off the excess acid and replace the crucible in the muffle furnace at 550 ± 25 °C to remove the last traces of carbon.

Give the ash a further treatment with the sulphuric acid (13.3), 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 sulphate. Allow the crucible to cool, add 2 to 3 g of potassium hydrogen sulphate (13.1) and, supporting the crucible on the asbestos board, apply strong heat from a burner until a clear melt is obtained. Cool the crucible and contents.

As an alternative to the above method of ashing, wrap 10 g of the test portion, weighed to the nearest 10 mg, in a piece of ashless filter paper about 150 mm in diameter and place in a crucible of about 80 cm^3 nominal capacity. Place about 5 g of the potassium hydrogen sulphate on top of the wrapped test portion, place the crucible in the furnace, maintained at 550 ± 25 °C and close the door. The furnace door must not be opened during the first hour. Also commence a blank determination using a similar filter paper and crucible and giving identical treatment throughout to the test and blank determinations. When all the carbon has been oxidized allow the crucible and contents to cool.

Add to the ash produced by either of the above procedures 20 cm^3 of dilute sulphuric acid (13.4) 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 a sintered glass filter 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 (13.5), 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 (13.2), heat the solution to boiling and maintain at the boiling point for 10 min. Hold the temperature above 90 °C for a further 10 min to ensure full development of the permanganate colour. After cooling, transfer the solution to a 50 cm^3 volumetric flask and dilute to the mark with stabilized water (13.6) 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 chloride.

Rinse the cell of the electrophotometer or spectrophotometer (14.1) first with approximately 0,001 N potassium permanganate solution (13.7), 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 curve. Correct the reading by subtracting the absorbance of the blank solution treated similarly. If the absorbance is measured on a double-beam or a null-point instrument, place the cell containing the blank solution in the reference beam and measure the absorbance of the test solution against that of the blank.

17 EXPRESSION OF RESULTS

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

Express the result as parts per million (ppm) of manganese (Mn) calculated by mass.

18 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

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[1] All precautions and safeguards required for the carrying out of trace metal analysis must be observed.