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INTERNATIONAL STANDARD ISO 1655

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Raw rubber and rubber latex — Determination of manganese content — Potassium periodate photometric method

Caoutchoucs bruts et latex de caoutchouc — Dosage du manganèse — Méthode photométrique au periodate de potassium

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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 1655 and found it technically suitable for transformation. International Standard ISO 1655 therefore replaces ISO Recommendation R 1655-1971 to which it is technically identical.

ISO Recommendation R 1655 was approved by the Member Bodies of the following countries :

Australia
Austria
Belgium
Brazil
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Czechoslovakia
Egypt, Arab Rep. of
France
Germany
Greece
Hungary
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Iran
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Netherlands
New Zealand
Peru
Poland
South Africa, Rep. of
Spain
Sri Lanka
Sweden
Switzerland
Thailand
Turkey
United Kingdom
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No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 1655 into an International Standard.

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Raw rubber and rubber latex — Determination of manganese content — Potassium 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 without degradation taking place, but no generally accepted method is available for distinguishing between the active and inactive forms. At present, therefore, there is 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 is less severe than is the case with natural rubber. Possibly for this reason the determination of manganese in synthetic rubbers is less frequently carried out; nevertheless, the method specified in this International Standard is applicable to most of the commonly used synthetic elastomers.

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a potassium periodate photometric method for the determination of small amounts of manganese in raw natural rubber, raw synthetic elastomers which do not contain chlorine, and the corresponding uncompounded latices.

For compounded rubber the methods given in ISO 1397, *Compounded rubber — Determination of manganese content — Sodium periodate photometric method,* should be used.

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, *Raw rubber — Sample preparation.*

3 PRINCIPLE

Ashing, in a silica crucible, of the dried latex solids or of the raw rubber. Treatment of the ash with potassium hydrogen sulphate and sulphuric acid to convert the manganese to a soluble form. After dissolution of the ash in dilute sulphuric acid, complexing of any iron present with orthophosphoric acid and oxidation of the manganese to permanganate by boiling with potassium 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 high purity analytical reagent quality suitable for use in trace metal analysis. Distilled water shall be used whenever water is specified.

4.1 Potassium hydrogen sulphate.

4.2 Potassium periodate.

4.3 Sulphuric acid, ρ 1,84 g/cm^3.

4.4 Sulphuric acid, dilute.

Mix 1 volume of concentrated sulphuric acid (4.3) with 19 volumes of water.

4.5 Orthophosphoric acid, 85 to 90 % H_3PO_4.

4.6 Stabilized water.

Dissolve about 0,1 g of potassium permanganate in 1 dm^3 of water to which a few drops of sulphuric acid have been added. 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.

4.7 Potassium permanganate, approximately 0,001 N solution.

4.8 Standard manganese solution.

Either of the following solutions may be used :

a) Prepare an approximately 0,1 N solution of potassium permanganate and standardize against sodium oxalate. Transfer the calculated amount of this standardized solution to contain 0,720 g of $KMnO_4$ to a small beaker and acidify with 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 with stabilized water. Pipette 20 cm^3 of this stock solution into a second 500 cm^3 volumetric flask and again dilute to the mark with stabilized water. This dilute solution contains the equivalent of 0,02 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 is stable for at least a month. Pipette 20 cm^3 of this stock solution into a second 500 cm^3 volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0,02 mg of manganese per cubic centimetre and shall 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 Silica crucibles, nominal capacity 80 cm^3.

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

For raw rubber, carry out the sampling in accordance with ISO 1795.

For latex, carry out the sampling in accordance with one of the methods specified in ISO 123.

7 PROCEDURE

7.1 Preparation of test portion

For the determination of manganese in rubber, cut at least 10 g from the sample in such a way that proper representation of the whole is achieved. Treat the piece or pieces comprising the test portion in accordance with ISO 1796.

For the determination of manganese in latex, take a portion of thoroughly mixed latex containing about 5 g of total solids and dry to constant mass as specified in ISO 124.

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 20 cm^3 of dilute sulphuric acid (4.4), 3 cm^3 of orthophosphoric acid (4.5), and potassium hydrogen sulphate (4.1) equal in amount to that used in ashing the test portion. To these solutions, add portions of the standard manganese solution (4.8) ranging from 0 to 15 cm^3, followed in each case by 0,3 g of potassium periodate (4.2). Bring the solutions to the boil, maintain at boiling point for 10 min, and hold at 90 °C or above for a further 10 min to ensure full development of the permanganate colour. Cool each solution, transfer to a 50 cm^3 volumetric flask and dilute to the mark with stabilized water (4.6).

Rinse the cell of the electrophotometer or spectrophotometer (5.1) first with approximately 0,001 N potassium permanganate solution (4.7), then with stabilized water (4.6), and finally with the appropriate standard matching solution. Fill the cell with the standard matching solution and measure the absorbance at the absorption maximum (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 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 Procedure[1]

Weigh, to the nearest 10 mg, a 10 g portion of the raw rubber or about 5 g of the dried latex solids, cut into small pieces, and place in a crucible (5.2) which is supported in the hole cut in the asbestos board (6.3). Heat the crucible and contents with a small gas flame until a dry carbonaceous residue remains and then transfer the crucible to the muffle furnace maintained (5.4) at a temperature of 550 ± 25 °C and heat until all carbon has been oxidized. Remove the crucible and allow to cool. Add concentrated sulphuric acid (4.3), delivered drop by drop from a pipette with a fine jet, round the sides of the crucible in amount just sufficient to moisten the ash. Fume off the excess acid by gentle heating and replace the crucible in the muffle furnace at 550 ± 25 °C to remove the last traces of carbon.

After cooling, give the ash a further treatment with sulphuric acid, adding the acid as before from a pipette, but heating only until fuming ceases in order to retain the ash as far as possible in the form of sulphate. Cool the crucible. Add 2 to 3 g of potassium hydrogen sulphate (4.1) 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.

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

As an alternative to the above method of ashing, wrap the 10 g portion, weighed to the nearest 10 mg, in a piece of ashless filter paper about 150 mm in diameter and place in a crucible (5.2). Place about 5 g of potassium hydrogen sulphate (4.1) on top of the wrapped test portion, place the crucible in the furnace at 550 ± 25 °C and close the door. Owing to the risk of ignition of flammable gases, the furnace door shall not be opened during the first hour. When all the carbon has been oxidized, allow the crucible and contents to cool.

In parallel with the determination and following the same procedure, carry out a blank test, using a similar crucible and filter paper and the same quantities of all the reagents as used for the determination. To the ash produced by either of the above procedures, add 20 cm^3 of dilute sulphuric acid (4.4), 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 boil the solution gently until no more will dissolve. Filter the solution through a sintered glass filter pad into a small conical flask, and wash the filter and insoluble material with two or three portions of water. Add 3 cm^3 of orthophosphoric acid (4.5) to the solution in the flask, making further additions of 1 ml as may be necessary to remove any yellow colour due to iron. Add to the solution 0,3 g of potassium periodate (4.2), bring the solution to the boil and maintain at 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 (4.6). After mixing, the colour should be stable for several hours; any tendency to fading indicates the incomplete removal of organic matter or chloride.

Rinse the cell of the electrophotometer, absorptiometer or spectrophotometer (5.1) first with approximately 0,001 N potassium permanganate solution (4.7), then with stabilized water (4.7), and finally with the test solution. Fill the cell 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. 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 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) or percentage 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.