INTERNATIONAL STANDARD ISO 1396

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Vulcanized and unvulcanized compounded rubber — Determination of copper content — Zinc diethyldithiocarbamate photometric method

Mélanges à base de caoutchoucs vulcanisés et non vulcanisés — Dosage du cuivre — Méthode photométrique au diéthyldithiocarbamate de zinc

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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 1396 and found it technically suitable for transformation. International Standard ISO 1396 therefore replaces ISO Recommendation R 1396-1970 to which it is technically identical.

ISO Recommendation R 1396 was approved by the Member Bodies of the following countries :

Australia
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Egypt, Arab Rep. of
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United Kingdom
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Yugoslavia

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 1396 into an International Standard :

Germany

Printed in Switzerland

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Vulcanized and unvulcanized compounded rubber – Determination of copper content – Zinc diethyldithiocarbamate photometric method

0 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 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 copper 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 copper in the rubber compound.

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 compounds based on the synthetic rubbers is less frequently carried out; nevertheless the method specified in this International Standard is applicable to all the commonly used elastomers. Furthermore, since the method is insensitive to chlorine, it may be applied to raw polymers which contain chlorine.

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a zinc diethyldithiocarbamate photometric method for the determination of trace amounts of copper in compounded rubber, both natural and synthetic. It may also be used for the determination of copper in raw polymers and in latices which contain chlorine, but is not applicable to rubber having a saturated polymer chain or to butyl rubber.

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

Digestion of the dried latex solids or of the raw rubber with concentrated sulphuric and nitric acids. Removal of excessive amounts of calcium as sulphate and complexing of any iron present with ammonium citrate. After alkalization, shaking of the aqueous solution with a measured volume of a chloroform solution of zinc diethyldithiocarbamate to form and extract the yellow copper complex. Photometric measurement of the absorbance of this solution, which is proportional to the concentration of copper.

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 sulphate**, anhydrous.

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

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

4.4 **Hydrogen peroxide**, 300 g/dm^3.

4.5 **Ammonia** solution, ρ 0,890 g/cm^3.

4.6 **Hydrochloric acid**, 5 N.

4.7 **Citric acid** solution.

Dissolve 50 g of citric acid in 100 cm^3 of water.

4.8 **Zinc diethyldithiocarbamate reagent.**

Dissolve 1 g of solid zinc diethyldithiocarbamate in 1 000 cm^3 of chloroform. If zinc diethyldithiocarbamate is not available the reagent may be prepared thus: Dissolve 1 g of sodium diethyldithiocarbamate in water and add 2 g of zinc sulphate. Extract the resulting zinc diethyldithiocarbamate by shaking with 100 cm^3 of chloroform, separating the chloroform solution and diluting to 1 000 cm^3. Stored in an amber-coloured bottle, this reagent is stable for at least 6 months.

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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.

4.9 Standard copper solution.

Weigh 0,393 g of copper sulphate pentahydrate ($CuSO_4.5H_2O$) into a small beaker and dissolve in water. Add 3 cm^3 of concentrated sulphuric acid. Transfer the solution to a 1 000 cm^3 volumetric flask and dilute with water to the mark to form the stock solution. Pipette 10 cm^3 of this stock solution into a 100 cm^3 volumetric flask and dilute with water to the mark.

This solution contains the equivalent of 0,01 mg of copper 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 435 nm, and **matched cells.**

5.2 Kjeldahl flask, 100 cm^3 capacity, of silica or borosilicate glass.

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 copper in rubber, cut at least 2 g of rubber 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 smaller portions each weighing approximately 0,1 g. For the determination of copper in latex, take from the sample a portion of thoroughly mixed latex containing at least 2 g of total solids and dry to constant mass as specified in ISO 124. Digestion of this portion can be facilitated by passing it six times between the cold rolls of a laboratory mill, rolling the rubber into a cylinder after each pass and presenting the cylinder end-on to the rolls for the next pass.

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

7.2 Preparation of calibration curve

Prepare a series of standard matching solutions each consisting of 5 cm^3 of sulphuric acid (4.2) diluted to 10 cm^3 with water. To these solutions add portions of the standard copper solution (4.9) ranging from 0 to 10 cm^3, followed by 5 cm^3 of citric acid solution (4.7). Add ammonia solution (4.5) drop by drop until the solutions are just alkaline to litmus paper. Cool the solutions, transfer individually to a separating funnel and add to each a further 2 cm^3 of ammonia solution (4.5). Using a pipette add to each solution 25 cm^3 of zinc diethyldithiocarbamate reagent (4.8) and shake for 2 min. Immediately after separation draw the chloroform layer into a stoppered flask containing about 0,1 g of anhydrous sodium sulphate (4.1). If turbidity persists after standing for about 30 min further small additions of anhydrous sodium sulphate (4.1) should be made.

Decant each chloroform solution through a plug of glass wool or a small filter paper into the cell of the electrophotometer or spectrophotometer (5.1) and measure the absorbance at the wavelength of maximum absorption (about 435 nm). Correct the reading by subtracting the absorbance of the solution containing no added copper. 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 copper.

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

7.3 Determination[1]

Cut the milled rubber into pieces of not more than 0,1 g, and place 2 g, weighed to the nearest 2 mg, in the Kjeldahl flask (5.2). Add 4,0 ml of sulphuric acid (4.2) and 3,0 ml of nitric acid (4.3) and warm the flask to start the reaction. Commence a blank determination in a similar flask using the same amounts of acid. Thereafter give identical treatment to the test and blank solutions.

If the reaction becomes too vigorous, cool the flask in a beaker of cold water. As soon as the initial reaction has subsided, heat the mixture gently until the vigorous reaction has ceased, and then more strongly until the mixture darkens. Add nitric acid in 1 cm^3 portions, heating after each addition until darkening takes place. Continue this treatment until the solution becomes colourless or pale yellow and fails to darken on further heating. If the digestion is prolonged it may be necessary to add about 1 cm^3 of sulphuric acid to prevent the contents of the flask from solidifying. To destroy the last traces of organic matter, cool the mixture and add 0,5 ml of hydrogen peroxide (4.4) and 2 drops of nitric acid. Then heat the solution to fuming, repeating the additions and the heating until there is no further reduction in the colour of the solution. Cool the solution, dilute with 10 cm^3 of water and evaporate to fuming. Finally, cool the solution and add 5 cm^3 of water.

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

If the test solution at this stage is free from insoluble matter, transfer the acid digest to a conical flask and rinse the Kjeldahl flask with three 5 cm^3 portions of water which are added to the conical flask. If, however, the test solution contains insoluble matter, filter the supernatant liquid through a small filter paper into a conical flask, retaining as much as possible of the insoluble residue in the Kjeldahl flask. Add 5 cm^3 of hydrochloric acid to the Kjeldahl flask, heat the solution to incipient boiling and swirl vigorously to wash the sides of the flask. Then pour the flask contents into the filter and collect in the conical flask.

Add 5 cm^3 of citric acid to the solution in the conical flask and if, on cooling, the solution remains clear, it should be neutralized by the drop by drop addition of ammonia solution using a small piece of litmus paper as indicator. If, however, calcium sulphate crystallizes out from the solution on cooling, chill the flask and contents to about 10 °C, filter into a second conical flask and wash the filter and contents with three 2 cm^3 portions of ice-cold water before neutralizing with ammonia solution. Cool the solution, for example by immersion in running water, transfer to a separating funnel, add a further 2 cm^3 of ammonia solution, and then dilute to about 40 cm^3 with water. Using a pipette add 25 cm^3 of zinc diethyldithiocarbamate reagent (4.8) to the solution and shake the funnel for 2 min. Immediately after separation draw the chloroform layer into a stoppered flask containing about 0,1 g of anhydrous sodium sulphate (4.1). If turbidity persists after standing for about 30 min, make further small additions of anhydrous sodium sulphate until the solution becomes clear.

Decant the chloroform through a plug of glass wool or a small filter paper into the cell of the electrophotometer or spectrophotometer (5.1), 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 copper corresponding to the corrected reading and from this calculate the copper content of the test portion.

Express the result as parts per million (ppm) of copper (Cu) 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.