IS 3660 (Part 5) : 1989

Indian Standard

METHODS OF TEST FOR NATURAL RUBBER

PART 5 DETERMINATION OF MANGANESE

(NR : 5)

(Second Revision)

भारतीय मानक

प्राकृतिक रबड़ की परीक्षण पद्धत्ति का मसौदा

भाग 5 मैंगनीज ज्ञात करना

(एन. आर. 5)

(दूसरा पुनरीक्षण)

[redacted]

UDC 678·4 : 543 : 546·711

[redacted]

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Price Group 2

October 1989

Rubber Sectional Committee, PCDC 14

FOREWORD

This Indian Standard (Part 5) (Second Revision) was adopted by the Bureau of Indian Standards on 8 May 1989, after the draft finalized by the Rubber Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

Methods of test for natural rubber had been originally covered in the following four parts of IS 3660:

Part 1 : 1972 Determination of ash, total copper, manganese, rubber hydrocarbon, viscosity (shearing disc viscometer), and mixing and vulcanizing of rubber in a standard compound (*first revision*)

Part 2 : 1968 Determination of solvent extract and nitrogen content

Part 3 : 1971 Plasticity and plasticity retention index

Part 4 : 1979 Determination of colour, accelerated storage-hardening test and vulcanization characteristics (MOD test)

While reviewing various test methods for natural rubber, the committee decided to align them with the corresponding international standards. No unification of test methods for natural and synthetic rubber has been considered necessary. However, in revising test methods for natural rubber, the Committee, had decided to revise and split the standard (IS : 3660) into further parts and publish individual test methods under natural rubber (NR) series. For proper referencing of the existing test methods and the new methods under revision, a table showing correspondence of the various methods of test covered in the previous 4 parts of IS 3660 with the presently split parts retaining the original NR : number have been given in Annex A.

In order to facilitate cross-reference, it has been decided to retain the original discrete NR series numbers assigned to various test methods in original IS 3660 (Parts 1, 2, 3 and 4), in the revised parts of IS 3660.

The test method given in this revised standard will supersede the test method as given under NR : 5 of IS 3660 (Part 1) : 1972. All the four parts of the original IS 3660 shall be withdrawn upon its complete revision.

The method of test for determination of manganese was originally published as NR : 5 of IS 3660 (Part 1) : 1966 wherein only photoelectric absorptiometer method was prescribed. Since at that time, most of the laboratories were not equipped with photoelectric absorptiometer, this standard was subsequently revised in 1972 and in the first revision. Nessler method for determination of manganese was included as routine method along with photoelectric absorptiometer method.

The Committee has now observed that most of the laboratories are equipped with photoelectric absorptiometer. Therefore, in view of the desirability of accuracy of test results and also to align it with the corresponding ISO standard, only the photoelectric absorptiometer method is being retained in this revision.

In the preparation of this standard, assistance has been derived from ISO 7780-1987 'Rubber and rubber lattices — Determination of manganese content — Sodium periodate photometric method', issued by the International Organisation for Standardisation (ISO) which specifies photometric methods for determination of manganese into two sections:

Section 1 specifies a method for compounded of vulcanized rubbers which do not contain chlorine, and

Section 2 specifies method for raw rubber, latex and compounded rubber which does not contain heavy loadings of inert silicate fillers.

This revision is based on Sec. 2 since it is applicable to raw natural rubber. Further the changes as given in ISO 7780/DAMI regarding hydrogen peroxide and hydrofluoric acid treatment prior to colour development has not been included in this revision since such treatment is not required for natural rubber.

Indian Standard

METHODS OF TEST FOR NATURAL RUBBER

PART 5 DETERMINATION OF MANGANESE

(NR : 5)

(Second Revision)

1 SCOPE

1.1 This standard (Part 5) prescribes a method for determination of total manganese in raw natural rubber.

2 REFERENCES

2.1 The following Indian Standards are necessary adjuncts to this standard:

IS No.	*Title*
IS 266 : 1977	Specification for sulphuric acid (*second revision*)
IS 1070 : 1977	Specification for water for general laboratory use (*second revision*)
IS 3660 (Part 1) : 1972	Methods of test for natural rubber: Part 1 Determination of ash, total copper, manganese, rubber, hydrocarbon, viscosity (shearing disc viscometer), and mixing and vulcanizing of rubber in a standard compound

3 QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070 : 1977) shall be employed in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the result of analyis.

4 OUTLINE OF THE METHOD

4.1 Raw natural rubber is ashed in a crucible and the ash is treated with potassium hydrogen sulphate and sulphuric acid to convert the manganese to a soluble form. After dissolution of the ash in dilute sulphuric acid, iron present is complexed with orthophosphoric acid and the manganese oxidized to permanganate by boiling with sodium periodate. The absorbance of this solution is measured photometrically which is proportional to the concentration of manganese.

5 APPARATUS

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

5.2 Silica Crucibles, nominal capacity 80 ml.

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 projects below the board.

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

6 REAGENTS

6.1 Potassium Hydrogen Sulphate

6.2 Sodium Periodate

6.3 Sulphuric Acid, Concentrated—*see* IS 266 : 1977.

6.4 Sulphuric Acid, Dilute, 1 volume of concentrated sulphuric acid mixed with 19 volumes of stabilized water.

6.5 Orthophosphoric Acid, ($H_3.PO_4.$), 85 to 90 percent (*v/v*)

6.6 Stabilized Water

Dissolve about 0·1 g of potassium permanganate in one litre 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 ml of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

6.7 Potassium Permanganate

Approximately 0·001 N solution.

6.8 Standard Manganese Solution

Either of the following solutions may be used:

a) Prepare an approximately 0·1 N solution of potassium permanganate ($KMNO_4$) 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 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 with stabilized water. Pipette 20 ml of this stock solution into a second 500 ml volumetric flask and again dilute to the mark with stabilized water. This dilute solution contains the equivalent of 0·02 mg of manganese per ml 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 ml of sulphuric acid. Transfer the solution to a 500 ml volumetric flask and dilute to the mark. This solution is stable for at least a month. Pipette 20 ml of this stock solution into a second 500 ml volumetric flask and again dilute to the mark. This dilute solution contains the equivalent of 0·02 mg of manganese per ml and shall be freshly prepared from the stock solution when required.

7 DETERMINATION OF MANGANESE

7.1 Preparation of Test Portion

For determination of manganese in natural rubber, cut the homogenized test portion prepared according to 3″ of IS 3660 (Part 1) : 1972.

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

7.2 Preparation of Calibration Curve

7.2.1 Prepare a series of standard matching solutions, each containing 20 ml of dilute sulphuric acid, 3 ml of orthophosphoric acid and potassium hydrogen sulphate equal in amount to that used in ashing the test portion. To these solutions, add portions of the standard manganese solution ranging from 0 to 15 ml, followed in each case by 0·3 g of sodium periodate. Bring the solutions to the boil, maintain at boiling point for 10 minutes, and hold at 90°C or above for further 10 minutes to ensure full development of the permanganate colour. Cool each solution, transfer to a 50-ml volumetric flask and dilute to the mark with stabilized water.

7.2.2 Rinse the cell of the electrophotometer or spectrophotometer first with approximately 0·001 N potassium permanganate solution, then with stabilized water 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 mm). 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.

7.2.3 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

7.3.1 Weigh to the nearest 10 mg, a 10 g portion of the raw rubber, cut into small pieces, and place in a crucible which is supported in the hole cut in the asbestos board. 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 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, 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 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.

7.3.2 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. Place about 5 g of potassium hydrogen sulphate 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.

7.3.3 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 ml of dilute sulphuric acid, 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 ml of orthophosphoric acid to the solution in the flasks, 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 sodium periodate, bring the solution to the boil and maintain at boiling point for 10 minutes. Hold the temperature above 90°C for further 10 minutes to ensure full development of the permanganate colour. After cooling, transfer the solution to a 50-ml volumetric flask and dilute to the mark with stabilized water. After mixing, the colour should be stable for several hours; any tendency to fading indicates the incomplete removal of organic matter or chloride.

7.3.4 Rinse the cell of the electrophotometer, absorptiometer or spectrophotometer first with approximately 0·001 N potassium permanganate solution, then with stabilized water, 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.

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

8 EXPRESSION OF RESULTS

8.1 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

9.1 The test report shall include the following information:

a) Type and identification of the test sample;

b) Reference to this standard;

c) Results as described in **8.1**;

d) Any unusual features noted during the determination; and

e) Any operation not included in this standard, or regarded as optional.

(*Continued from Second Cover*)

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 may be present without degradation taking place. However, there is always the possibility in case of compounded rubbers that under the influence of some constituents (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 rubber.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.