

Transformed

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 1397

DETERMINATION OF MANGANESE IN COMPOUNDED RUBBER

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BRIEF HISTORY

The ISO Recommendation R 1397, *Determination of manganese in compounded rubber*, was drawn up by Technical Committee ISO/TC 45, *Rubber*, the Secretariat of which is held by the British Standards Institution (BSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1397 which was circulated to all the ISO Member Bodies for enquiry in December 1967. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia
Austria
Czechoslovakia
France
Greece
Hungary
India
Iran

Ireland
Israel
Italy
Japan
Netherlands
New Zealand
Poland
Spain

Sweden
Switzerland
U.A.R.
United Kingdom
U.S.A.
Yugoslavia

The following Member Body opposed the approval of the Draft :

Germany

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in April 1970, to accept it as an ISO RECOMMENDATION.

DETERMINATION OF MANGANESE IN COMPOUNDED RUBBER

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 no alternative therefore to determining the total amount of manganese in the rubber compound.

Little is known concerning the influence of manganese on the catalytical 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 recommended in this ISO Recommendation are applicable to all the commonly used elastomers except those which contain chlorine.

Of the two recommended 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.

1. DETERMINATION OF MANGANESE – GENERAL METHOD

1.1 Scope

This section describes a method suitable 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.

1.2 Principle of method

Ten grammes of the rubber are ashed in a platinum crucible and the ash fused with sodium fluoroborate. After treating with dilute sulphuric and nitric acids, insoluble matter is removed and the manganese oxidized to permanganate by boiling with sodium periodate. The colour of the solution is measured photometrically and is proportional to the concentration of manganese.

1.3 Reagents

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

1.3.1 *Sodium fluoroborate*. If analytical grade is not available, this reagent should be prepared as follows : Dissolve 110 g of technical grade sodium fluoroborate in 100 ml of water warmed to about 35 °C. After filtering through paper cool the solution to room temperature and add 100 ml 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.

1.3.2 *Sodium periodate*.

1.3.3 *Sulphuric acid*, concentrated, ρ 1.84 (g/ml).

1.3.4 *Nitric acid*, concentrated, ρ 1.42 (g/ml).

1.3.5 *Stabilized water*. To approximately 1 litre 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 ml of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

1.3.6 *Potassium permanganate*, approximately 0.001 N solution.

1.3.7 *Standard manganese solution*. Either of the following alternative solutions may be used :

- (a) Weigh 0.720 g of potassium permanganate (KMnO_4) into a small beaker and dissolve in water containing 2 ml of sulphuric acid. Add sulphur dioxide-saturated water until the solution is colourless. Boil the solution for 15 minutes, cool, transfer to a 500 ml volumetric flask and dilute to the mark. Pipette 10 ml of this solution into a second 500 ml volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0.01 mg of manganese per millilitre and should be freshly prepared from the stock solution when required.
- (b) Weigh 0.770 g of manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) into a small beaker and dissolve in water containing 2 ml of sulphuric acid. Transfer the solution to a 500 ml volumetric flask and dilute to the mark. This solution should be stable for at least a month. Pipette 10 ml of this solution into a second 500 ml volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0.01 mg of manganese per millilitre and should be freshly prepared from the stock solution when required.

1.4 Apparatus

1.4.1 *Electrophotometer, absorptiometer, or spectrophotometer* capable of measuring optical density at approximately 525 nm.

1.4.2 *Platinum crucible* (30 ml capacity is suitable).

1.4.3 *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.

1.4.4 *Muffle furnace*, with thermocouple and thermostat for control of temperature.

1.5 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. Then homogenize the piece or pieces comprising the test portion by passing a few times between the cold rolls of a laboratory mill to produce a thin sheet or rough crumb. Alternatively the test portion may be prepared by cutting the rubber into small portions each weighing approximately 0.1 g.

At all stages of sample preparation care should be taken to avoid contamination of the rubber.

1.6 Procedure

NOTE. — All precautions and safeguards for the carrying out of trace metal analysis must be observed.

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 (1.4.2) which is supported in the hole in the asbestos board (1.4.3). 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 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 (1.3.3) dropwise 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 (1.3.1), 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 ml of water and 4 ml of sulphuric acid (1.3.3). After warming very gently to dissolve the solidified mass, rinse the contents into a 100 ml conical flask and give the platinum crucible a further treatment with 10 ml of water and 2 ml of sulphuric acid (1.3.3) which should also be added to the conical flask. Add to the flask 5 ml of nitric acid (1.3.4) and pass through a sintered glass filter (porosity grade 3), washing the filter once with 5 ml of hot water. Transfer the filtrate to another conical flask with washings made up to about 40 ml, add 0.3 g of sodium periodate (1.3.2) and heat the solution to boiling. Continue boiling gently for 10 minutes to ensure full development of the colour. After cooling, transfer the solution to a 50 ml volumetric flask and dilute to the mark with stabilized water (1.3.5) 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, absorptiometer or spectrophotometer (1.4.1) first with approximately 0.001 N potassium permanganate solution (1.3.6), then with stabilized water (1.3.5) and finally with the test solution. Then fill with the test solution and measure the optical density at the wavelength used in preparing the calibration curve (about 525 nm). Correct the reading by subtracting the optical density of the blank solution treated similarly. If the optical density is measured on a double beam or a null point instrument the cell containing the blank solution should be placed in the reference beam and the optical density of the test solution measured against that of the blank. The reading thus obtained, used in conjunction with the calibration curve, gives the concentration of manganese in the test solution and hence in the rubber.

A calibration curve is prepared as follows :

Prepare a series of standard solutions each containing 25 ml of stabilized water (1.3.5), 6 ml of sulphuric acid (1.3.3) and 5 ml of nitric acid (1.3.4). To these solutions add portions of the standard manganese solution (1.3.7) ranging from 0 to 10 ml followed in each case by 0.3 g of sodium periodate (1.3.2). Boil the solutions and treat exactly as described for the test solution, finally cool and dilute to 50 ml in volumetric flasks. Rinse the cell of the electrophotometer, absorptiometer or spectrophotometer first with approximately 0.001 N potassium permanganate solution (1.3.6) then with stabilized water (1.3.5) and finally with the appropriate standard solution. Fill with the standard solution and measure the optical density at the wavelength of maximum absorption (about 525 nm).

Correct the reading by subtracting the optical density of the solution containing no added manganese. If the optical density is measured on a double beam or null point instrument the cell containing the blank solution should be placed in the reference beam and the optical density of each standard solution measured 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 should be checked periodically according to local conditions and the type of instrument used.

1.7 Expression of results

The results should be expressed as parts of manganese (Mn) in a million parts of the rubber.

2. DETERMINATION OF MANGANESE – RESTRICTED METHOD

2.1 Scope

This section describes 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.

2.2 Principle of method

Ten grammes of the rubber are ashed in a silica crucible and the ash is treated with sulphuric acid and potassium hydrogen sulphate to convert the manganese to the soluble form. After dissolving the sulphated ash in dilute sulphuric acid, any iron present is complexed with orthophosphoric acid, and the manganese oxidized to permanganate by boiling with sodium periodate. The colour of the solution is measured photometrically and is proportional to the concentration of manganese.

2.3 Reagents

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

2.3.1 *Potassium hydrogen sulphate.*

2.3.2 *Sodium periodate.*

2.3.3 *Sulphuric acid*, concentrated, ρ 1.84 (g/ml).

2.3.4 *Sulphuric acid*, dilute. Mix 1 volume of concentrated acid with 19 volumes of water.

2.3.5 *Orthophosphoric acid*, 85 to 90 % H_3PO_4 .

2.3.6 *Stabilized water.* To approximately 1 litre 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 ml of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

2.3.7 *Potassium permanganate*, approximately 0.001 N solution.

2.3.8 *Standard manganese solution.* Either of the following alternative solutions may be used :

(a) Weigh 0.720 g of potassium permanganate (KMnO_4) into a small beaker and dissolve in water containing 2 ml of sulphuric acid. Add sulphur dioxide-saturated water until the solution is colourless. Boil the solution for 15 minutes, cool, transfer to a 500 ml volumetric flask and dilute to the mark. Pipette 10 ml of this solution into a second 500 ml volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0.01 mg of manganese per millilitre and should be freshly prepared from the stock solution when required.

(b) Weigh 0.770 g of manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) into a small beaker and dissolve in water containing 2 ml of sulphuric acid. Transfer the solution to a 500 ml volumetric flask and dilute to the mark. This solution should be stable for at least a month. Pipette 10 ml of this solution into a second 500 ml volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0.01 mg manganese per millilitre and should be freshly prepared from the stock solution when required.