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R 1654

RAW RUBBER AND RUBBER LATEX

DETERMINATION OF COPPER

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BRIEF HISTORY

The ISO Recommendation R 1654, *Raw rubber and rubber latex – Determination of copper*, 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. 1645, which was circulated to all the ISO Member Bodies for enquiry in July 1968. It has been approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia
Austria
Brazil
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Ceylon
Colombia
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France
Germany
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Hungary
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Thailand
Turkey
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United Kingdom
U.S.A.
U.S.S.R.

No Member Body opposed the approval of the Draft.

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

ISO Recommendation | R 1654 | August 1971

RAW RUBBER AND RUBBER LATEX

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INTRODUCTION

Copper 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 copper 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 copper in the rubber.

Little is known concerning the influence of copper 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 copper in synthetic rubbers is less frequently carried out; nevertheless this ISO Recommendation is applicable to most of the commonly used synthetic elastomers.

1. SCOPE

This ISO Recommendation describes a method suitable for the quantitative determination of small amounts of copper in raw natural rubber, raw synthetic elastomers which do not contain chlorine, and the corresponding uncompounded latices.

For compounded rubber and for rubbers and latices which contain chlorine, the methods given in ISO Recommendation R 1396, *Determination of copper in compounded rubber (vulcanized and unvulcanized)*, should be used.

2. PRINCIPLE

5 g of the dried latex solids or of the raw rubber are ashed in a silica crucible. The ash is extracted with a hydrochloric/nitric acid mixture and the solution made alkaline with ammonium hydroxide. Any iron present is complexed with ammonium citrate. The aqueous solution is then shaken with a solution in chloroform of zinc diethyldithiocarbamate to form and extract the yellow copper complex. The optical density of this solution is measured photometrically and is proportional to the concentration of copper.

3. REAGENTS

All reagents should be of recognized high purity analytical reagent quality suitable for use in trace metal analysis.

Distilled water should be used whenever water is specified.

3.1 *Light magnesium oxide.*

3.2 *Sodium sulphate*, anhydrous.

3.3 *Hydrochloric acid/nitric acid* mixture, prepared as follows

Mix together :

2 volumes of hydrochloric acid, ρ 1.18 g/ml;
1 volume of nitric acid, ρ 1.42 g/ml;
3 volumes of water.

3.4 *Citric acid solution.*

Dissolve 50 g of citric acid (solid) in 100 ml of water.

3.5 *Ammonia solution*, ρ 0.890 g/ml.

3.6 *Litmus paper.*

3.7 *Zinc diethyldithiocarbamate reagent.*

Dissolve 1 g of solid zinc diethyldithiocarbamate in 1 litre of chloroform.

If zinc diethyldithiocarbamate is not available the reagent may be prepared as follows :

Dissolve 1 g of sodium diethyldithiocarbamate in water and add 2 g of zinc sulphate. Extract the resulting zinc diethyldithiocarbamate by shaking with 100 ml of chloroform and separate the chloroform solution. Dilute to 1 litre. Store in an amber coloured bottle; this reagent is stable for at least six months.

3.8 *Copper standard solution.*

Weigh 0.393 g of copper sulphate pentahydrate ($CuSO_4.5H_2O$) into a small beaker and dissolve in water. Add 3 ml of concentrated sulphuric acid. Transfer the solution to a 1000 ml one-mark volumetric flask and dilute to the mark with water to form the stock solution. Pipette 10 ml of this stock solution into a 100 ml one-mark volumetric flask and dilute to the mark with water. This solution contains the equivalent of 0.01 mg of Cu per millilitre and should be freshly prepared from the stock solution when required.

4. APPARATUS

4.1 *Electrophotometer, absorptiometer*, or *spectrophotometer*, capable of measuring optical density at approximately 435 nm.

4.2 *Matched absorption cells*, 10 to 50 mm in path length.

4.3 *Silica crucibles*, nominal capacity 50 or 80 ml.

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

5. PREPARATION OF TEST PORTION

For the determination of copper in rubber, cut at least 5 g from the sample in such a way that proper representation of the whole sample is achieved. 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. Alternatively the test portion may be prepared by cutting the constituent pieces into smaller portions each weighing approximately 0.1 g.

For the determination of copper in latex, take a portion of thoroughly mixed latex containing about 5 g of total solids and dry to constant mass as described in ISO Recommendation R 124, *Determination of total solids of latex.*

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

6. PREPARATION OF CALIBRATION CURVE

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

If the magnesium oxide method of ashing is to be used, prepare a series of standard solutions, each containing 0.1 g of magnesium oxide dissolved in 10 ml of the dilute hydrochloric acid/nitric acid mixture. If the rubber is to be ashed by wrapping in filter paper and then placing directly in the muffle furnace, omit the magnesium oxide. To these solutions add portions of the standard copper solution ranging from 0 to 10 ml followed in each case by 5 ml of citric acid solution. Add ammonia solution drop by drop until the solutions are just alkaline to litmus paper. Cool the solutions, transfer individually to a separating funnel and add a further 2 ml of ammonia solution to each. Pipette 25 ml of zinc diethyldithiocarbamate reagent into each solution and shake for 2 minutes. Immediately after separation, draw the chloroform layer into a stoppered flask containing about 0.1 g of anhydrous sodium sulphate. If turbidity persists after standing for about 30 minutes, make further small additions of anhydrous sodium sulphate until the solution becomes clear.

Decant each chloroform solution through a plug of glass wool or a small filter paper into the cell of the electrophotometer, absorptiometer or spectrophotometer, and measure the optical density at the absorption maximum (about 435 nm). Correct the reading by subtracting the optical density of the solution containing no added copper. 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 copper. Plot the reading thus obtained for each solution against the appropriate concentration of copper to give the calibration curve, which should be checked periodically according to local conditions and the type of instrument used.

7. PROCEDURE

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

Weigh, to the nearest 5 mg, a 5 g test portion of the dried latex film or of the raw rubber, and place in a silica crucible (4.3) containing 0.1 g of magnesium oxide distributed over the base and partly up the side of the crucible. Support the crucible in a hole cut in an asbestos board so that about two-thirds of the crucible projects below the asbestos. Commence a blank determination using a similar crucible and the same amount of magnesium oxide, and give identical treatment throughout to the test and blank determinations. Heat the crucible and contents with a small gas flame until a dry carbonaceous residue remains, and then transfer the crucible to a muffle furnace (4.4) at a temperature of 550 ± 25 °C and heat until all carbon has been oxidized. Remove the crucible and allow to cool.

As an alternative to the above method of ashing, wrap the 5 g test portion, weighed to the nearest 5 mg, in a piece of ashless filter paper about 150 mm in diameter and place in a transparent silica crucible having clean unetched walls. Place the crucible and contents in a furnace at 550 ± 25 °C and close the door. Because of the risk of igniting flammable gases the furnace door should not be opened during the first hour. Also commence a blank determination using a similar filter paper and crucible, and give identical treatment throughout to the test blank determinations. When all the carbon has been oxidized, remove the crucible and allow it to cool.

Moisten the contents of the crucible with 0.5 to 1 ml water, then add 10 ml of the dilute hydrochloric acid/nitric acid mixture (3.3) and heat the crucible, covered with a clockglass, on a steam bath for 30 to 60 minutes. Wash the contents of the crucible into a small beaker or flask, add 5 ml of citric acid solution (3.4) and then add ammonia solution (3.5) drop by drop until the solution is just alkaline to litmus paper. Cool the solution, for example by immersion in running water, transfer to a separating funnel, add a further 2 ml of ammonia solution and then dilute to about 40 ml with water. Pipette 25 ml of zinc diethyldithiocarbamate reagent (3.7) into the solution and shake the funnel for 2 minutes. After separation, immediately transfer the chloroform layer into a stoppered flask containing about 0.1 g of anhydrous sodium sulphate. If turbidity persists after standing for about 30 minutes, make further small additions of anhydrous sodium sulphate until the solution becomes clear.

Decant the chloroform solution through a plug of glass wool or a small filter paper into the cell of the electrophotometer, absorptiometer or spectrophotometer, and measure the optical density at the wavelength used in preparing the calibration curve (about 435 nm). Correct the reading by subtracting the optical density of the blank solution. 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 the test solution measured against that of the blank. The reading thus obtained, used in conjunction with the calibration curve, gives the concentration of copper in the test solution and hence in the rubber.

8. EXPRESSION OF RESULT

The result should be expressed as parts per million (ppm) of copper (Cu) calculated by mass.

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